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Dissertation

**Removal of Polymer Coating with Supercritical
Carbon Dioxide**

Submitted by

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Department of Mechanical Engineering

**In partial fulfillment of the requirements
for the degree of Doctor of Philosophy**

**Colorado State University
Fort Collins, Colorado**

Fall, 2001

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COLORADO STATE UNIVERSITY

October 18, 2001

WE HEREBY RECOMMEND THAT THE DISSERTATION PREPARED UNDER OUR SUPERVISION BY LAURIE L. WILLIAMS ENTITLED REMOVAL OF POLYMER COATINGS WITH SUPERCRITICAL CARBON DIOXIDE BE ACCEPTED AS FULFILLING IN PART REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

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Abstract of Dissertation

Removal of Polymer Coatings with Supercritical Carbon Dioxide

This work investigates the use of supercritical fluids, and carbon dioxide in particular, for the removal of polymer coatings. Research into new supercritical fluid applications is nearly always based on a trial and error approach, and frequently requires evaluating each operation on a case-by-case basis. A significant improvement in this approach is accomplished with the development of a framework in which polymer-CO₂ interactions can be evaluated and the number of experimental trials reduced.

The basic model developed is built upon the three-component solubility parameter (HSP) concept, which is widely used in the coatings industry to aid in the selection of solvents. Temperature and pressure dependent HSP values have been developed for supercritical CO₂, using a methodology extendable to other supercritical fluids. Equations were also developed to calculate HSP's for cosolvents and polymers. With the solvent, cosolvent, and polymer thus fully characterized in terms of the HSP values, the systems are then analyzed in terms of the like and unlike (solvent/polymer, cosolvent/polymer, and solvent/cosolvent) binary pairs. In addition to this study, consideration of specific interactions, such as Lewis acid/base interactions between the solvent and polymer or between the cosolvent and polymer are examined for their role in determining a favorable (polymer coating removal) result.

The model was tested on two real-world applications: involving poly(methyl methacrylate) (PMMA) and polycarbonate (PC) coatings. Several organic liquids were

evaluated as cosolvents, including at least one example of a non-polar fluid, a Lewis acid, and a Lewis base. Results of this study found the following interactions, listed in order of importance in the removal of polymer coatings, to be (1) specific interactions between the solvent and polymer, in the case of PMMA and CO₂, or specific interactions between the cosolvent and polymer, in the case of PC and CO₂, (2) weaken polymer/polymer interactions as a result of polymer swelling and subsequent lowering of the polymer HSP values, (3) specific interactions between the solvent and cosolvent are not necessary and in the case of specific interactions between the cosolvent and polymer, may be undesirable.

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Acknowledgments

I'd like to take this opportunity to acknowledge the support of Colorado State University and the National Science Foundation for the fellowship in Environmental Conscious Manufacturing, Grant No. 5-33391. I'd also like to thank Los Alamos National Laboratory for both their support and the availability of the Supercritical Fluid Facility while completing my doctorate work for Colorado State University.

To the many people who have made this work possible, I am very grateful: Dr. Eric Mas for his assistance and expertise in mathematical relationships, Tom Marquis and the Huntsman Corporation for technical assistance in cosolvent chemistries and funding the propylene carbonate/carbon dioxide vapor-liquid equilibrium data, Dr. Charles Hansen for numerous correspondences regarding the development of carbon dioxide three-component solubility parameters, and Dr. Peter Fogg for his thoughts and expertise in gas solubility data.

I'd also like to thank my husband Rolly for his continuous love and encouragement, even when I didn't always deserve it; and to Hal, whose spirit is always with me.

.....*"I hear and I forget, I see and I remember, I do and I understand."*

Confucius

To Jim Rubin, for taking the trip with me and making the journey worthwhile.....

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List of Symbols

T	Temperature
T_c	Critical temperature
T_r	Reduced temperature, T/T_c
T_{br}	Reduced boiling temperature, T_b/T_c
T_g	Glass transition temperature
P	Pressure
P_c	Critical pressure
P_r	Reduced pressure, P/P_c
V	Volume
ρ	Density
ρ_r	Reduced density, ρ/ρ_c
α^p	Polarizability
μ	Dipole moment
I	Ionization potential
σ	Collision diameter
r	Distance between molecules
r_o	Equilibrium distance between molecules
Q	Quadrupole moment
U	Total energy of a system
${}_1Q_2$	Heat transferred to a system
${}_1W_2$	Work transferred to a system
E	Internal energy
n	Ratio, $\left(\text{Internal Pressure} / \text{Cohesive energy density} \right)$
S	Entropy

H	Enthalpy
G	Gibbs free energy
δ	Total solubility parameter
δ_{λ}	Solubility parameter – nonpolar component
δ_{τ}	Solubility parameter – polar component
δ_d	Solubility parameter – dispersion component
δ_p	Solubility parameter – polar component
δ_h	Solubility parameter – hydrogen bonding component
x	Mole fraction
ϕ	Volume fraction
R_o	Interaction radius
R_a	Distance (expressed as a radius) between two different HSP points
R_o^{liq}	Interaction radius based on polymer dissolution behavior in liquid solvents
R_o^{SCF}	Interaction radius based on polymer behavior in SCF
n_D	Index of refraction
ε	Dielectric constant
α	Thermal expansion coefficient
β	Isothermal compressibility
p_s	Saturation vapor pressure
$B(T)$	Tait parameters
B_0	Material dependent parameter
B_1	Material dependent parameter
A_0	Material dependent parameter
A_1	Material dependent parameter
A_2	Material dependent parameter
γ	Surface tension
P_s	Parachor parameter
k_D	Henry's law constant

1 Introduction

Polymer coatings are applied to surfaces (a) to impart desirable properties to the finished product (corrosion resistance, to reduce wear and friction, and to improve appearance), or (b) as part of an intermediate processing step (photolithography, etc.). If the coating is applied as part of an intermediate step, then it is required that this coating be removed prior to subsequent processing operations. Coating removal is also required for recycling/recovery of used or obsolete products (computer chassis, compact discs, etc.). At present, the removal of polymeric coatings is typically done using liquid organic solvents. However, the numerous environmental regulations faced by manufacturers who currently utilize solvents for these applications, and the wide range of concerns pertaining to their environmental release paths, is leading industries to seek less-hazardous, zero-discharge coating removal technologies.

During the last two decades, the concept of supercritical fluids (SCFs) as a solvent has grown out of knowledge developed through supercritical extraction and purification processes. In the U.S., commercial supercritical fluid (SCF) applications include coffee decaffeination, hops extraction, extraction of organic wastes from water, fats from foods, essential oils and spices from plants, and purification processes in the petrochemical industry.¹ While the technology is in widespread commercial use it has dealt primarily with simple molecules that dissolve in fluids such as carbon dioxide (CO₂). Therefore, the current commercial applications can be broadly described as selective extractions of

organic molecules (compounds) from organic matrices. This ability of supercritical CO₂ to solubilize organic compounds has recently extended the scope of applications to include commercial de-greasing and precision cleaning of machined parts contaminated with oil and greases. These cleaning applications are similar to the selective extraction and purification applications in that the objective is to solubilize, and thereby separate, organic compounds from matrices. There are two major differences, however, between these two types of applications. First, in a cleaning application, it is not the bulk of the “matrix” which is subjected to the supercritical fluid, but rather only the (typically inorganic) surface. Second, it is frequently required in cleaning applications that the supercritical fluid solvent not have any deleterious effects on the substrate, in contrast to the selective extraction and purification applications, where the effects on the matrix are generally inconsequential.

The removal of polymer coatings can be considered to be a cleaning application, since it is the selective separation of the polymer from the surface of the substrate which is desired. Also, whether or not the coating removal technique is inert with respect to the substrate will depend on the reason for the coating removal, i.e., whether it is part of an intermediate processing step or part of a recovery/recycling process. Finally, there is one more important aspect to the use of supercritical fluids for the removal of polymer coatings. While the use of organic liquid solvents may achieve the end result of polymer coating removal, it is nearly always the case that a liquid solvent based process does not allow for simple recovery of the polymer, if this is desired. Also, there will nearly always be a waste treatment and/or disposal issue associated with the spent liquid solvent.

This work represents an investigation into the use of supercritical fluids, and carbon dioxide in particular, for the removal of polymer coatings. At this initial stage of coatings removal research, substrate/polymer interactions will not be considered, though those interactions could be significant in some applications. It will be shown in this work that the removal of a polymer coating depends on the dissolution of the supercritical fluid solvent into the polymer, and the resulting swelling of the polymer. Pure, supercritical CO₂ is limited in its ability to dissolve most polymers. Rather, it is the sorption of supercritical CO₂ into a wide variety of polymers and the resulting swelling of the polymer that can be utilized to achieve the desired interactions. In fact, near its critical point, CO₂ is as soluble in many polymers as are typical liquid organic solvents, ranging from (approximately) 10% to more than 30% by mass.² Maximizing CO₂ solubility and the subsequent polymer swelling, or disruption of the polymer/polymer interactions, followed by rapid depressurization, causes the polymer coating to fracture and/or debond from the substrate. This research illustrates a method to select the optimum composition of supercritical fluid solvent, which can include not only a pure solvent but also one or more dissolved co-solvents, given a known polymer. Further, the method allows for the prediction of the optimum processing conditions of temperature and pressure in order to achieve maximum polymer impregnation and swelling. This method relies on the use of solubility parameters. Traditionally, the solubility parameter concept has been almost exclusively confined to mixtures of ambient-pressure liquids. It is shown in this work how the solubility parameter concept can be applied to each of the components (pure fluid, cosolvent(s), and polymer) in the liquid, gas, and supercritical fluid states.

The solubility parameter method will be applied to two specific polymer coating removal applications - stripping of hardened photoresist-coated silicon wafers, an example of coating removal as part of an intermediate processing operation, and removal of a photoconductive polymer coating from laser printer drums, which is an example of a recovery/recycling operation.

1.1 Example Application #1: Removal of Photoresist Coatings from Silicon Wafers

The fabrication of integrated circuits (IC) relies heavily on an intermediate processing step called photolithography to define the shape and pattern of individual components. In the photolithography process, Figure 1-1, a film of photo-reactive polymer, known as a photoresist, is applied to the surface of a semiconductor wafer and cured by exposure to light. The areas of the photoresist which are exposed to the light source cause the polymer film to undergo either chain scission in the case of a positive-acting photoresist, or chain cross-linking in the case of a negative acting photoresist. Subsequent immersion in a developing solution causes dissolution of that part of the photoresist that has undergone chain scission (for the positive acting polymer) or has not undergone cross-linking (for the negative acting). This selective dissolution uncovers well-defined regions of the substrate (wafer) surface. The remainder of the photoresist film is then baked at high temperature to evaporate excess solvent, thereby “hardening” the photoresist so that it can withstand subsequent fabrication steps, such as ion implantation or metal deposition. Once the subsequent fabrication step has been completed, the hardened photoresist must be removed before the next step in manufacturing can begin. Current techniques for “hardened” photoresist removal utilize

highly acidic or highly alkaline aqueous solutions, or mixtures of regulated organic solvents. To ensure that all traces of organic solvents and inorganic residues are removed from the wafer surface, the manufacturing process incorporates a final rinse step during the photoresist-stripping process. Up to 4 million gallons of water per day are used in the removal and cleaning steps during this process, generating more waste than any other single step in the IC manufacturing process³. The production of a complete IC can involve many iterations of the photolithography process as shown in Figure 1-1. The cost associated with the treatment and disposal of this waste, as well as employee health and safety considerations, are driving a search for alternative, environmentally benign, cost-effective solutions.

The Photolithography Process

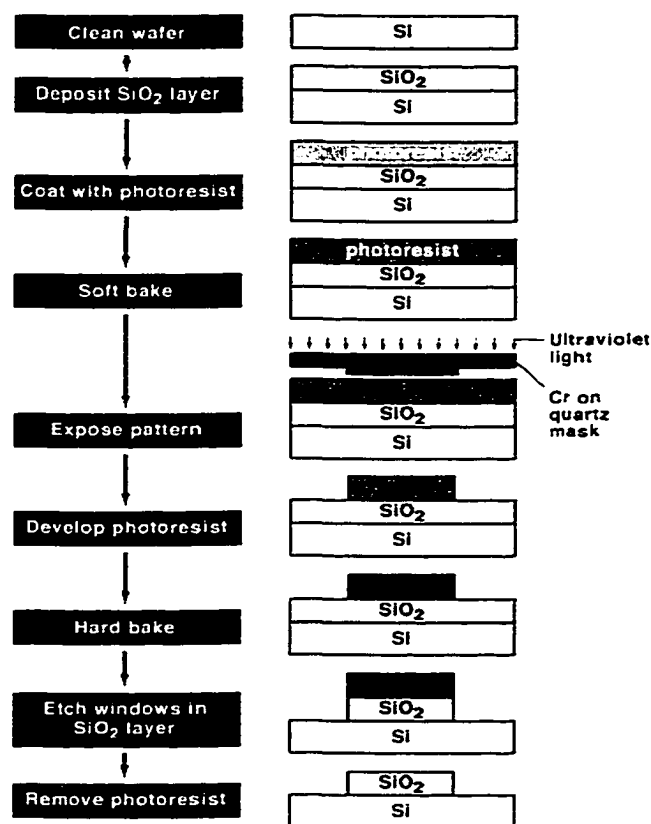


Figure 1-1. Schematic illustration of the photolithography process, showing the production of a polymer (photoresist) coating onto a silicon wafer substrate, and its subsequent removal.

1.2 Example Application #2: Removal of Photoconductor Coating from Aluminum Drums

The removal of polymer coatings from manufactured components is also important in the application of recovery of improperly coated components or for the recycling of used or obsolete components. At Lexmark International Inc., a global developer, manufacturer, and supplier of laser and inkjet printers and associated supplies, components manufactured for their laser printers are photoconductor drums. Constructed

of anodized aluminum, these photoconductor drums are coated with a charge-generating layer of polyvinyl butyral (PVB) overlaid with a charge transporting film of polycarbonate (PC).

The polymer films, shown in a schematic cross section in Figure 1-2, are applied to a photoconductor drum in a two-step dipping process. The inner PVB coating is affixed by dipping the drum into a 3% solid/97% solvent solution. The solid is 50% PVB/50% pigment, while the solvent is methyl ethyl ketone (MEK). The dip coating is followed by a drying step to evaporate the solvent (100°C for 20 minutes), resulting in a dried PVB coating approximately 1 μm thick. The outer PC layer is applied by dipping the drum into a 20% solid (70% PC/30% transport molecule) and 80% solvent solution (tetrahydrofuran and 1,4-dioxane). Coating is again followed by a drying step (130°C for 1 hour) to evaporate the solvent. The dried PC coating is approximately 25 μm thick.

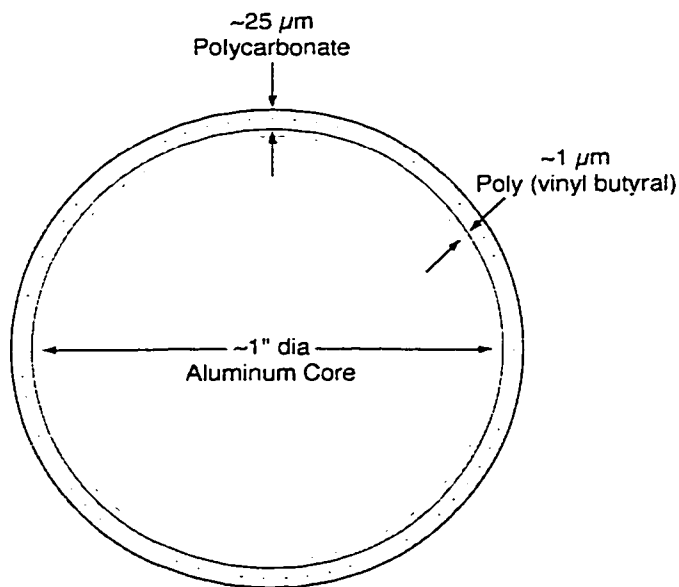


Figure 1-2. Cross-sectional view of a photoconductor drum with polymer coatings.

In a laser printing process, also known as electrophotography, the photoconductor drum is analogous to a reusable film. In the printing process, the entire surface of the drum is charged to approximately -800 volts. The laser print head then begins writing characters to the charged drum surface. The charge generation layer, which has a photosensitive dye, undergoes a reaction that produces charge carriers in the local areas addressed by the laser. Due to the presence of the charged drum surface, charge-transport molecules in the transport layer transfer the photo-generated charges to the drum surface. Additionally, the charge transport layer provides protection to the charge generation layer from the abrasion of the paper, cleaning blades, toner, etc. The net result of the charge generation and transport process is the generation of localized regions of lower charge (approximately -150 volts), in the shape of the laser-generated characters on the drum surface. These “discharged” areas attract toner particles, which are also charged, resulting in toner adhering only to specific locations. The toner is then transferred to the paper and fused by a heating element. The drum is then recharged to -800 volts, erasing the latent image, and the entire cycle repeated.

Approximately 5% of the coated drums manufactured by Lexmark are discarded for quality reasons. Of these drums, approximately one-third are rejected due to defects in the aluminum substrate with the remaining two-thirds rejected due to defects in the polymer coatings. Quality control consists of visual inspection of all the drums and electrostatic and print testing on a “lot sample” basis. Removal of the polymer films from rejected drums requires manually stripping the polymer films with hazardous solvents such as tetrahydrofuran (THF) and MEK. Currently, all rejected drums are sent offsite for recycling of the aluminum. Removal of the defective polymer coating would

result in an estimated annual 200,000 reclaimed cores suitable for reuse. In addition, an unknown number of photoconductor drums could be reclaimed from used components returned from buyers following their useful life.

1.3 Research Methodology and Results

Chapter 2 discusses the details of supercritical fluids with an emphasis on supercritical CO₂. It is shown by reference to physical properties why supercritical fluids are useful as processing solvents, and why supercritical fluids are gaining attention for cleaning and polymer coating removal. Also, the different types of macroscopic interactions, such as those leading to the removal of a coating, which can occur between polymers and a supercritical fluid are illustrated by examples where such interactions are, or can be, commercially applied.

Chapter 3 reviews the microscopic forces that operate between the molecules of a pure substance and between unlike molecules in a mixture. The purpose is to give a brief introduction to the nature and variety of forces acting between molecules which must be accounted for in any description of a fluid-polymer processing application.

Chapter 4 introduces the various solubility parameter models which have been used to evaluate the range of molecular interactions discussed in Chapter 3. The development of the solubility parameter methodology and the model chosen for expansion in this dissertation are examined and established.

Chapter 5 make use of the solubility parameter models for expressing the cohesive properties of pure components (solvent, cosolvent(s), and polymer). In addition, because a supercritical fluid application typically operates at pressures far above

atmospheric and at greater than ambient temperatures, the effects of temperature and pressure on the pure component solubility parameter values are considered.

Chapter 6 continues with characterization of solubility parameters of binary pairs of components (solvent/cosolvent, solvent/polymer, and cosolvent/polymer). Other considerations, such as Lewis acid/base interactions between the solvent and polymer or polymer functional group, as well as between the cosolvent and polymer or polymer functional group, are examined.

Chapter 7 is an example of vapor liquid equilibrium modeling with CO₂ and propylene carbonate.

Chapter 8 compares experimental results with the model framework developed.

Chapter 9 is a summary and discussion of the present work, while Chapter 10 contains references.

There are four Appendices included at the end of the dissertation, (A) CO₂ equation of state and respective partial derivatives; (B) CO₂ Ideal solubility discussion, details of the published CO₂ solubility data in 103 solvents, and results of the RED (relative energy difference) calculations; (C) CO₂ HSP Values for a range of pressures and temperature; and (D) Equation of state references.

2 Polymer/CO₂ Interactions

2.1 Supercritical fluids

Supercritical fluids are fluids (a generic term encompassing liquids and gases) that are at a temperature and pressure greater than, or equal to, the critical temperature (T_c) and pressure (P_c) of that fluid. Figure 2-1 is a temperature-pressure phase diagram showing the phase transitions for a pure substance such as carbon dioxide. In the region $T \geq T_c$ and $P \geq P_c$, shown by the shaded region, the liquid and vapor regions merge into single, homogeneous fluid, a SCF.

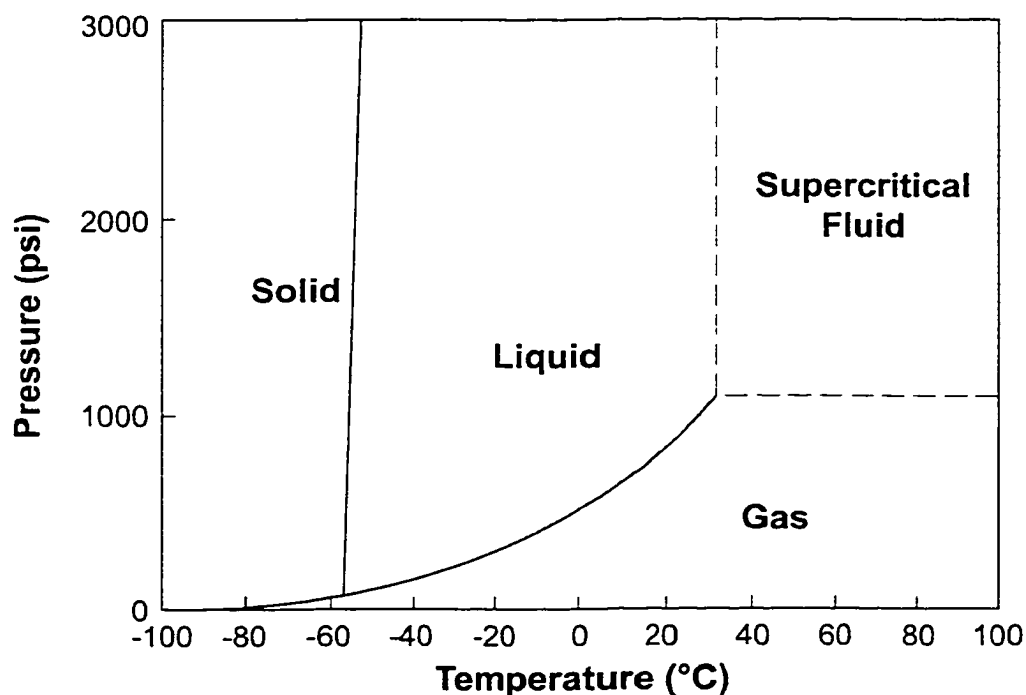


Figure 2-1. Schematic pressure-temperature diagram showing the solid, liquid, gas, and supercritical fluid phases for a pure, one component system.

While the existence of supercritical fluids has been known since 1822⁴ it has only been in the last two decades that the value of SCFs as a medium for extraction, cleaning, and synthesis has been recognized. The attractiveness of SCFs as process solvents stems from their unique combination of liquid-like and gas-like properties. SCFs exhibit gas-like transport properties of diffusivity and viscosity yet possess liquid-like mechanical properties, such as density. Table 2-1 gives a comparison of the diffusivity, viscosity and density of a typical organic fluid in the liquid, gas, and supercritical fluid states.⁵

Table 2-1. *Comparison of physico-chemical properties of a typical organic fluid in the liquid, gas, and supercritical fluid states.*

	Diffusivity (cm ² /s)	Viscosity (mN s/m ²)	Density (g/cm ³)
Liquid	10 ⁻⁵	10 ⁰	1
Supercritical fluid	10 ⁻³ - 10 ⁻⁴	10 ⁻¹ - 10 ⁻²	0.5 - 1.1
Gas	10 ⁻¹	10 ⁻²	0.001

To a first approximation, the ability of a solvent to solubilize other compounds is related to its density^{6,7,8,9} (the reason for this will be discussed in Chapter 3). As seen in Table 2-1 high liquid-like densities, > 1 g/cm³, are achievable in SCFs, allowing for substantial solubilities. The combination of properties illustrated in Table 2-1 shows why SCFs are ideal for cleaning substrates having porous, intricate, or rough surfaces, and for confined work areas. The solvent is able to penetrate into otherwise inaccessible regions due to the gas-like viscosity, and is then able to solubilize and remove contaminants, due to its liquid-like dissolving power.

Table 2-1 might suggest that the density of supercritical fluids is always liquid-like. However, it is also the ability to *continuously* vary the density of a SCF from liquid-

like to gas-like by altering the temperature and/or pressure that is their true hallmark. Figure 2-2 illustrates how relatively small changes in temperature and pressure near the critical point result in large changes in density and therefore the solubilizing power of the fluid. It is this “tunability” of solubilizing power that makes SCFs such attractive solvent for manufacturing processes. In terms of developing predictive models for solvent/polymer interactions, however, it is this ability to assume liquid-like or gas-like properties, over such a wide range of temperatures and pressures, that presents the most difficulty.

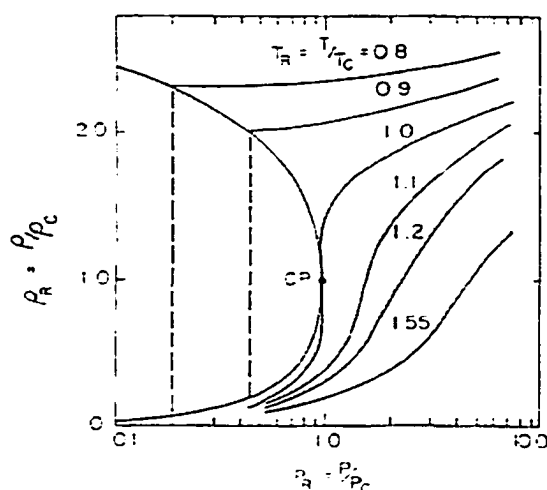


Figure 2-2. Variation of the reduced density in the vicinity of its critical point.¹⁰

2.1.1 Supercritical CO₂

The critical values of temperature and pressure are unique for every compound. The critical temperature of CO₂ is 31.1°C and the critical pressure is 73.8 bar. Figure 2-3 shows the pressure-temperature-density surface of pure CO₂, with the critical point shown by a large solid circle. As can be seen in Figure 2-3 the density of supercritical

CO₂ can vary over a wide range from gas-like values of 0.0018 g/cm³ (STP), to liquid-like values of over 1.0 g/cm³. This reflects a density change of several orders of magnitude by relatively modest variations of temperature and pressure

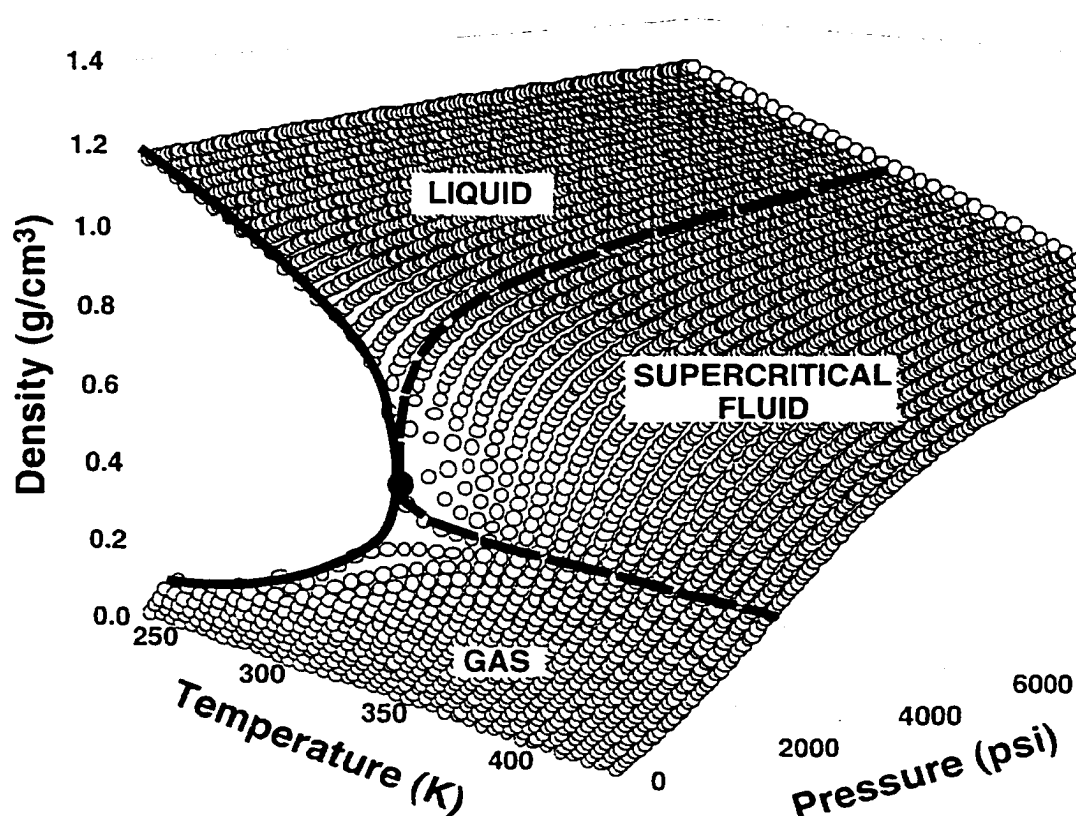


Figure 2-3. Pressure-temperature-density surface of pure CO₂.

In addition to the high liquid-like densities achievable in supercritical CO₂, it also possesses gas-like diffusivity, shown in Figure 2.4.

Use of SCFs, especially supercritical CO₂, as an alternative coating removal technology, offers many potential advantages over conventional organic solvents. CO₂ is generally chemical inert with respect to inorganic materials and is therefore compatible with a variety of substrates. CO₂ is noncombustible, readily available in high purity,

environmentally friendly (not ozone depleting), and has a low human toxicity. Supercritical CO₂ is also attractive from the viewpoint of waste minimization. After the cleaning step, carbon dioxide is easily separated from the extracted/dissolved polymers, resulting in streams of concentrated polymer (or polymer residue) and pure, reusable CO₂. Also, since supercritical CO₂ evaporates completely when depressurized, leaving no residue, supplemental aqueous rinsing and drying steps are also not required.

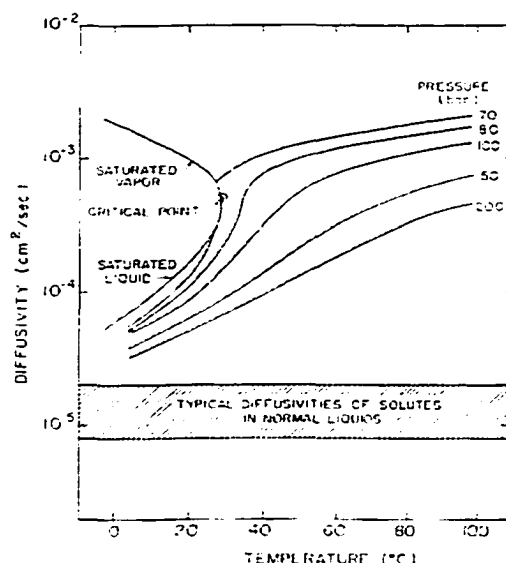


Figure 2-4. Diffusivity behavior of supercritical CO₂.

2.2 Polymer/CO₂ Interactions

To further exploit the use of SCFs as a cleaning/polymer coating removal technology it is essential to understand their properties and how SCFs interact with materials. In general, because of their high crystallinity, high density, and resulting impermeability to gases, most metal and glass materials will have little interaction with CO₂.¹¹ On the other hand, polymeric materials, which are most often amorphous or semi-crystalline, exhibiting lower than theoretical densities, are known to interact with a

variety of gases and may be expected to show a wide range of behaviors in the presence of a SCF, varying from no effect to very pronounced effects.

Mixtures of polymers and supercritical fluids (SCFs) have many features in common with mixtures of polymers and conventional organic liquid solvents.¹² As a result, a variety of operations, such as swelling, plasticization, crystallization, extraction of impurities, polymerization, and fractionation can be carried out on polymers using SCFs. The following discussion of CO₂/polymer interactions will be limited to interactions where (a) the supercritical fluid is inert with respect to the overall composition of the polymer, or (b) where changes produced in the polymer composition are the result of polymerization and depolymerization, and not by chemical incorporation of CO₂. This means that certain types of polymer/SCF interactions will not be considered, such as the chemical reaction of the SCF with the polymer, forming a new compound. One example of such a reaction is that between a primary aliphatic amine and CO₂, forming a carbamic acid.¹³

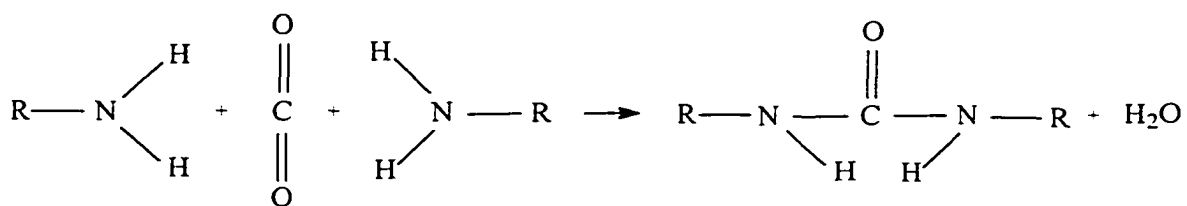


Figure 2-5. The chemical reaction of CO₂ with a primary amine to produce a carbamic acid.

All CO₂/polymer interactions require either some amount of polymer solubility in the SCF, or SCF solubility in the polymer. With the notable exception of some siloxane and fluorinated polymers, few polymers are soluble in supercritical CO₂. CO₂ is, however, readily absorbed into a wide variety of polymers at elevated pressures,

especially carbonyl-containing polymers, frequently plasticizing the polymer and lowering its glass transition temperature significantly below that observed at atmospheric pressure.¹⁴ The ability of a polymer to solublize CO₂ depends on its chemical structure. Particularly, because CO₂ is a potential electron acceptor compound (Lewis acid),^{15,16,17} the presence of a basic site in the polymer's structure is favorable for the sorption of CO₂. However, the presence of crystallinity in the polymer will inhibit the sorption of CO₂, since CO₂ sorption is believe to occur only in the amorphous regions.¹⁸ Also, highly crosslinked polymers will expand less freely than those with less crosslinking.¹⁹

The interaction between a supercritical fluid and a polymer can have pronounced effects on the polymer. Many of these effects are, or can be, the basis of commercial processes. Figure 2-6 illustrates the types of macroscopic interactions that can be achieved by processing a polymer in a supercritical fluid environment. These known and observed interactions between supercritical CO₂ and polymers are here classified according to the effect of the interaction on the molecular weight distribution (MWD) of the polymer. Figure 2-6 is intended to highlight *end-processes* that are, or could be, commercially viable, and there will nearly always be some overlap between the general end-processes shown. For example, fractionation involves both permeation of the supercritical fluid into the polymer, and therefore, swelling, followed by solubilization of the polymer, and therefore, selective extraction.

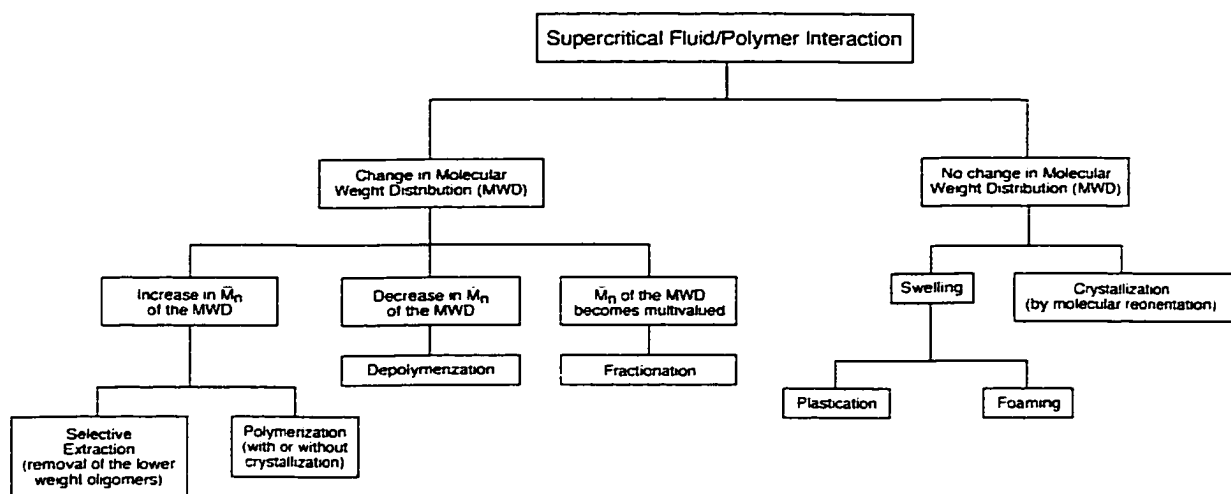


Figure 2-6. Supercritical CO₂-polymer interactions.

By classifying the various CO₂/polymer interactions by their effect on the MWD, we immediately separate those interactions which rely on the solubility of the polymer in the supercritical fluid from those which rely on the solubility of the supercritical fluid in the polymer. A change in the MWD can be either an increase, a decrease, or the development of a multimodal number average molecular weight, $\bar{M}_n$, distribution. All of the end-processes in Figure 2-6 that involve a change in the MWD depend on having the *polymer soluble in the supercritical fluid*. Interactions where an increase in the $\bar{M}_n$ of the MWD is expected include selective extraction and polymerization. While a decrease in $\bar{M}_n$ of the MWD is assumed to be the result of depolymerization, and the creation of a multivalued $\bar{M}_n$ distribution is characterized as polymer fractionation. Simple illustrations of these changes are shown in Figure 2-7.

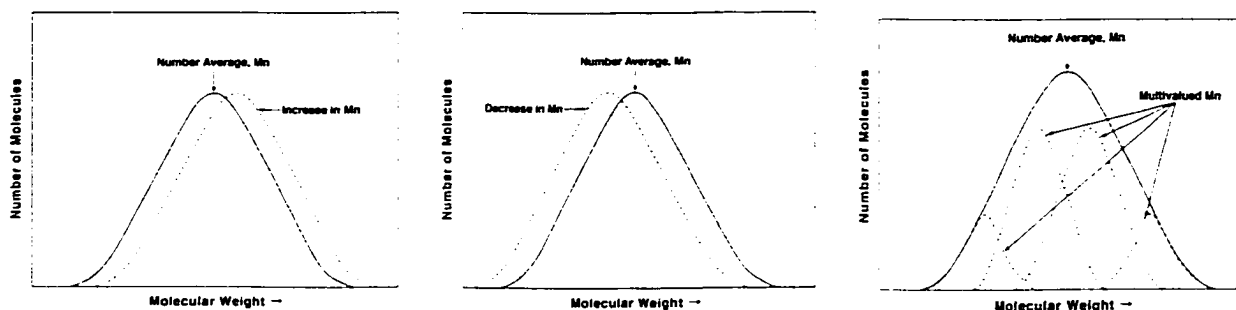


Figure 2-7. Variations in the number average molecular weight, M_n .

The simplest interactions between a supercritical fluid and a polymer, from a physical point of view, are those that do not change the MWD. From Figure 2-6, these end-processes are swelling and recrystallization,^{20,21,22,23,24,25,26,27,28} and these interactions are characterized by *solubility of the supercritical fluid in the polymer*.

2.2.1 Selective Extraction

Selective extraction^{29,30,31,32,33} is a process of selective or sequential removal of components from within a polymer matrix, including unreacted monomers, initiators, catalysts, and low molecular weight oligomers. Traditional SCF extraction falls into this category if the matrix is a natural polymer. Current methods for selective extraction include distillation, precipitation, filtration, or liquid solvent extraction. However, many specialty monomers and polymers are difficult to process and purify by these techniques. CO₂, however, because it can act as a Lewis acid, interacts favorably with many basic polymers. Combined with its small molecular diameter, CO₂ can then diffuse into polymers more quickly than conventional liquid solvents accelerating swelling.³⁴

Solubility of the targeted component(s) in supercritical CO₂ is essential for this application. In addition, the lack of solubility of the "parent" polymer matrix in CO₂ is,

in this case, a benefit. As an example, it has been shown that by suitable tuning of processing conditions (temperature and pressure), CO₂ can effectively extract selected components or liquid solvents while leaving 100% of the parent polymer intact.³⁵ Current commercial applications include the removal of impurities that are coproduced with monomer synthesis and which interfere with polymerization (e.g., diacetone acrylamide, BisGMA, and monomers synthesized with dimethylsiloxane backbones), and the removal of low molecular weight oligomers from polyphenylmethyilsiloxane (designated OV-17).³⁶

Selective extraction can also result in detrimental effects if CO₂ polymer interactions are not considered. An example is the extraction of plasticizers, such as esters of the benzenedicarboxylic acid terephthalic acid, whose removal from the parent polymer can affect its mechanical properties.

2.2.2 Polymerization

Polymerization is the process of joining together small structural repeat units to produce a compound of higher molecular weight. The prospect of using supercritical CO₂ as an alternative to traditional volatile organic solvents and chlorofluorocarbons, is promising and has been reviewed in several publications.^{37,38,39,40,41,42} This approach has been somewhat limited, however, because the polymers which dissolve in supercritical or near-critical CO₂ are limited,^{43,44} and in some cases the pressures required for dissolution are extremely high.

Polymers that have been demonstrated to dissolve in CO₂ include hydrocarbon polymers containing fluorinated octyl acrylates. Hydrocarbon-fluorocarbon block and graft copolymers also exhibit a high degree of solubility. Krukonis⁴⁵ has shown that CO₂ at or near room temperature and at pressures typically below 600 bar also dissolves many poly(dimethyl)- and poly(phenylmethyl) silicones, perfluoroalkylpolyethers, and chloro- and bromotrifluoroethylene polymers. Beckman and coworkers⁴⁶ found poly(perfluoropropylene oxide) and also poly(dimethyl siloxane) to exhibit solubility in CO₂ as well. CO₂ can also dissolve very low molecular weight, slightly polar polymers, such as polystyrene, or telechelic polyisobutylene if the molecular weight is below 1000.⁴⁷ The high solubilities of siloxane and fluorinated based polymers^{48,49,50,51,52} has resulted in the synthesis polymerization of amorphous fluoropolymers in supercritical CO₂.^{53,54,55}

To enhance solubility of additional polymers, there is considerable research focusing on new monomer and polymer chemistries that achieve enhanced solubilities in CO₂, and in designing new surfactants that can disperse many polymers, as emulsions, in CO₂.^{56,57} Other polymerization operations in supercritical CO₂ that have been demonstrated include chain-growth free-radical polymerization of styrenics, acrylates, and methacrylates, and cationic polymerization of isobutylene, vinyl ethers, and styrene. Also, step-growth reactions in CO₂ have produced polycarbonates, polyamides, polyesters, polypyrrole, polyphenoxides, and silica gels.⁵⁸

2.2.3 Depolymerization

Depolymerization is the "reverse" of reactions that occur during polymerization, resulting in smaller chain lengths and therefore a decrease in the number average molecular weight.^{59,60,61,62} This can potentially, lead to extraction of the lower molecular weight components, partial fractionation of the polymer, and/or scission of a polymer's intermolecular interactions.^{63,64,65,66} Depolymerization reactions of polymers in supercritical fluids would be of great value for environmental remediation and recycling of mixed polymer wastes. One application that is currently receiving attention is the conversion or breakdown of tires into lower molecular weight components that could be recovered as a chemical feedstock.⁶⁷

This reaction may also have tremendous potential for the use of supercritical CO₂ in the removal of polymer coatings. In this application, however, complete depolymerization or polymer/polymer chain scission is not anticipated. However, some deformation of the polymer matrix will occur as a result of the supercritical CO₂ sorption. This deformation, as swelling, has the potential to disrupt the polymer/polymer bonds, degrading and weakening the polymer, promoting its removal.

2.2.4 Fractionation

Many synthetic polymers are produced with a distribution of chain lengths, and therefore molecular weights. Since the solubility of a given polymer fraction in a given solvent is related to the solvent's density, and since the density of supercritical CO₂ can be varied over a wide range, supercritical CO₂ could be used to fractionate polymers

according to molecular weight. This has, in fact, been demonstrated,^{68,69,70,71,72,73} and, in addition, it has been found that fractionation into molecular weight ranges more narrow than is generally achievable by traditional distillation or separation techniques is possible. Supercritical fluid fractionation of a polymer is typically carried out in multiple, sequential pressure reduction steps. The number of fractions obtained is dependent on the number of pressure reduction stages, and the molecular weight range of each fraction is related to the ratio of pressure reduction per stage.⁷⁴ The heaviest fraction leaving the system is the fraction with the highest molecular weight that has not been dissolved, based upon the extraction pressure and temperature.

Choosing an appropriate supercritical solvent is one of the most important considerations in polymer fractionation. The specific choice of a supercritical fluid solvent for a given polymer is highly dependent on intermolecular forces, such as hydrogen bonding and dipole-dipole interactions between the solvent-solvent, solvent-polymer, and polymer-polymer molecule pairs in solution. This, of course, applies to all the end-processes which rely on the polymer being soluble in the supercritical fluid. Chapter 3 will discuss these forces in further detail.

2.2.5 Swelling

As noted previously, the number of polymers that dissolve in supercritical CO₂ is quite limited. However, CO₂ is readily absorbed into a wide variety of polymers that frequently results in polymer swelling. Polymer swelling can be further characterized as temporary (in-situ or reversible), known as plasticization, and permanent (ex-situ or irreversible), often referred to as foaming.^{75,76,77,78,79} Foaming of polymers is achieved by

the injection of high-pressure gas into the molten polymer, followed by rapid depressurization and expansion of the gas. The production of foam using supercritical CO₂ is, in fact, a commercialized process for the manufacture of ultra-low density materials (primarily for use as packing materials, etc.) and ultra-low dielectric constant materials (for use in antennas, etc.).

Reversible, or in-situ, swelling is commercially exploited in the impregnation of polymers with additives. The reversible swelling of polymers in supercritical CO₂ is well known, and has often been reported to plasticize the polymer. Plasticization is a very important commercial operation and is typically achieved by the incorporation of low molecular weight diluents into polymer materials during their manufacture to improve workability and increase flexibility.

Plasticization by supercritical CO₂ processing increases polymer flexibility essentially through a decrease in the polymer's glass transition temperature, T_g .⁸⁰ The temperatures at which polymers soften, represented by T_g , and melt are important for their processing, end-use, and potentially for their removal as coatings. T_g reflects the onset of long-range motions of polymer chains and is intimately related to free volume. According to the "free volume" theory,⁸¹ molecular mobility is controlled by that part of the excess volume which can be randomly redistributed with no or little energy requirement. The glass transition is the result of the temperature-dependent decrease of this free volume of the amorphous phase below some small characteristic value, which limits further molecular rearrangement. Consequently, below the glass transition temperature, further molecular rearrangements of the polymer become energy intensive, so mobility of the polymer is "frozen in".⁸² Above the glass transition temperature,

amorphous polymers enter the rubbery state where polymer segments are free to move. Many of the physical properties of an amorphous material change when the material is heated above its glass-transition temperature since above T_g the amorphous phase can be considered to be an undercooled liquid.

In the absence of any solvent, the free-volume of a polymer decreases with applied pressure and the T_g therefore increases. However, the T_g of a polymer exposed to a (pressurized) supercritical fluid, although affected by a decrease in free-volume due to hydrostatic pressure, is more significantly influenced by the pressure dependence of the sorption of the supercritical fluid. The softening of the polymer by lowering of its T_g enhances penetration and impregnation of polymer materials with additives at much lower temperatures. The advantage to using supercritical fluids over vapors or liquid for polymer impregnation is the ability to tune the solvent strength by changing temperature and pressure, thus allowing the degree of polymer swelling and portioning of penetrants to be adjusted.

Two distinct types of reversible swelling and sorption isotherms have been identified for polymers in the presence of CO_2 at elevated pressures. One isotherm is characterized by swelling and sorption that begin to level off and reach limiting values at elevated pressures. The other isotherm is characterized by sorption and swelling that continue to increase with pressure.⁸³ The sorption isotherm behavior is found to depend on the glass transition of the amorphous or semi-crystalline polymer in the presence of compressed CO_2 . In the absence of a glass transition, the equilibrium solubility of CO_2 in a polymer will exhibit a maximum with increasing pressure owing to free volume effects. Therefore, at a given temperature, if the pressure corresponding to the maximum

gas solubility is reached before the glass transition, the first type of isotherm described above characterizes the sorption and swelling. However, if the glass transition occurs below the pressure corresponding to maximum CO₂ solubility, the second type of isotherm characterizes sorption and swelling. It is expected that these isotherms will also eventually level off at some high pressure due to free volume effects in the polymer melt.⁸⁴

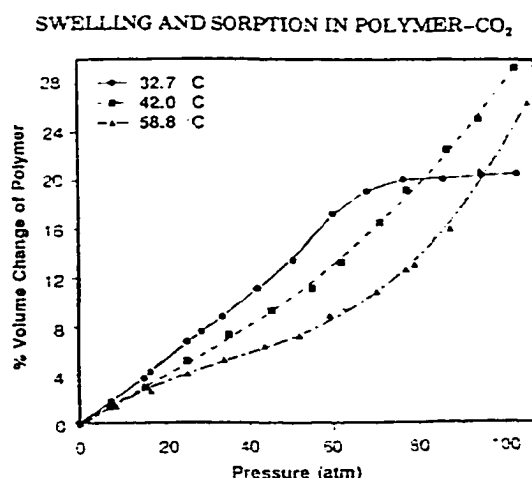


Figure 2-8. Isotherms characterizing polymer sorption and swelling behavior with CO₂. Isotherms at $T = 42.0^{\circ}\text{C}$ and $T = 58.8^{\circ}\text{C}$, are characterized by swelling and sorption which increase with pressure. Isotherms at $T = 32.7^{\circ}\text{C}$, are characterized by swelling and sorption that levels off with increasing pressure.

The use of high-pressure liquid and supercritical CO₂ to lower the glass transition temperature of various polymers has been extensively studied, and a compilation of reported results is presented in Table 2-2

Table 2-2. Index of polymers and related studies on T_g depression.

Polymer	Reference
Poly(methyl methacrylate), PMMA	85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96
Poly(urethane)s	97, 98

Polycarbonate, PC	99, 100, 101, 102, 103, 104, 105, 106, 107
Tetramethyl polycarbonate, TMPC	108
	109
Tetrachloro polycarbonate, TCPC	110
Tetrabromo polycarbonate, TBPC	
Polystyrene, PS	111, 112, 113, 114, 115, 116, 117, 118
High Impact Polystyrene, HIPS	119
Poly(ethyl methacrylate), PEMA	120, 121, 122
Poly(2,6-dimethyl phenylene oxide), PPO	123, 124, 125
Poly(vinyl chloride), PVC	126, 127
Poly(vinylidene fluoride)	128, 129
Poly(amic acid)	130, 131
Polyimide	132, 133
Poly(p-phenylene sulfide)	134
Poly(vinyl benzoate)	135, 136
Poly(vinyl butyral)	137, 138
Poly(4-methyl-1-pentene)	139, 140
Poly(ethylene terephthalate), PET	141, 142, 143, 144, 145
Poly(ethylene terephthalate) glycol modified, PETG	146
Poly(dimethyl siloxane), PDMS	147, 148, 149
Poly(methyl methacrylate-co-styrene), SMMA60	150
Acrylonitrile butadiene styrene, Royalite	151
Cellulose acetate butyrate, Uvex	152
Poly(vinyl acetate), PVA	153
Poly(p-methoxystyrene)	154
Nitrile Rubber	155
Poly(vinyl alcohol), PVOH	156
Polyhydroxybutyrate, PHB	157
Chitosane	158
Hydroxypropylcellulose, HPCL	159

Plasticization with supercritical CO₂, as a replacement for conventional vapor or liquid solvents, can be used to facilitate the incorporation of additives into polymers.^{160,161,162,163,164,165,166,167} The principle is to swell the polymer with the SCF, allowing the additive, dissolved in the SCF, to migrate into the polymer matrix. The pressure is then released, forcing the CO₂ out of the polymer matrix, while trapping the additive within the bulk of the polymer.¹⁶⁸ The impregnation of colorants or dyes for

textiles and other synthetic polymers with supercritical CO₂ is currently commercialized in Germany.¹⁶⁹ For successful impregnation of a polymer, it must be amenable to swelling by and the additive species soluble in supercritical CO₂. (It is also possible to use supercritical CO₂ to reversibly swell a polymer for in-situ molding, without the need for incorporated plasticizers.)

2.2.6 Crystallization

The second type of polymer/CO₂ interaction which does not produce a change in MWD is crystallization. The degree of crystallinity in polymers influences many of its properties and end-use characteristics.^{170,171,172,173,174,175} Crystallinity in polymers, requiring the cooperative movement of polymer chains throughout the matrix, develops in the range between T_g and the melting temperature, T_m .¹⁷⁶ Crystallization can therefore be induced either by raising the temperature of the polymer into the range between T_g and T_m (known as thermal crystallization), or by the sorption of liquid solvents to swell the polymer and lower T_g to below the ambient (known as solvent crystallization). As discussed earlier, supercritical fluids can swell polymers leading to a depression in T_g . Polymer crystallization accomplished through a controlled cycle of pressurization and depressurization using supercritical fluid solvents is an area that is receiving recent attention. Numerous studies of crystallization kinetics of polymers in high pressure CO₂ has been reported.^{177,178,179,180,181,182,183,184} It has been observed that with increasing CO₂ pressure, a polymer's characteristic time for crystallization can decrease by an order of magnitude for each MPa increase in pressure, leading to

significantly increased crystallization rates.¹⁸⁵ (The characteristic time for crystallization is defined as the time required for the crystallinity to reach one-half its maximum value.) The advantage of using supercritical CO₂ is that the sorption can be controlled by changing the pressure, providing a highly tunable technique for changing the crystallinity in a controlled manner. Also, after bringing about the desired crystallinity change, the supercritical CO₂ is easily removed from the polymer by simply depressurizing the system, whereas sorbed liquids cannot be desorbed easily. It is possible to completely eliminate the need for liquid solvents in some instances.

2.3 Polymer/CO₂/Cosolvent Interactions

Given the broad range of possible supercritical fluid applications in polymer processing, combined with the almost unlimited varieties of polymers used, it cannot be expected that a single SCF will possess all the characteristics necessary for favorable interactions in all cases. To enhance the characteristics of a SCF for a particular application, additional compounds, or modifiers, may be dissolved in the SCF as cosolvents. The addition of a small amount of cosolvent can have dramatic effects on SCF behavior, especially in the presence of specific molecular interactions between the cosolvent and the solute, or in the case of this research, the cosolvent and the polymer.

Because the focus of this research is to utilize supercritical CO₂ as the solvent in coating removal applications, and because of the wide differences in the types of polymers used, it is assumed that cosolvents will be necessary. In addition, if the result

of this work is to be of general applicability, the methodology must be as nearly as possible independent of the nature of the solvent, cosolvent, and polymer.

The most accurate description of the interactions between a given set of components (solvent, cosolvent, and polymer) would be one which considers those components in isolation, that is, the evaluation of molecular interactions between those three specific components taken three at a time. Such an evaluation is clearly possible, but would involve a large number of individual experimental trials, and the results of the evaluation would be applicable to that specific ternary system only. The next most general treatment would be a method which could evaluate any given set of three components. This would require not only the evaluation of a complex ternary interaction parameter, but a theoretical framework in which to use the data. Such a framework does not appear to exist. An alternative approach is to evaluate the interactions between three components, taken two components at a time. This is equivalent to evaluating the ternary system as a set of nine binary systems, Figure 2-9. The analysis to follow will further assume that the interaction between two components is symmetric, so that, for example, the solvent/cosolvent interaction is equivalent to the cosolvent/solvent interaction, etc. This reduces the number of binary pairs from nine to six. The results of these binary system evaluations would then be combined according to "mixing rules". The immediate advantage of this approach is the ability to easily exchange any one component (solvent, cosolvent, or polymer) without having to re-evaluate the interactions between the two remaining components. Further, methods for evaluating unlike binary interactions have been considered by various authors for various solvent/cosolvent, solvent/polymer, and cosolvent/polymer systems.

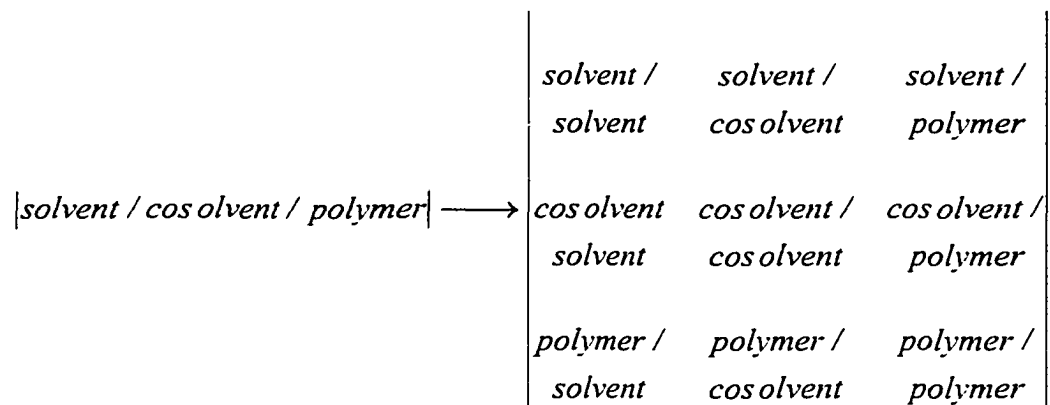


Figure 2-9. A Ternary solvent/cosolvent/polymer system described as a set of binary systems.

Evaluation of the binary pair interactions must necessarily involve an understanding of the intermolecular interactions within the pure components and between unlike component pairs, as well as the ability to optimize the characteristics of the components to predict an ultimately favorable result: the removal of a polymer coating.

3 Molecular Interactions

Intermolecular forces that operate between the molecules of a pure substance determine the thermodynamic properties of that substance. In the case of a mixture, however, consideration must be given not only to interactions between like molecules, but also to interaction between unlike molecules.¹⁸⁶ The purpose of this section is to give a brief introduction to the nature and variety of forces acting between molecules.

When a molecule is in the proximity of another, forces of attraction and repulsion strongly influence its behavior. For example, if there are no forces of attraction, gases would not condense to form liquids and solids, and in the absence of repulsive forces, condensed matter would not show resistance to compression. The net energy of interaction, or potential energy, E , of non-bonded atoms or molecules is the result of both these attractive ($-E_A$) and repulsive effects (E_R). There is one major repulsive interaction, the tendency of two molecules to avoid occupying the same space (known as the occluded space). There are several components to the overall attractive interaction energy (including induced dipole-induced dipole, dipole-induced dipole, dipole-dipole and quadrupole), collectively known as *van der Waals'* forces, as well as specific forces (including Lewis acid-base interactions and hydrogen bonding).

To determine the magnitude of interaction between a solute and a given solvent, it is necessary to consider the balance of the intermolecular forces between solvent-solvent, solute-solute, and solvent-solute pairs of molecules in solution. These intermolecular

forces are considered in terms of the electrical properties of the molecules. The electrical behavior of individual molecules may be classified as (a) electrically neutral and symmetric, usually giving rise to nonpolar molecules; (b) electrically neutral but asymmetric, that is, possessing permanent dipole moments, giving rise to polar molecules; and (c) those having residual valences, giving rise to specific interactions such as Lewis acid/base interactions and hydrogen bonding.¹⁸⁷

3.1 Dispersion Interactions

Every molecule possess an instantaneous electric dipole due to electron oscillations that induce dipoles in neighboring molecules. The result is a net attractive interaction that determines the solubility of a non-polar solute in a non-polar solvent. For non-polar molecules, such as CO₂, these instantaneous dipoles average to zero over time due to their rapidly changing direction and magnitude. A simplified expression can be used to describe the potential energy of this induced dipole-induced dipole interaction, known as dispersion or *van der Waals-London* energy,¹⁸⁸

$$-E_d = \frac{3I_i I_j \alpha_i^p \alpha_j^p}{2(I_i + I_j)r^6} \quad (3-1)$$

Where E_d is the dispersion energy between molecules “ i ” and “ j ”, α^p is the *polarizability* (the ease with which the molecule’s electron “cloud” can be deformed by an electric field), r is the distance between the two molecules, and I is the ionization potential. From eqn. (3-1), it is the *polarizability* which is the key molecular property of the solute and solvent molecules that provides an indication of the strength of their interaction.

London's equation, eqn. (3-1), does not hold at very small separations where the electron clouds overlap and the forces between molecules are repulsive rather than attractive.¹⁸⁹ Figure 3-1 is a representation of Mie's potential energy function, of which the Lennard-Jones potential function (E_{LJ}) is a special case,¹⁹⁰ commonly used to describe the repulsive and attractive potential energies as a function of intermolecular distance r .

$$E_{LJ} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (3-2)$$

As seen in the figure, the component of repulsive interaction rises very steeply to high positive values (E_R) when the intermolecular separation falls below a certain distance ($r < \sigma$) but otherwise has little effect on the net energy, which is seen to be attractive ($-E_A$).

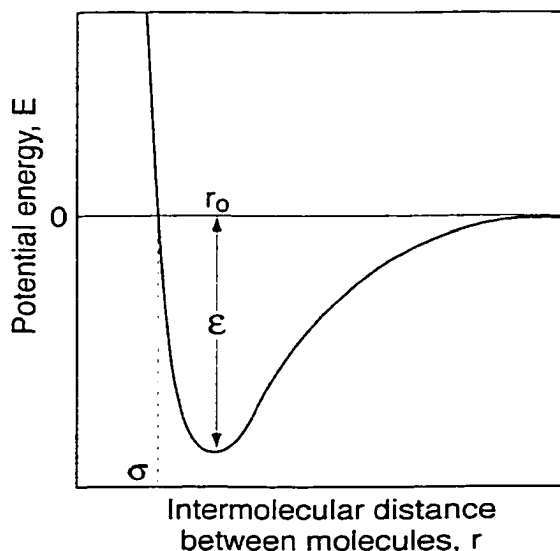


Figure 3-1. Mie's potential, where σ is the collision diameter, at which the potential energy is zero, and the maximum depth of the potential is ϵ and occurs at an equilibrium separation r_0 .

3.2 Polar Interactions

In addition to van der Waals-London dispersion forces, which are always present for all molecules, there can be additional forces of attraction between two molecules if one or both of these has a permanent dipole moment. A permanent dipole moment, μ , is a result of an unsymmetrical charge distribution present in some electrically neutral molecules. If the magnitude of the two equal and opposite charges of this molecular dipole is denoted by q , and the distance of separation l , the dipole moment is given by

$$\mu = q \cdot l \quad (3-3)$$

Apart from hydrocarbons (such as n-hexane, cyclohexane, benzene, etc.) and some symmetrical compounds (such as carbon disulfide, tetrachloromethane, and tetrachloroethene) all common organic solvents possess a permanent dipole moment between 0 and 5.4 Debye (D).¹⁹¹ (1 D is equal to 1.0×10^{-18} electrostatic units or 3.336×10^{-30} coulomb meters).

3.2.1 Dipole-Induced Dipole Interactions

If one of the molecules possesses a permanent dipole moment, μ , it can induce a dipole in the second, neighboring molecule. This induced moment always lies in the direction of the inducing dipole. Thus, attraction always exists between the two molecules, which is independent of temperature.¹⁹² The resulting permanent dipole-induced dipole, or *van der Waals-Debye* interaction energy, can be described by

$$-E_i = \frac{\alpha_i^p \mu_j^2 + \alpha_j^p \mu_i^2}{r^6} \quad (3-4)$$

where E_i is the dipole-induced dipole energy between molecules “ i ” and “ j ”. For *van der Waals-Debye* interactions, it is the strength of the *dipole moment* in D which defines the strength of the molecular interaction.¹⁹³

3.2.2 Dipole- Dipole Interactions

Finally, if both molecules have permanent dipole moments, there will be a force of attraction between the molecules whose strength and direction are fixed as a result of their molecular structure. This situation only exists, however, when the attractive energy is larger than the thermal energy which can prevent the dipoles from optimal orientation, leading to a net attraction which is strongly temperature dependent. The simplified expression that accounts for permanent dipole-permanent dipole, or *van der Waals-Keesom*, potential energy is

$$-E_p \approx \frac{2\mu_i^2 \mu_j^2}{3r^6 kT} \quad (3-5)$$

where E_p is the dipole energy between molecules “ i ” and “ j ”, μ is the strength of the *dipole moment* in D, T is the absolute temperature, and k is Boltzmann’s constant. As with the *van der Waals-Debye* energy, the key parameter which determines the strength of the interaction is the *dipole moment*. It is observed that *van der Waals-Debye* and *van der Waals-Keesom* forces can be significant if the magnitude of either molecular dipole is greater than about ≈ 1.0 Debye. Such large values of μ are commonly associated with functional groups of atoms, such as -OH, -CN, -NH₂, -COOH, and -NO.

Substances that are highly polar at ambient conditions, such as acetone, ammonia, and water, typically have high critical temperatures, as shown in Table 3-1. However, while a polar solvent such as acetone will always have a permanent dipole moment due to its molecular structure, regardless of its physical state, it will exhibit interactions more like those of a non-polar solvent at the elevated temperatures and pressures needed to make it supercritical. This is because as the temperature increases, the attractive interaction energies decrease in magnitude until, at some higher temperature, all dipole orientations are equally populated and the net interaction energy is zero. In fact, it is these high critical temperatures and the inverse temperature-interaction energy relationship that precludes the possibility of finding a highly polar liquid solvent that is also a polar SCF solvent.

Table 3-1. Critical temperature and pressure of some common fluids.

Fluid	Critical Temperature (°C)	Critical Pressure (psi)
Neon, Ne	-229	400
Nitrogen, N ₂	-147	492
Argon, Ar	-122	706
Xenon, Xe	17	858
Carbon dioxide, CO ₂	31	1072
Sulfur hexafluoride, SF ₆	46	545
Propane, C ₃ H ₈	97	617
Ammonia, NH ₃	133	1654
Acetone, C ₃ H ₆ O	235	682
Water, H ₂ O	374	3209

3.2.3 Quadrupolar Interactions

Molecules can also have higher-order polar moments such as a quadrupole moment. CO₂, perhaps the most commonly used SCF, has a rather large quadrupole

moment (-4.3×10^{-26} esu, the sign indicating that the oxygen atoms are negative with respect to the carbon atom¹⁹⁴). In this instance, the simplified formula for the intermolecular quadrupole-quadrupole potential energy is¹⁹⁵

$$-E_Q \approx C_1 \frac{Q_i^2 Q_j^2}{r^{10} kT} \quad (3-6)$$

where E_Q is the quadrupole energy between molecules “ i ” and “ j ”, C_1 is a constant, and Q is the *quadrupole moment*. For this type of interaction, Q , is the important parameter in determining interaction strength. Like dipolar forces of attraction, quadrupolar forces of attraction are inversely proportional to temperature, but decrease in magnitude with intermolecular distance much faster than dipolar forces. Therefore, the effect of a quadrupole moment on thermodynamic properties is expected to be much less significant than a dipole moment.

Quadrupoles and dipoles can also interact according to the simplified expression,¹⁹⁶

$$-E_{Qp} \approx C_2 \frac{\mu_i^2 Q_j^2}{r^8 kT} + C_3 \frac{\mu_j^2 Q_i^2}{r^8 kT} \quad (3-7)$$

where all variables are as described previously.

3.3 Donor-acceptor Interactions

In addition to dispersion and polar interactions, specific donor-acceptor interactions may exist between pairs of molecules. Lewis acid-base interactions are completely

3.4 Strengths of Intermolecular Interactions

Dispersion (van der Waals-London) forces are universal for all atoms and molecules, and it is they that are responsible for the aggregation of molecules which possess neither free charges nor permanent electrical dipole moments. Even for many molecules possessing permanent dipole moments, the major part of the cohesion may be due to dispersion forces. For example, the calculated cohesion energy of methyl ethyl ketone ($\mu = 3.3\text{D}$) at 40°C consists of 22% polar energy, and 78% dispersion energy.¹⁹⁹ In addition, typically, induced intermolecular potentials are negligibly small in comparison with potentials caused by permanent moments. Table 3-2 and 3-3 gives examples of the relative magnitude of van der Waal forces between identical and different molecules, respectively.

Table 3-2. Relative magnitude of van der Waals forces between two identical molecules.²⁰⁰

Molecule	Dipole Moment (D)	VDW Forces between Two Identical Molecules at 0°C ($\text{erg cm}^6 \times 10^{60}$)		
		Dipole Eqn. (3-5)	Induction Eqn. (3-4)	Dispersion Eqn. (3-1)
Carbon Tetrachloride, CCl_4	0	0	0	1460
Cyclohexane, C_6H_{12}	0	0	0	1560
Carbon Monoxide, CO	0.10	0.0018	0.0390	64.3
Hydrogen bromide, HBr	0.80	7.24	4.62	188
Hydrogen chloride, HCl	1.08	24.1	6.14	107
Ammonia, NH_3	1.47	82.6	9.77	70.5
Water, H_2O	1.84	203	10.8	38.1
Acetone, $\text{C}_3\text{H}_6\text{O}$	2.87	1200	104	486

The computed values in Table 3-2 indicate that the contribution of induction forces is small and that even for strongly polar substances, like ammonia, water, or acetone, the contribution of dispersion forces is far from negligible.

Table 3-3. Relative magnitude of van der Waals forces between two different molecules.²⁰¹

Molecules		Dipole Moment (D)		VDW Forces between Two Different Molecules at 0°C (erg cm ⁶ x 10 ⁶⁰)		
(1)	(2)	(1)	(2)	Dipole Eqn. (3-5)	Induction Eqn. (3-4)	Dispersion Eqn. (3-1)
Carbon Tetrachloride, CCl ₄	Cyclohexane, C ₆ H ₁₂	0	0	0	0	1510
Carbon Tetrachloride, CCl ₄	Ammonia, NH ₃	0	1.47	0	22.7	320
Acetone, C ₃ H ₆ O	Cyclohexane, C ₆ H ₁₂	2.87	0	0	89.5	870
Carbon Monoxide, CO	Hydrogen chloride, HCl	0.10	1.08	0.206	2.30	82.7
Water, H ₂ O	Hydrogen chloride, HCl	1.84	1.08	69.8	10.8	63.7
Acetone, C ₃ H ₆ O	Ammonia, NH ₃	2.87	1.47	315	32.3	185
Acetone, C ₃ H ₆ O	Water, H ₂ O	2.87	1.84	493	34.5	135

Again, it is noticed that polar forces are not important when the dipole moment is less than about 1 D and induction forces always tend to be smaller than dispersion forces.

Donor-acceptor interactions between solute and solvent molecules generally have a greater influence than the combined van der Waals forces, due to their greater bond energies. Strong Lewis acid-base bond energies lie between -42 and -188 kJ/mol, and weaker complexes, while less than approximately -42 kJ/mol, are usually still larger than van der Waals forces, which range from -4 to -40 kJ/mol.²⁰² The bond dissociation

energy for normal hydrogen bonds is from -13 to -42 kJ/mol,²⁰³ while the strongest hydrogen bonds, those formed with the most electronegative elements (i.e. fluorine), are as large as -155 kJ/mol. The greater strength of hydrogen bonds as compared with van der Waals forces is due to the much smaller size of the hydrogen atom relative to any other atom, which allows it to approach another atom more closely. Table 3-4 gives a summary of the strengths of the various intermolecular interactions.

Table 3-4. Interaction strengths.

Interaction Type	Interaction Strength
Van der Waals	- 4 to - 40 kJ/mol
Hydrogen bonds (normal - large)	- 13 to - 42 kJ/mol (up to - 155 kJ/mol)
Weak Lewis acid/base	< - 42 kJ/mol but generally larger than van der Waals
Strong Lewis acid/base	- 42 to - 188 kJ/mol

4 Solubility Parameters

In the previous chapter, the types of interactions which can occur between solvent, cosolvent, and polymer molecules were described. The selection of a “good” solvent, which we will assume will be a solvent/cosolvent mixture, for a given polymer requires some method of quantifying the type and magnitude of each of these intermolecular interactions, both within each pure component and between components. If the type and strength of the interactions occurring within the solvent and polymer can be matched, then the thermodynamic conditions are tuned to provide favorable (attractive) interactions between them. The most widely used method for quantifying intermolecular interactions in condensed (liquid and solid) systems is the solubility parameter. The solubility parameter is obtained from an approximation of a system’s cohesive energy density, which, in turn, is intimately connected to the thermodynamic concept of internal pressure.

4.1 Cohesive Energy Density and Internal Pressure

The foundation of the first solubility parameter theory was developed as early as 1916²⁰⁴ and was formalized by Hildebrand and Scott in 1950.²⁰⁵ This theory was derived from an approximation of the internal pressure of a fluid, which was later termed the cohesive energy density, based on work conducted in 1928,²⁰⁶ 1929,²⁰⁷ 1932,²⁰⁸ and 1950²⁰⁹ where the two terms, internal pressure and cohesive energy density, were in fact

found to be nearly equivalent for nonpolar liquids. Subsequently, because of the ease in calculating the cohesive energy density of liquids at normal conditions, later workers have followed this approximation, so that the distinction between internal pressure and cohesive energy density has become blurred. This Section will examine the basis of internal pressure and the derivation of cohesive energy density in order to understand the significance of the two quantities, and their differences.

The first law of thermodynamics for a system that undergoes a change of state is

$$U_2 - U_1 = \Delta U = {}_1Q_2 - {}_1W_2 \quad (4-1)$$

where U_1 and U_2 are the initial and final values of the total energy U of the system, ${}_1Q_2$ is the heat transferred to the system during the change from state 1 to 2, and ${}_1W_2$ is the work done by the system during the change. In differential form, eqn. (4-1) is written as follows,

$$dU = \delta Q - \delta W \quad (4-2)$$

The physical significance of the property U is that it represents *all* the energy of the system in the given state. This energy might be present in a variety of forms, including the kinetic or potential energy of the system as a whole with respect to the chosen coordinate frame, energy associated with motion and position of the molecules, energy associated with structure of the atom, chemical energy such as is present in a storage battery, energy present in a charged condenser, etc.²¹⁰

It is convenient to separate the kinetic energy (KE) and potential energy (PE) of the system as a whole, and then to consider all the remaining energy of the system in a single property called the internal energy, E . Therefore,

$$E + KE + PE = U \quad (4-3)$$

The first law for a change of state of a system may therefore be written as

$$dE + d(KE) + d(PE) = \delta Q - \delta W \quad (4-4)$$

If we assume that there are no changes in kinetic or potential energy of the system as a whole and that the only work done by the system during the process is the work of expansion by the system against its surroundings, then

$$dE = \delta Q - PdV \quad (4-5)$$

where $PdV = \delta W$. At this point we may define another property called entropy, designated by S . Entropy is defined as a property of a substance in accordance with the relation²¹¹

$$dS = \left(\frac{\delta Q}{T} \right)_{rev} \quad (4-6)$$

so that

$$\delta Q = TdS \quad (4-7)$$

for a reversible process. This leads to the following important thermodynamic relation for a simple compressible substance,

$$dE = TdS - PdV \quad (4-8)$$

Differentiating eqn. (4-8) with respect to V at constant T

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P\left(\frac{\partial V}{\partial V}\right)_T \quad (4-9)$$

and using the Maxwell relation,

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad (4-10)$$

gives “the thermodynamic equation of state”

$$\boxed{\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P} \quad (4-11)$$

The individual terms in eqn. (4-11) can be defined as,

$$\left(\frac{\partial E}{\partial V}\right)_T = \text{Internal Pressure,}$$

$$T\left(\frac{\partial P}{\partial T}\right)_V = \text{Thermal Pressure,} \quad (4-12)$$

P = External Pressure.

Equation (4-11) forms the basis of the cohesive energy density, developed by Hildebrand and Scott.²¹² A brief outline of this work is as follows.

In general, a functional relationship among any three-system properties, for a one-component system, could be called an equation of state. However, by common usage the expression equation of state usually refers to relationships between pressure, temperature and specific volume.²¹³ Three broad classifications of equations of state can be identified, namely, generalized, empirical, and theoretical. The best known of the generalized equation of state is also the oldest, the van der Waals equation, which was presented in 1873 as a semi-theoretical improvement over the ideal gas equation.²¹⁴ The van der Waals equation of state is,

$$P + \frac{a}{V^2} = \frac{RT}{V - b} \quad (4-13)$$

where a , b are called the attraction and repulsion parameter, respectively and are usually assumed to be constant for a given substance.²¹⁵ Differentiating the van der Waals equation with respect to T and constant V

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{R}{V - b} \quad (4-14)$$

Substituting the result of eqn. (4-14) into eqn. (4-13) and comparing to eqn. (4-11) implies that

$$\left(\frac{\partial E}{\partial V} \right)_T = \frac{a}{V^2} \quad (4-15)$$

Scott went on to state that “over a small range of volumes”, E could be represented in the functional form,²¹⁶

$$E = -\frac{a}{V^n} \quad (4-16)$$

so that by differentiating eqn. (4-16) with respect to volume at constant temperature, $(\partial E/\partial V)_T$ can be expressed as²¹⁷

$$\left(\frac{\partial E}{\partial V}\right)_T = \frac{na}{V^{n+1}} = \frac{-nE}{V} \quad (4-17)$$

Further, Scott states that for most practical purposes the cohesive energy per mole E may be replaced by $-\Delta E$ ²¹⁸ so that eqn. (4-17) can be rewritten as

$$\boxed{\left(\frac{\partial E}{\partial V}\right)_T = \frac{n\Delta E}{V}} \quad (4-18)$$

Thus $(\Delta E/V)$, referred to by Hildebrand as the cohesive energy density, and $(\partial E/\partial V)_T$, the internal pressure, are related by the quantity n . It can be shown that for a liquid obeying van der Waals equation of state, eqn. (4-13), $n = 1$, and the cohesive energy density is therefore equal to the internal pressure. Further, Hildebrand and coworkers found that for nonpolar/nonassociating liquids, where intermolecular interactions are weak, n is, in fact, not far from unity.^{219,220,221} Whereas for polar or associating liquids or liquids which are not greatly expanded over their close-packed structure, where repulsive forces play an important role (such as mercury at room temperature), the internal pressure is not equivalent to the cohesive energy density.

Table 4-1 gives a comparison of cohesive energy density and internal pressure for the solids and liquids, as evaluated by Hildebrand and Scott.

Table 4-1. Values of n for pure organic and inorganic liquids.²²²

Liquid	μ (D) ²²³ dipole momer	$V^2 \left(\frac{\partial E}{\partial V} \right)_T$ (kcal liters)	$V \Delta E^V$ (kcal liters)	n
n-Heptane	0.0	13.14	12.01	1.09
Silicon tetrachloride	0.0	8.23	7.56	1.09
Carbon tetrachloride	0.0	7.56	7.04	1.07
Benzene	0.0	7.07	6.70	1.05
Silicon tetrabromide	0.0	12.90	12.40	1.04
Stannic chloride	0.0	10.95	10.55	1.04
Titanium tetrachloride	0.0	10.15	9.98	1.02
Chloroform	1.1	5.76	5.67	1.02
Ethyl ether	1.3	6.58	6.49	1.01
Acetone	2.9	4.33	4.86	0.89
Carbon disulfide	0.0	3.27	3.67	0.89
Methanol	1.7	1.16	3.46	0.34
Mercury	-	0.69	2.11	0.33

In regards to the low value of n found for carbon disulfide Hildebrand²²⁴ stated that while carbon disulfide has practically no dipole moment it is less symmetrical than carbon tetrachloride and it is therefore reasonable to expect a value less than unity. However in a similar experiment conducted in 1976,²²⁵ a much different value for n was found for carbon disulfide (1.06) and it was suggested in this article that the earlier value was incorrect.

Since this early work of Hildebrand and others was conducted (spanning from 1928 to 1950), other studies^{226,227,228,229,230} have evaluated the internal pressure and cohesive energy density for a range of liquid solvents. An expanded tabulation of $(\partial E / \partial V)_T$ and $(\Delta E / V)$, along with the corresponding value of n , is given in Table 4-2

Table 4-2. Reported values of internal pressure, cohesive energy density, and n for pure liquids (sorted by decreasing values of n).

Solvent	$\left(\frac{\partial E}{\partial V}\right)_T$ (J/cm ³)	$\left(\frac{\Delta E}{V}\right)$ (J/cm ³)	μ (D) dipole moment	n	Ref
1,4-dioxane	493.7	396.2	0.45	1.2	231
Cyclohexane	321.8	282.3	0	1.14	232
Methylcyclohexane	296.7	260.2	0	1.14	233
Benzene	368.2	350.6	0	1.1	231
Carbon tetrachloride	338.9	307.9	0	1.1	231
Octane	266.1	242.3	0	1.1	233
Nonane	276.1	249.0	0	1.1	233
Decane	280.3	253.1	0	1.1	233
Benzene	363.1	342.6	0	1.06	231
Carbon disulfide	445.8	420.6	0	1.06	231
Hexane	238.9	225.1	0	1.06	233
Pentane	220.5	210.0	0	1.05	233
Toluene	354.8	337.2	0.36	1.05	233
Diethyl ether	263.6	250.6	1.2	1.05	233
o-Xylene	356.1	341.8	0.50	1.04	233
Ethyl acetate	355.6	341.8	1.88	1.04	231
Trichloromethane	369.5	361.9	1.1	1.02	233
Methyl acetate	372.4	374.0	1.61	0.99	231
Dichloromethane	407.9	414.2	1.9	0.98	233
Methyl ethyl ketone	341.8	382.8	2.76	0.89	233
Acetone	330.5	394.6	2.88	0.84	231
Dimethylformamide	479.5	582.4	3.82	0.82	231
Dimethyl sulphoxide	520.9	705.4	4.49	0.74	231
Dimethyl sulphoxide	516.7	704.7	4.49	0.733	234
t-Butyl alcohol	338.9	473.8	1.67	0.72	233
Propylene carbonate	543.5	762.7	4.94	0.71	231
Acetonitrile	394.6	582.4	3.84	0.68	231
Butanol	300.0	485.4	1.66	0.62	233
Ethylene glycol	502.1	892.0	2.31	0.56	231
Propanol	287.9	606.7	1.68	0.47	233
Ethanol	292.9	674.9	1.68	0.43	231
Formamide	554.4	1574.9	3.37	0.35	231
Methanol	293.0	860.1	1.66	0.34	234
Methanol	288.3	873.6	1.66	0.33	231
Water	150.6	2302.0	1.84	0.07	231

The additional data shown in Table 4-2 further demonstrates that n is near unity for nonpolar liquids, and also for polar liquids where the dipole moment is less than 2 D and where specific interactions (particularly hydrogen bonding) is largely absent. Also, while no direct evaluation of the value of n has been found in the literature, a comparison of the values in Tables 4-1 and 4-2 strongly suggests that the value of n for CO₂, is expected to be near unity, and as a result, the internal pressure and cohesive energy density are approximately equal. In the remainder of this work, the equivalence of internal pressure and cohesive energy density, at least for the case of CO₂, is assumed.

However, in the presence of strong self-association (again, primarily hydrogen bonding), n is significantly less than unity. The divergence between internal pressure and cohesive energy density in the presence of strong specific interactions can be understood if we examine the physical meaning of $(\Delta E/V)$ and $(\partial E/\partial V)_T$. The cohesive energy density is a measure of the total molecular cohesion, or sum total of the attractive interactions per unit volume when all intermolecular bonds associated with that volume are broken, (i.e., vaporized to an ideal gas). Internal pressure, on the other hand, is a measure of the change in internal energy of 1 mole of solvent as it undergoes a very small isothermal expansion. This small expansion does not necessarily disrupt all the intermolecular interactions associated with 1 mole of solvent. The most important contributions to internal pressure will therefore come from those interactions which vary most rapidly near the equilibrium molecular separation in the solvent (recall r_0 from Figure 3-1). Dispersion, repulsion, and dipole-dipole interactions all vary rapidly with intermolecular separation, see eqns. (3-1), (3-4), and (3-5), and so we might expect the internal pressure to reflect mainly these interactions.²³⁵ This is why, in Tables 4-1 and 4-

2, the values of internal pressure approach those of cohesive energy density for non-polar solvents, and polar liquids where the dipole moment is less than 2 D, where only dispersion and repulsion and weak polar interactions (i.e., no specific interactions) exist. That is, the small volume expansion associated with the internal pressure disrupts the dispersion and repulsion and weak polar interactions as effectively as complete vaporization.

4.2 Empirical Models of Solubility Parameters

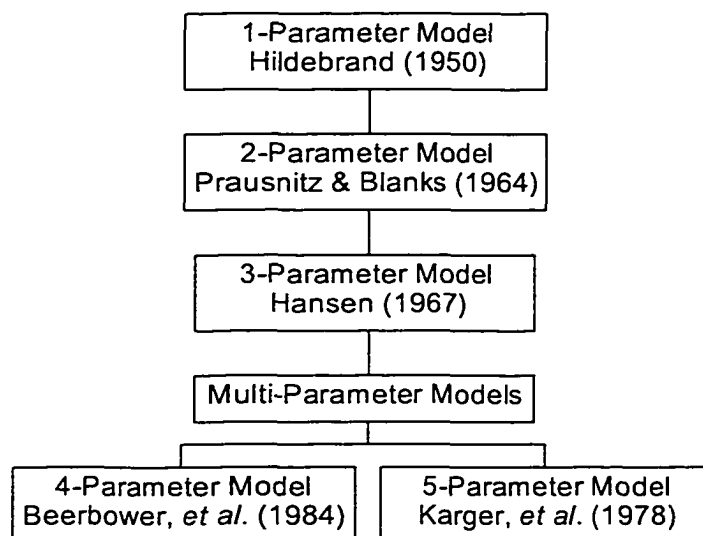


Figure 4-1. Chronological evolution of empirical solubility parameter models.

4.2.1 One Parameter Model – (Hildebrand)

The thermodynamic criteria of solubility are based on the Gibbs free energy of mixing, $\Delta_m G$. Two substances are mutually soluble if $\Delta_m G$ is negative. By definition,

$$\Delta_m G = \Delta_m H - T\Delta_m S \quad (4-19)$$

where $\Delta_m H$ and $\Delta_m S$ are the enthalpy and entropy of mixing, respectively; and T is the temperature. As the entropy change of a mixing process, $\Delta_m S$, is positive, $\Delta_m H$ must be negative or slightly positive to have $\Delta_m G \leq 0$. Therefore, the miscibility of two compounds depends on the magnitude of $\Delta_m H$.

As early as 1916 Hildebrand tried to correlate solubility with the cohesive properties of solvents. In 1949 he proposed the Scatchard-Hildebrand equation for the calculation of the enthalpy of mixing of two liquids.²³⁶

$$\frac{\Delta_m H}{V} = \left[\left(\frac{E_1}{V_1} \right)^{1/2} - \left(\frac{E_2}{V_2} \right)^{1/2} \right]^2 \phi_1 \phi_2 \quad (4-20)$$

where V is the total molar volume of the mixture, E_i is the molar potential energy or energy of attraction of species 1 and 2 respectively, V_1 , V_2 are the molar volumes of species 1 and 2, respectively, and ϕ_1 , ϕ_2 are the volume fraction of species 1 and 2, respectively.

The energy of attraction, E , divided by the condensed molar volume was termed by Hildebrand the cohesive energy density, eqn. (4-18), and is the basis of the original definition by Hildebrand and Scott of what is now generally called the *Hildebrand solubility parameter*, δ . In this definition, Hildebrand equates the energy of attraction E , with the energy of isothermal vaporization to the gas at zero pressure (i.e. infinite separation of the molecules), ΔE . Accordingly, Hildebrand's solubility parameter, defined as the square root of the cohesive energy density,²³⁷ is expressed as

$$\delta = \left(\frac{\Delta E}{V} \right)^{1/2} \quad (4-21)$$

The Scatchard-Hildebrand equation can then be rewritten as

$$\frac{\Delta_m H}{V} = [\delta_1 - \delta_2]^2 \phi_1 \phi_2 \quad (4-22)$$

Examination of eqn. (4-19) shows that the solubility is maximized when $\Delta_m H$ is minimized, and from eqn. (4-22) it is seen that that this occurs when the respective solubility parameters are equal or when their difference is small. This is in accordance with the general rule that chemical and structural similarity favors solubility, or “like dissolves like”.

In Hildebrand’s development of the solubility parameter approach, the existence of polar interactions and of specific interactions such as hydrogen bonding, were explicitly neglected, in other words, he assumed $n = 1$. Therefore, the Hildebrand parameter is limited to nonpolar or weakly polar systems where no specific interactions are expected, as in *regular* solutions. Hildebrand describes the term regular solution as “one involving no entropy change when a small amount of one of its components is transferred to it from an ideal solution of the same composition, the total volume remaining unchanged.”²³⁸ It is also necessary to emphasize that the Hildebrand parameter is, fundamentally, a liquid state property. When gases are considered they are treated as hypothetical “liquid” solutes at atmospheric pressure, while substances that are solids at normal temperatures are treated as supercooled liquids.

4.2.2 Two Parameter Model – (Prausnitz and Blanks)

A shortcoming of the early solubility parameter work of Hildebrand is that the approach was limited to solutions of weakly interacting components, as defined by Hildebrand and Scott, and did not account for association between molecules, such as those which polar and hydrogen bonding interactions would require. An early extension of the solubility parameter approach was to systems containing compounds with permanent dipoles. van Arkel,²³⁹ Small,²⁴⁰ and Prausnitz and co-workers²⁴¹ accounted for polar interactions by dividing the total solubility parameter into two components, defining a nonpolar cohesion parameter (δ_λ) and a polar parameter (δ_τ). Dividing the energy of vaporization of a polar compound into nonpolar and polar parts leads to the following definitions,

$$\text{Nonpolar solubility parameter } \delta_\lambda = \left(\frac{\Delta E_{(np)}}{V} \right)^{1/2} \quad (4-23)$$

$$\text{Polar solubility parameter } \delta_\tau = \left(\frac{\Delta E_{(p)}}{V} \right)^{1/2} \quad (4-24)$$

where $\Delta E_{(np)}$ and $\Delta E_{(p)}$ are the nonpolar and the polar contributions to the energy of vaporization, and

$$\Delta E_{(total)} = \Delta E_{(np)} + \Delta E_{(p)} \quad (4-25)$$

The energy of vaporization of a polar compound was then divided into polar and nonpolar contributions using the homomorph method of Brown.²⁴² The homomorph method will be described in detail in the next chapter, but, in brief, postulates that the homomorph of a polar molecule is a nonpolar molecule having nearly the same size and shape as that of the polar molecule. This concept is relatively easy to apply, as the energy of vaporization of the polar molecule is simply the difference between the experimentally determined total energy of vaporization and the energy of vaporization of the homomorph molecule, at the same reduced temperature. Blanks and Prausnitz²⁴³ published a homomorphic plot of the energy of vaporization for straight chain hydrocarbons. Similarly, Weimer and Prausnitz²⁴⁴ prepared homomorph plots of the cohesive pressure against molar volume at various reduced temperatures for alkanes, cycloalkanes, and aromatic hydrocarbons. These figures also have been reproduced elsewhere.^{245,246}

4.2.3 Three Parameter Model – (Hansen)

In 1967, Hansen²⁴⁷ proposed a further extension of the Prausnitz and Blanks 2-parameter model by separating the single polar contribution to the total cohesive energy density into two distinct polar and hydrogen bonding contributions. Therefore, the basis of Hansen Solubility Parameters (HSP) is the assumption that the total cohesive energy (E) is made up of the additive contributions from nonpolar (dispersion) interactions (E_d), polar (dipole-dipole and dipole-induced dipole) interactions (E_p), and hydrogen bonding or other specific association interactions (including Lewis acid-base interactions) (E_h):

$$E = E_d + E_p + E_h \quad (4-26)$$

Dividing each contribution by the molar volume gives the square of the total solubility parameter as the sum of the squares of the Hansen dispersion (δ_d), polar (δ_p), and hydrogen bonding (δ_h) components.

$$\frac{E}{V} = \frac{E_d}{V} + \frac{E_p}{V} + \frac{E_h}{V} \quad (4-27)$$

so that

$$\boxed{\delta_T^2 = \delta_d^2 + \delta_p^2 + \delta_h^2} \quad (4-28)$$

where

$$\delta_d^2 = \frac{E_d}{V}; \quad \delta_p^2 = \frac{E_p}{V}; \quad \text{and } \delta_h^2 = \frac{E_h}{V} \quad (4-29)$$

Hansen's total solubility parameter, δ_T , should equal the Hildebrand solubility parameter, eqn. (4-21), although the two quantities may differ for materials with specific interactions when these specific interactions are determined by different methods.²⁴⁸

Hansen's development of the HSP methodology is tied to the reasoning that materials having similar HSP have high affinity for each other, and the extent of the similarity in a given situation will determine the extent of the (favorable) interaction. The same cannot be said of the Hildebrand solubility parameter. Ethanol and nitromethane, for example, have similar Hildebrand solubility parameters (26.1 vs. 25.1 MPa^{1/2}), but their affinities are quite different. Ethanol is water soluble, while

nitromethane is not.²⁴⁹ Hansen has applied the HSP approach, with general success, in predicting polymer solubility that could not have been predicted by Hildebrand parameters. In fact, Hansen demonstrated that mixtures of nitroparaffins and alcohols, which by themselves are nonsolvents for a given polymer, are successfully predicted, through addition of their HSP's, to generate a synergistic mixture which will dissolve the polymer, in agreement with experiment.

It has been shown through numerous examples, by various authors, that the 3-parameter approach of Hansen represents a significant improvement in the description of solubility behavior of real fluids. In addition to polymer solubility (swelling) studies, HSP's have been applied to biological materials, barrier properties of polymers, as well as the characterization of surfaces, pigments, fillers, and fibers.²⁵⁰ Being able to characterize organic and inorganic solids, liquids, and gases with the same 3-parameter parameter model also enables interpretation of situations involving mutual solubility and material compatibility.

4.2.4 Multi-Parameter Models

Other multicomponent solubility parameter approaches have been developed. Beerbower, Martin, and Wu²⁵¹ developed a four-component approach and a five-component approach has been used by a variety of researchers.^{252,253,254} In the five parameter approach, the total solubility parameter consists of separate terms for dispersion (induced dipole-induced dipole) interactions (δ_d), orientation (dipole-dipole) interactions (δ_o), induction (dipole-induced dipole) interactions (δ_i), Lewis acid

interactions (δ_a), and Lewis base interactions (δ_b). Hildebrand's total solubility parameter was related to these component parameters by²⁵⁵

$$\delta^2 = \delta_d^2 + \delta_o^2 + 2\delta_i\delta_d + 2\delta_a\delta_b \quad (4-30)$$

In the four-component approach, the induction interaction is ignored on the grounds that its inclusion did not improve significantly the solubility predictions, so eqn. (4-30) reduces to²⁵⁶

$$\delta^2 = \delta_d^2 + \delta_o^2 + 2\delta_a\delta_b \quad (4-31)$$

Identifying δ_o with δ_p and δ_h^2 with $2\delta_a\delta_b$ reduces the 4- parameter model to the 3- parameter (Hansen) model, eqn. (4-28).

Table 4-3 is a comparison of the parameter values obtained with the various solubility parameter models.

Table 4-3. Solubility parameter values – empirical models.²⁵⁷

Compound	One-Parameter Hildebrand	Two-Parameter	Three-Parameter Hansen	Four-Parameter	Five-Parameter
Chloroform, CHCl ₃	$\delta = 19.0$	$\delta_{\lambda} = 14.9$	$\delta_d = 17.8$	$\delta_d = 17.8$	$\delta_d = 16.6$
		$\delta_{\tau} = 10.0$	$\delta_p = 3.1$	$\delta_o = 3.1$	$\delta_o = 6.1$
		$\delta_T = 17.9$	$\delta_h = 5.7$	$\delta_a = 6.1$	$\delta_i = 1.0$
			$\delta_T = 18.9$	$\delta_b = 2.7$	$\delta_a = 13.3$
				$\delta_T = 18.9$	$\delta_b = 1.0$
					$\delta_T = 19.3$
Chlorobenzene, C ₆ H ₅ Cl	$\delta = 19.4$	$\delta_{\lambda} = 18.9$	$\delta_d = 19.0$	$\delta_d = 19.0$	$\delta_d = 18.8$
		$\delta_{\tau} = 6.0$	$\delta_p = 4.3$	$\delta_o = 4.3$	$\delta_o = 3.9$
		$\delta_T = 19.8$	$\delta_h = 2.0$	$\delta_a = 2.0$	$\delta_i = 0.6$
			$\delta_T = 19.6$	$\delta_b = 1.0$	$\delta_a = -$
				$\delta_T = 19.6$	$\delta_b = 2.1$
					$\delta_T = 19.9$
Dimethyl- formamide C ₃ H ₇ NO	$\delta = 24.8$	$\delta_{\lambda} = 17.0$	$\delta_d = 17.4$	$\delta_d = 17.4$	$\delta_d = 16.2$
		$\delta_{\tau} = 16.5$	$\delta_p = 13.7$	$\delta_o = 13.7$	$\delta_o = 12.7$
		$\delta_T = 23.7$	$\delta_h = 11.3$	$\delta_a = 7.0$	$\delta_i = 4.9$
			$\delta_T = 24.9$	$\delta_b = 9.0$	$\delta_a = -$
				$\delta_T = 24.8$	$\delta_b = 9.4$
					$\delta_T = 24.1$
Dimethyl- sulfoxide, C ₂ H ₆ OS	$\delta = 24.5$	$\delta_{\lambda} = 17.5$	$\delta_d = 18.4$	$\delta_d = 18.4$	$\delta_d = 17.2$
		$\delta_{\tau} = 19.4$	$\delta_p = 16.4$	$\delta_o = 16.4$	$\delta_o = 12.5$
		$\delta_T = 26.1$	$\delta_h = 10.2$	$\delta_a = 4.5$	$\delta_i = 4.3$
			$\delta_T = 26.7$	$\delta_b = 11.7$	$\delta_a = -$
				$\delta_T = 26.7$	$\delta_b = 10.6$
					$\delta_T = 24.9$
Acetone, C ₃ H ₆ O	$\delta = 20.2$	$\delta_{\lambda} = 15.7$	$\delta_d = 15.5$	$\delta_d = 15.5$	$\delta_d = 13.9$
		$\delta_{\tau} = 12.6$	$\delta_p = 10.4$	$\delta_o = 10.4$	$\delta_o = 10.4$
		$\delta_T = 20.1$	$\delta_h = 7.0$	$\delta_a = 4.9$	$\delta_i = 3.1$
			$\delta_T = 20.0$	$\delta_b = 4.9$	$\delta_a = -$
				$\delta_T = 20.0$	$\delta_b = 6.1$
					$\delta_T = 19.6$
1,4-Dioxane, C ₄ H ₈ O ₂	$\delta = 20.5$	$\delta_{\lambda} = 17.5$	$\delta_d = 19.0$	$\delta_d = 19.0$	$\delta_d = 16.0$
		$\delta_{\tau} = 9.5$	$\delta_p = 1.8$	$\delta_o = 1.8$	$\delta_o = 10.6$
		$\delta_T = 19.9$	$\delta_h = 7.4$	$\delta_a = 2.1$	$\delta_i = 2.0$
			$\delta_T = 20.5$	$\delta_b = 13.3$	$\delta_a = -$
				$\delta_T = 20.5$	$\delta_b = 9.4$
					$\delta_T = 20.7$

As can be observed from Table 4-3, the three, four, and five parameter approaches generally result in similar values for the total solubility parameter.

However, of all the solubility parameter models, the most widely used has been the 3-parameter approach proposed by Hansen. As a result, there is a large body of tabulated HSP data, both measured and calculated, for a large number of compounds. (The four-parameter approach, should a larger set of data be developed, may become a generally acceptable improvement on the 3-parameter model, as it takes into account the unsymmetrical nature of Lewis acid-base interactions. The five-component approach, which was developed for the optimization of liquid chromatography, has proved too cumbersome for widespread use.²⁵⁸) Therefore, because the Hansen 3-parameter model approach provides a reasonable compromise between descriptive accuracy and simplicity, and is well established in the field of solubility characterization, this methodology was chosen for the current work.

5 Pure Component Solubility Parameters

5.1 Hildebrand Solubility Parameters – Pure CO₂

In his high pressure gas chromatography work, Giddings²⁵⁹ recognized that gases subjected to high pressures, where densities approach those of liquids, acquire solvent properties much like liquids (see Table 2-1). This similarity with liquid solvents led Giddings to develop a corresponding states approach, based on Hildebrand's (liquid) solubility parameter concept.

5.1.1 Giddings Approximation

Hildebrand and Scott,²⁶⁰ developed a relationship between the solubility parameter and the critical pressure, P_c , from the equality of eqn (4-18), when $n = 1$, eqn. (4-15), and eqn. (4-21).

$$\left(\frac{\partial E}{\partial V}\right)_T = \frac{\Delta E}{V}; \quad \left(\frac{\partial E}{\partial V}\right)_T = \frac{a}{V^2}; \quad \text{and } \delta = \left(\frac{\Delta E}{V}\right)^{1/2} \quad (5-1)$$
$$\therefore \delta = \frac{a^{1/2}}{V}$$

where a is known as the van der Waals attraction parameter and the volume, V , is identified with van der Waals parameter b . This determination of V was originally proposed by van Laar,²⁶¹ who assumed that liquids not significantly expanded could be

approximated by the minimum volume according to the van der Waals equation, namely the parameter b ,²⁶²

$$\delta = \frac{a^{1/2}}{b} \quad (5-2)$$

Expressing the van der Waals parameters a and b in terms of critical properties,

$$a = \frac{27R^2T_c^2}{64P_c}, \text{ and } b = \frac{RT_c}{8P_c} \quad (5-3)$$

so that

$$\therefore \delta = \frac{\left(\frac{27R^2T_c^2}{64P_c} \right)^{1/2}}{\frac{RT_c}{8P_c}} = (27P_c)^{1/2} \quad (5-4)$$

However, Hildebrand found that to obtain satisfactory agreement with directly measured values of $(\partial P/\partial T)_v$, referred to by Hildebrand as the “thermal pressure coefficient”,²⁶³ the numerical constant $\sqrt{27}$ should be replaced with 1.25, so that

$$\delta = 1.25P_c^{1/2} \quad (5-5)$$

where P_c is the critical pressure in atmospheres and δ is in $(\text{cal}/\text{cm}^3)^{1/2}$.

Hildebrand²⁶⁴ compared the accuracy of eqn. (5-5) with solubility parameter values calculated from eqn. (5-1) and eqn. (5-77) (reviewed later in this chapter). The result of his comparison is reproduced in Table 5.1.

Table 5-1. Comparison of solubility parameter equations.

Substance	Eqn. (5-77) $\delta \cong \left(\frac{\Delta H^v - RT}{V_m} \right)^{1/2}$	V (L)	a (liter ² atm)	Eqn. (5-1) $\delta \cong \frac{a^{1/2}}{V}$	P _c (atm)	Eqn. (5-5) $\delta = 1.25 P_c^{1/2}$
n-Hexane	7.3	132	24.4	5.8	29.5	6.8
Ethyl ether	7.5	105	17.4	6.2	35.5	7.4
Cyclohexane	8.2	109	22.8	6.8	40.4	8.0
Carbon tetrachloride	8.6	97	20.4	7.2	45.0	8.4
Benzene	9.15	89	18.0	7.4	47.7	8.6
Chloroform	9.3	81	25.4	9.7	65.8	10.1
Carbon disulfide	10.0	61	11.6	8.7	76	10.9

All values were determined at 25°C; δ units in cal^{1/2} cm^{-3/2}.

As can be seen from the table, the approximate ranking of the solvents according to solubility parameter value is retained, but the numerical values for individual substances differ considerably.

Giddings followed the development of Hildebrand and Scott, but instead of using the van Laar assumption, eqn. (5-2), he substituted van der Waals' constants and used reduced variables,

$$a = \frac{27R^2T_c^2}{64P_c}, \quad b = \frac{RT_c}{8P_c} \quad \text{and} \quad b = \frac{V_c}{3} \quad (5-6)$$

$$V_r = \frac{V}{V_c} \Rightarrow V = V_r V_c = 3V_r b$$

and

$$\delta = \frac{\left(\frac{27R^2T_c^2}{64P_c}\right)^{1/2}}{3V_r b} = \frac{\left(\frac{27R^2T_c^2}{64P_c}\right)^{1/2}}{3V_r \left(\frac{RT_c}{8P_c}\right)} = \frac{(3P_c)^{1/2}}{V_r} = (3P_c)^{1/2} \rho_r \quad (5-7)$$

Giddings then adopted Hildebrand's empirical constant of 1.25 in place of $\sqrt{3}$,

$$\delta = 1.25 P_c^{1/2} \rho_r \quad (5-8)$$

Giddings extended this equation, strictly applicable only to liquids, to supercritical fluids by assuming the equivalence of gases and liquids at a common density. This equivalence says simply that the solubility parameter remains a simple linear function of density in the liquid, gas, and supercritical fluid regions. That is, density changes smoothly and continuously as you trace a path, shown in Figure 5-1, from the liquid region, around the critical point (in the supercritical fluid region), and into the gas region.

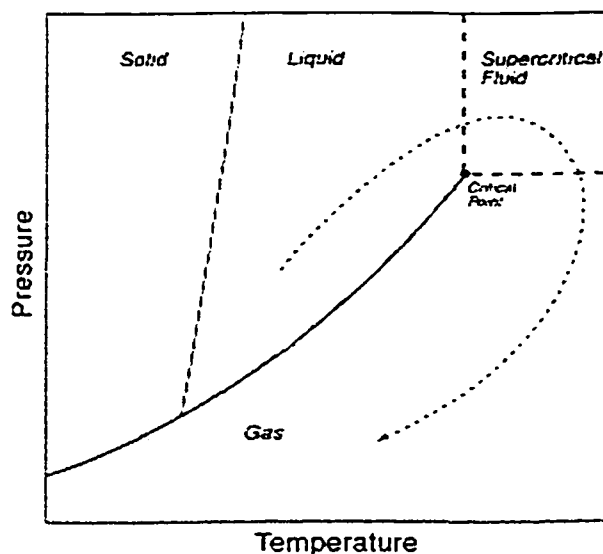


Figure 5-1. Schematic illustration of the continuous change in fluid density on going from a liquid, to a supercritical fluid, to a gas.

This corresponding states assumption leads to the following equation for describing the solubility parameter of a fluid, applicable to the liquid, supercritical, or gas state

$$\delta = 1.25 P_c^{1/2} \left(\frac{\rho_r}{\rho_{r(liq)}} \right) \quad (5-9)$$

where $\rho_{r(liq)}$ is reduced density of the liquid phase at its normal boiling point. Giddings made an analysis of some fluids “commonly used as chromatographic stationary phases” and determined an average value of $\rho_{r,liq} = 2.66$, so that,

$$\begin{aligned} \delta &= 1.25 P_c^{1/2} \rho_r^{SCF} / 2.66 \\ &= 0.47 P_c^{1/2} \rho_r^{SCF} \end{aligned} \quad (5-10)$$

Equation (5-10) has become the most widely used method to calculate the (1-component) solubility parameter for supercritical fluids.^{265,266,267,268} Unfortunately, little or no experimental verification of relations such as the one presented by Giddings exists, and hence their accuracy cannot be assessed. This type of empirical correlation, however, is expected to be less accurate for fluids that are gases at room temperature and pressure and for polar and/or hydrogen bonding fluids where specific interactions occur.

The liquid solvents evaluated by Giddings to arrive at the value $\rho_r^{liquid} = 2.66$ are unknown. In Tables 5-2, 5-3, and 5-4, values of $\rho_r^{liquid} = \rho_{1 atm BP} / \rho_c$ are given for a range of fluids, including those which are gases and liquids at room temperature and pressure

(RTP). CO₂ sublimates from a gas to solid phase at 25°C and 1 atm, and therefore boiling point data are not available, at the stated conditions, for this compound.

Table 5-2. Reduced density of (gaseous) fluids at the normal boiling point.

Fluid (Gas at RTP)	ρ_C (g/cm ³)	$\rho_{1 \text{ atm BP}}$ (g/cm ³)	$\frac{\rho_{1 \text{ atm BP}}}{\rho_C}$
Sulfur Dioxide	0.524	1.462	2.79
Argon	0.536	1.39	2.59
Nitrogen	0.311	0.808	2.60
Helium	0.0696	0.125	1.80
Krypton	0.9085	2.412	2.65
Hydrogen	0.031	0.0708	2.28
Oxygen	0.436	1.141	2.62
Methane	0.1625	0.4241	2.61
Propane	0.225	0.582	2.59
Average = 2.50			

Table 5-3. Reduced density of (liquid) fluids at the normal boiling point.

Fluid (Liquid at RTP)	ρ_C (g/cm ³)	$\rho_{1 \text{ atm BP}}$ (g/cm ³)	$\frac{\rho_{1 \text{ atm BP}}}{\rho_C}$
<i>n</i> -Pentane	0.232	0.609	2.63
Benzene	0.3063	0.818	2.67
Toluene	0.291	0.779	2.68
Acetone	0.2683	0.745	2.78
Acetic acid	0.351	0.911	2.60
Formic acid	0.4322	1.059	2.45
Acetonitrile	0.2373	0.708	2.98
<i>p</i> -Dioxane	0.369	0.936	2.54
Pyrrolidine	0.2856	0.793	2.78
Pyridine	0.3268	0.889	2.72
Aniline	0.340	0.868	2.55
Average = 2.67			

Additional errors will likely arise when empirical relations designed for pure fluids are used to calculate the solubility parameter for fluid mixtures, particularly if one or more of the components is highly polar.

Table 5-4. *Reduced density of (polar liquid) fluids at the normal boiling point.*

Fluid (Polar Liquid at RTP)	ρ_C (g/cm ³)	$\rho_{1 \text{ atm BP}}$ (g/cm ³)	$\frac{\rho_{1 \text{ atm BP}}}{\rho_C}$
Methanol	0.2715	0.75	2.76
Phenol	0.4104	1.16	2.83
Isopropyl alcohol	0.2735	0.713	2.61
Ammonia	0.235	0.683	2.91
<i>Average = 2.78</i>			
<i>Overall Average of All Fluids = 2.63</i>			

5.1.2 Thermodynamic Equation of State

As previously discussed, Hildebrand derived an approximation of the internal pressure, calling this approximation the cohesive energy density, by assuming a particular volume dependence of E (see eqn. (4-16)).

$$\delta^2 = \left(\frac{\Delta E}{V} \right)_T \approx \left(\frac{\partial E}{\partial V} \right)_T \quad (5-11)$$

but from the thermodynamic equation of state, eqn. (4-11)

$$\left(\frac{\partial E}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P \quad (5-12)$$

so that

$$\delta^2 \approx \left(\frac{\partial E}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P \quad (5-13)$$

Total (1-component) solubility parameters can therefore be calculated using an equation of state (EOS) of the form, $P = f(\rho, T)$. This approach has been used in this work to calculate the total solubility parameter for pure CO₂, using the empirical EOS of Huang *et al.*²⁶⁹

$$P = \rho R T \left[\begin{aligned} &1 + b_2 \rho' + b_3 \rho'^2 + b_4 \rho'^3 + b_5 \rho'^4 + b_6 \rho'^5 + b_7 \rho'^2 \exp(-c_{21} \rho'^2) + b_8 \rho'^4 \exp(-c_{21} \rho'^2) \\ &+ c_{22} \rho'^2 \exp[-c_{27} (\Delta T)^2] + c_{23} \frac{\Delta \rho}{\rho'} \exp[-c_{25} (\Delta \rho)^2 - c_{27} (\Delta T)^2] \\ &+ c_{24} \frac{\Delta \rho}{\rho'} \exp[-c_{26} (\Delta \rho)^2 - c_{27} (\Delta T)^2] \end{aligned} \right] \quad (5-14)$$

where

$$T' = T/T_c; \quad \Delta T = 1 - T'; \quad \rho' = \rho/\rho_c; \quad \Delta \rho = 1 - 1/\rho' \quad (5-15)$$

Table 5-5. Huang equation of state constants, C_i .

i	C_i	i	C_i
1	0.376194	15	-2.79498
2	0.118836	16	5.62393
3	-3.04379	17	-2.93831
4	2.27453	18	0.988759
5	-1.23863	19	-3.04711
6	0.250442	20	2.32316
7	-0.115350	21	1.07379
8	0.675104	22	-0.599724×10^{-4}
9	0.198861	23	0.885339×10^{-4}
10	0.216124	24	0.316418×10^{-2}
11	-0.583148	25	10
12	0.119747×10^{-1}	26	50
13	0.537278×10^{-1}	27	80,000
14	0.265216×10^{-1}		

and,

$$\begin{aligned}
 b_2 &= \left(c_1 + \frac{c_2}{T} + \frac{c_3}{T^2} + \frac{c_4}{T^3} + \frac{c_5}{T^4} + \frac{c_6}{T^5} \right); & b_6 &= \left(\frac{c_{14}}{T} \right) \\
 b_3 &= \left(c_7 + \frac{c_8}{T} + \frac{c_9}{T^2} \right); & b_7 &= \left(\frac{c_{15}}{T^3} + \frac{c_{16}}{T^4} + \frac{c_{17}}{T^5} \right) \\
 b_4 &= \left(c_{10} + \frac{c_{11}}{T} \right); & b_8 &= \left(\frac{c_{18}}{T^3} + \frac{c_{19}}{T^4} + \frac{c_{20}}{T^5} \right) \\
 b_5 &= \left(c_{12} + \frac{c_{13}}{T} \right) & &
 \end{aligned} \tag{5-16}$$

These equations and the appropriate derivatives (presented in the Appendix A) have been written into a computer program and CO₂ solubility parameters have been calculated over the temperature and pressure range for which the EOS is stated to be valid ($220 \text{ K} \leq T \leq 420 \text{ K}$, and $1 \text{ atm} \leq P \leq 600 \text{ atm}$). Figure 5-2 is a plot of the resulting solubility parameters.

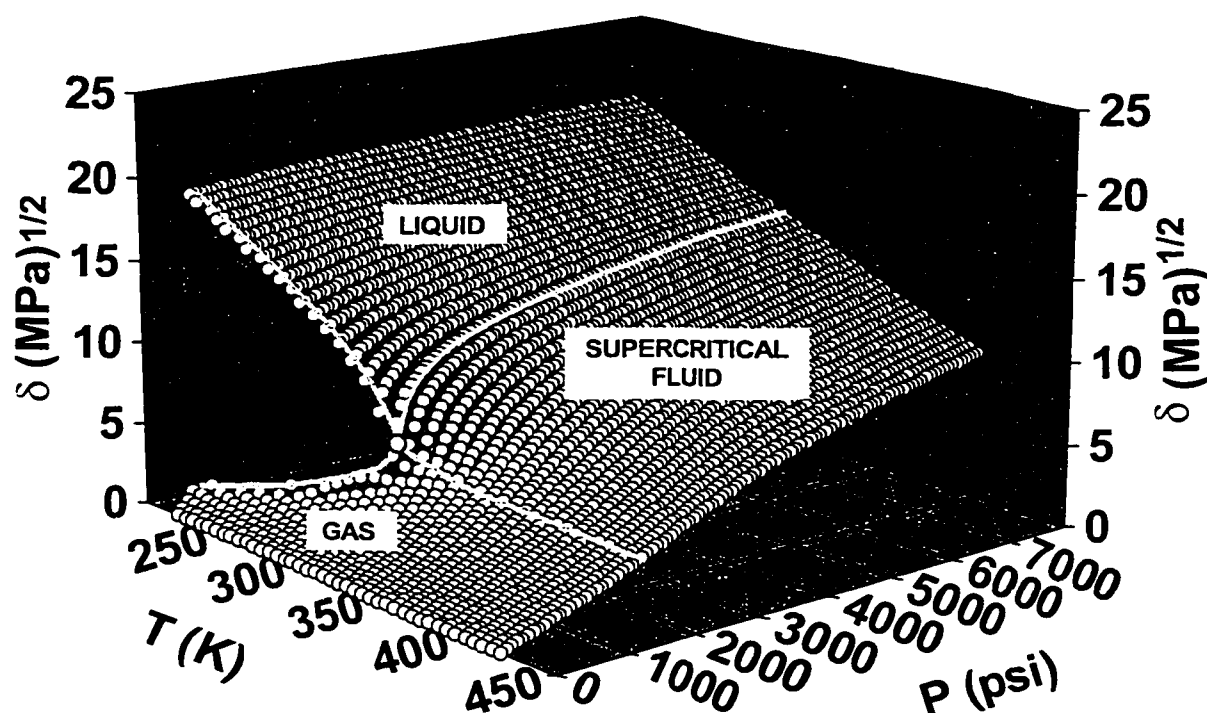


Figure 5-2. Total (1-component) solubility parameter of pure CO_2 , calculated using eqns. (5-13) and (5-14).

Figure 5-3 is a contour plot comparison of CO_2 solubility parameter values calculated with Giddings approximation, eqn. (5-10), versus CO_2 solubility parameter values calculated from the CO_2 equation of state eqn. (5-14) and eqn. (5-13). Values on the contour plot lines represent values of $\left(\frac{\delta \text{ from Giddings}}{\delta \text{ from EOS}} \right)$. In the supercritical fluid region (identified by the dashed lines), the solubility parameters obtained from Giddings' approximation are 10 to 20 % greater than those calculated from the EOS. Similarly, in the low-temperature gas region, Giddings' equation underestimates the true solubility parameter by about 15%.

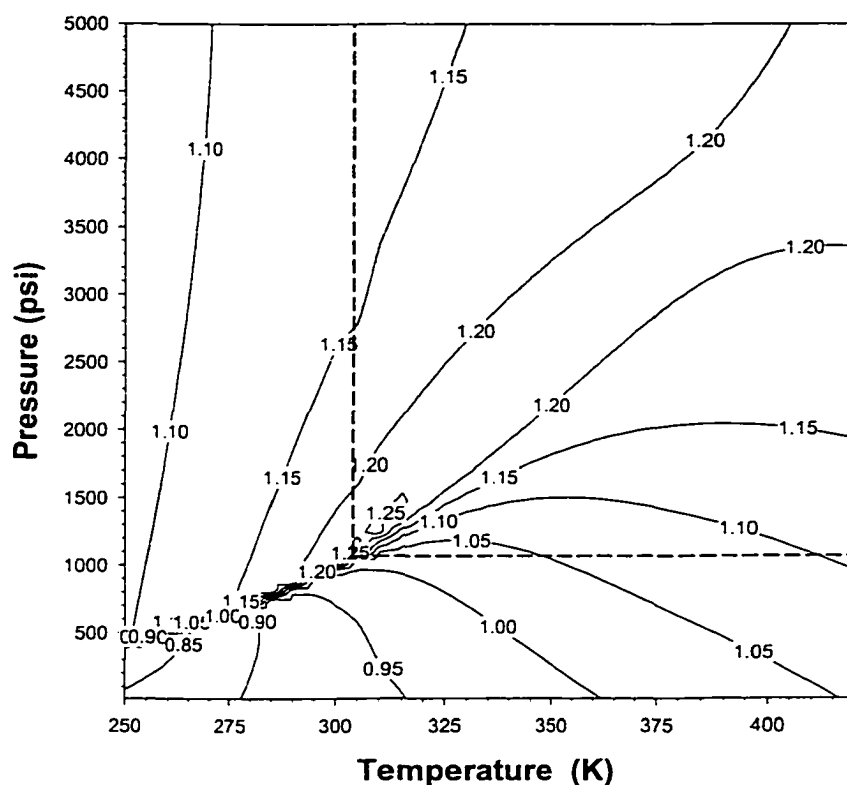


Figure 5-3. Contour plot comparison of Giddings solubility parameter approximation (eqn. 5-10) versus equation of state solubility parameter calculation (eqn. 5-13) for CO₂.

5.2 3-Component (Hansen) Solubility Parameters – Pure CO₂

While the thermodynamic equation of state method gives an accurate representation of the total (1-component) solubility parameter for CO₂ over a range of temperatures and pressures, we have seen that the (Hildebrand) 1-component model does not accurately predict the solubility behavior of a real fluid. We need to be able to express the solubility behavior of CO₂ in terms of 3-component (Hansen) Solubility Parameters (δ_d , δ_p , δ_h). Extending the HSP methodology to supercritical fluids would significantly enhance the understanding of their solvent properties; however, no such studies appear to have been

done. For strictly nonpolar gases (gases with no permanent dipole or higher moments, such as argon), the values of δ_p and δ_h will be zero, and we could equate δ_d with the total solubility parameter, δ_{Total} . However, CO₂, which possesses a large quadrupole moment and can display Lewis acid-base characteristics, has non-zero values for both δ_p and δ_h .²⁷⁰

Determination of HSP's for (ambient condition) gases is usually based on room temperature solubility of the gas in different liquids of known δ_d , δ_p , and δ_h . Those liquids that show the highest solubility for the gas are assumed to have HSP's closer to those of the gas than those liquids which have lower solubilities for CO₂. In the following section, published data of CO₂ gas solubility (at 25 °C and a CO₂ partial pressure of 1 atmosphere) in a large number of liquid solvents is evaluated. From this data, a set of HSP values at a particular temperature and pressure can be determined. HSP values at other pressures and temperatures will be based on this set of HSP values, using pressure and temperature derivative functions, which will be derived subsequently.

5.2.1 Optimized CO₂ HSP Values from Published Solubility Data

Published CO₂ solubility data at 25°C and 1 atmosphere partial pressure of CO₂ in various liquid solvents are collected in Appendix B. CO₂ HSP values were calculated based on a simple weighted average,

$$\delta_d^{CO_2} = \frac{\sum_{i=1}^n x_i \delta_{d_i}}{\sum x_i}, \quad (5-17)$$

$$\delta_p^{CO_2} = \frac{\sum_{i=1}^n x_i \delta_{p_i}}{\sum x_i}, \quad (5-18)$$

$$\delta_h^{CO_2} = \frac{\sum_{i=1}^n x_i \delta_{h_i}}{\sum x_i}. \quad (5-19)$$

using the entire data set of 101 solvents, hereafter called data set #1, as well as the subset of data where the measured CO₂ solubility was greater than the ideal solubility at 25 °C and 1 atmosphere, $x_{CO_2}^{ideal} = 0.0229$ (CO₂ ideal solubility development is included in the Appendix B). This subset of data, hereafter called data set #2, is comprised of 10 solvents.

These analyses resulted in the following HSP values for CO₂ at 25°C

$$\begin{aligned} \text{Data set \#1:} \quad & \delta_d = 16.4 \text{ MPa}^{1/2} \\ & \delta_p = 5.5 \text{ MPa}^{1/2} \\ & \delta_h = 5.8 \text{ MPa}^{1/2} \end{aligned}$$

$$\begin{aligned} \text{Data set \#2:} \quad & \delta_d = 15.6 \text{ MPa}^{1/2}, \\ & \delta_p = 5.2 \text{ MPa}^{1/2} \\ & \delta_h = 5.8 \text{ MPa}^{1/2} \end{aligned}$$

The experimental CO₂ solubilities and HSP values for the solvents included in data set #2 are shown in Table 5-6, while the values for data set #1 are given in Appendix B.

Table 5-6. CO₂ solubility, and HSP values for the solvents included in Data Set #2.

Solvent	$x_{CO_2}^{Exptl}$	δ_d (MPa) ^{1/2}	δ_p (MPa) ^{1/2}	δ_h (MPa) ^{1/2}
Tributyl phosphate, (C ₁₂ H ₂₇ O ₄ P)	0.03550	16.3	6.3	4.3
Amyl acetate, (C ₇ H ₁₄ O ₂)	0.02800	15.8	3.3	6.1
Butyl oleate, (C ₂₂ H ₄₂ O ₂)	0.02790	14.7	3.4	3.4
Tetrahydrofuran (C ₄ H ₈ O)	0.02700	16.8	5.7	8.0
Methyl oleate (C ₁₉ H ₃₆ O ₂)	0.02690	14.5	3.9	3.7
Isobutyl acetate (C ₆ H ₁₂ O ₂)	0.02500	15.1	3.7	6.3
Methyl ethyl ketone (C ₄ H ₈ O)	0.02444	16.0	9.0	5.1
Propyl acetate (C ₅ H ₁₀ O ₂)	0.02429	15.3	4.3	7.6
Ethyl acetate (C ₄ H ₈ O ₂)	0.02300	15.8	5.3	7.2
Methyl acetate (C ₃ H ₆ O ₂)	0.02253	15.5	7.2	7.6

A second approach, known as the solubility sphere,^{271,272,273} was also used to evaluate the published solubility data. The solubility sphere approach is essentially a trial and error method, whereby all the “good” solvents are included within the sphere and all the “bad” ones are excluded, and the radius of this sphere is known as the interaction radius, or R_o . The criterion of “good” versus “bad” can vary, based on the interaction being studied. This can include percentage polymer swelling, dissolution, breakthrough times, permeation coefficients higher than a given value, long-time suspension of a pigment, etc. Based upon the criteria selected, spheres are then produced for three plots, δ_d vs. δ_p , δ_d vs. δ_h , and δ_p vs. δ_h , and the sphere radius R_o is adjusted until an identical radius for each of the three plots can be found which incorporates the “good” interactions

and excludes the “bad” interactions. Using this approach, other solvents or compounds of interest can be screened to determine if they are within the interaction radius, R_o , and therefore appropriate (“good”), or inappropriate (“bad”) for the application they are being considered. This type of evaluation or predictability is aided by an equation developed by Skaarup for determining the distance, R_a , between two materials based on their respective HSP values,²⁷⁴

$$(R_a)^2 = 4(\delta_{d2} - \delta_{d1})^2 + (\delta_{p2} - \delta_{p1})^2 + (\delta_{h2} - \delta_{h1})^2 \quad (5-20)$$

where δ_{d2} , δ_{p2} , and δ_{h2} are associated with a given solvent and δ_{d1} , δ_{p1} , and δ_{h1} with the center of the solubility sphere. This equation was developed from plots of experimental data where the constant “4” was found convenient and correctly represented the solubility data as a sphere encompassing the good solvents. Figure 5-4 is a schematic representation of this approach.

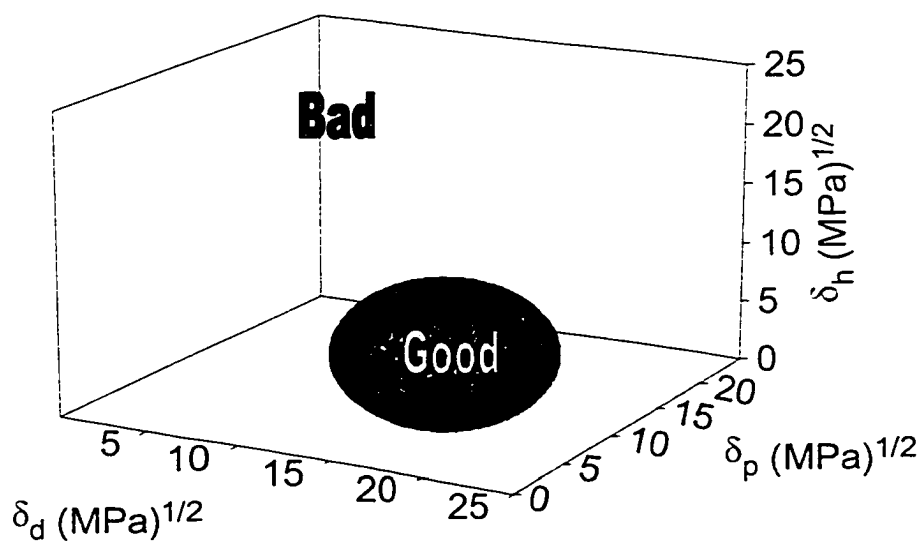


Figure 5-4. Interaction radius, where R_o incorporates all “good” solvents and excludes all “bad” solvents.

For this evaluation, “good” was defined as solvents with the CO₂ solubility greater than ideal and “bad” were those solvents where the CO₂ solubility is less than ideal. It is clear that for cases where CO₂ solubility is greater than ideal (where the (attractive) CO₂/solvent interactions are greater than solvent/solvent interactions) R_a should be less than R_o . A convenient index for relative “goodness” of a solvent is the ratio R_a/R_o , which has been called the relative energy difference (RED) number

$$RED = R_a / R_o \quad (5-21)$$

For an individual solvent, an RED less than 1 indicates high affinity, while an RED value close to 1 is a boundary condition (between “good” and bad”). Progressively higher RED numbers indicate progressively lower affinities.²⁷⁵ Computing R_a from eqn. (5-20) and the RED from eqn. (5-21) allows for easy scanning of large data sets, such as the 101 solvents in data set #1 used for the HSP optimization. The solubility spheres optimized for data set #1 and data set #2 with the two HSP center points are shown in Figures 5-5a, b, and c. As can be seen from these spheres, an interaction radius $R_o = 4.0$ for data set #2 incorporates the “good” solvents as defined, whereas for data set #1, an interaction radius $R_o = 4.7$ is necessary to incorporate the “good” solvents. In addition, the solubility sphere for data set #1 results in the inclusion of 7 “bad” solvents (2-Methylcyclohexanone, cyclohexanone, oleic acid, dichloromethane, trichloromethane, propylene bromide, and 1,2-dibromoethane) whereas the sphere generated for data set #2 results in the inclusion of only 1 “bad” solvent (oleic acid), for which the high CO₂ solubility may be a result of a chemical reaction with CO₂, similar to the type of reaction described in Section 2.2. In terms of the Sphere technique, occurrences of “good”

solvents falling outside of the sphere radius, and “bad” solvents falling inside the sphere radius are known as errors and can be viewed as an indication of the “goodness” of the fit. The Excel[®] spreadsheet of RED calculations is given in Appendix B.

Literature Ro values for the polymers evaluated in Chapter 6 are reportedly based on the dissolution behavior of the respective polymers in a range of liquid solvents. These Ro values will be identified in this work by R_o^{liq} .

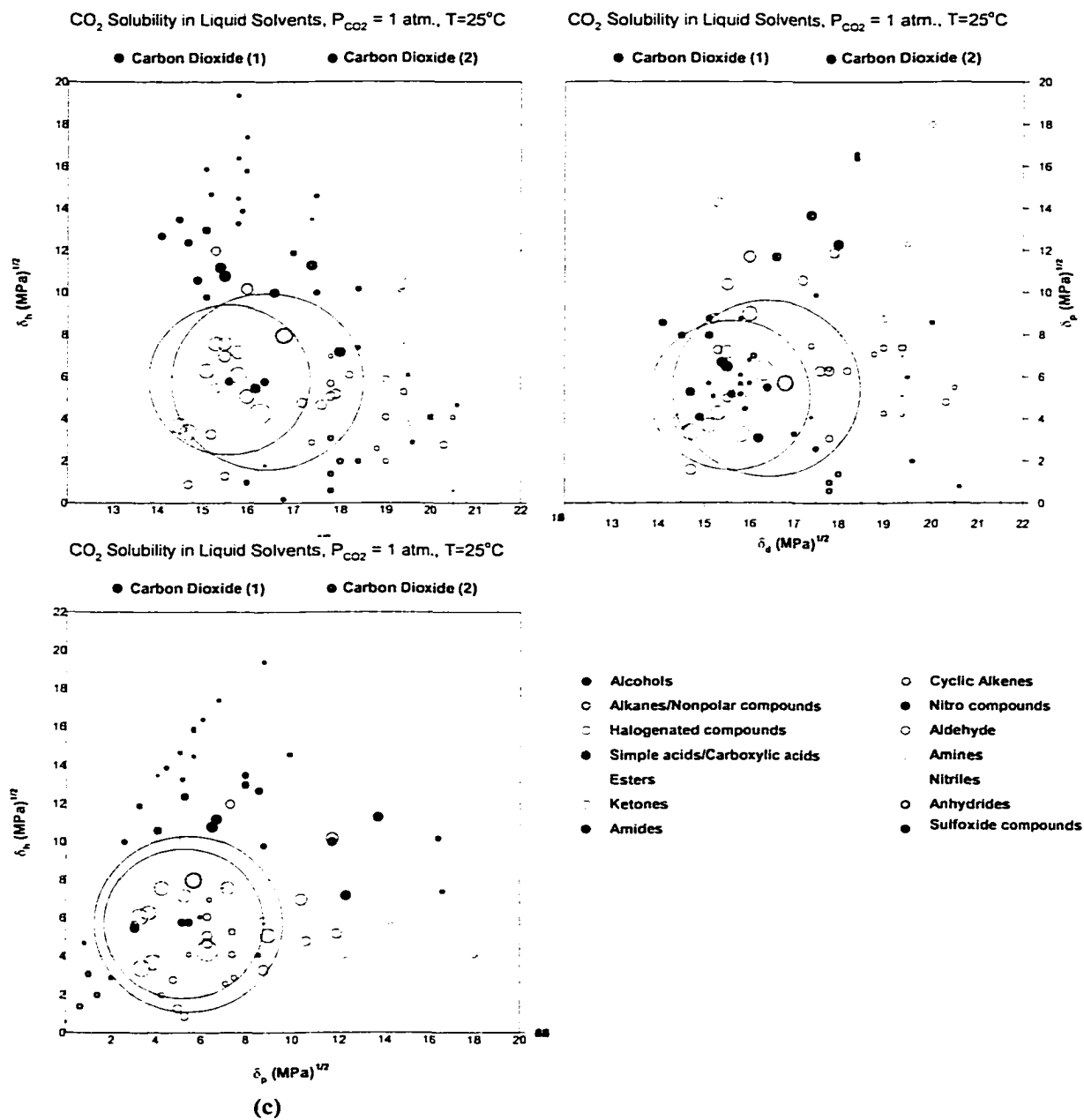


Figure 5-5. Solubility sphere plots of CO₂ in organic solvents. (a) δ_h versus δ_d , (b) δ_p versus δ_d , and (c) δ_h versus δ_p .

Using the optimization routines to identify CO₂ HSP points and then the solubility sphere as a graphical representation of “good” and “bad” solvents, it has been determined that the set of HSP’s optimized from data set #2,

$$\begin{aligned} \delta_d &= 15.6 \text{ MPa}^{1/2} \\ \delta_p &= 5.2 \text{ MPa}^{1/2} \\ \delta_h &= 5.8 \text{ MPa}^{1/2} \end{aligned} \quad (5-22)$$

best characterize CO₂ at $T = 25^\circ\text{C}$. The rational of this choice is further supported by problems noted by Hansen,²⁷⁶ who notes the approach of using all solvents to establish the center of a solubility sphere results in this sphere boundary (and center) being determined by the poor solvents or nonsolvents, rather than the best solvents in the middle.

It is next necessary to establish a pressure corresponding to this $T = 25^\circ\text{C}$ set of HSP values in order to use them to determine HSP’s at arbitrary conditions of T and P. From eqn. (4-27), the determined HSP values for CO₂ result in a total CO₂ solubility parameter of $17.4 \text{ MPa}^{1/2}$,

$$\begin{aligned} \delta_T^2 &= \delta_d^2 + \delta_p^2 + \delta_h^2 \\ &= (15.6)^2 + (5.2)^2 + (5.8)^2 = 304.04 \text{ MPa} \\ &= 17.4 \text{ MPa}^{1/2} \end{aligned} \quad (5-23)$$

The PVT equation of state, which calculates total CO₂ solubility parameters (Section 5.1.2) was used to determine the combination of pressure and molar volume corresponding to $T = 25^\circ\text{C}$ and $\delta_T = \left(\frac{\partial P}{\partial T} \right)_v - P = 17.4 \text{ MPa}^{1/2}$, which gave

$$\begin{array}{l} P = 13,300 \text{ psi} \quad (905 \text{ atm}) \\ V^{CO_2} = 39.13 \text{ cm}^3/\text{mole} \end{array} \quad (5-24)$$

5.3 Temperature and Pressure Effects

Both temperature and pressure will influence total solubility parameters. However, other than Giddings' extension of the 1-component (Hildebrand) solubility parameter model to supercritical fluids (Section 5.1.1), there appears to be no published reports on methods to calculate total solubility parameters as a function of pressure, and only limited reports on the calculation of solubility parameters as a function of temperature.^{277,278,279} Generally, an increase in pressure at constant temperature will increase the total solubility parameter through an increase in the solvent density. Similarly, an increase in temperature at constant pressure will decrease the total solubility parameter. Both of these trends can be seen in Figure 5-2, where the total CO₂ solubility parameter, calculated using eqns. (5-13) and (5-14), is seen to be similar in appearance to the PVT surface, shown in Figure 2-3, illustrating the predominant dependence of solubility parameter on density.

The temperature and pressure dependence of individual HSP's, as a function of temperature and pressure, has apparently not been evaluated for any liquid, gas or supercritical fluid. An approximate approach for this calculation is outlined in the following Sections, where the temperature derivatives, originally derived by Hansen and Beerbower,²⁸⁰ are verified. Pressure derivatives, not found in any literature search, are

derived in a manner parallel to the temperature derivatives. In addition, integrals forms are developed

5.3.1 Temperature and Pressure Effects on HSP's : δ_d

From Section 4.2.3, the dispersion solubility parameter, δ_d , was defined as

$$\delta_d^2 = \frac{E_d}{V} \quad (5-25)$$

where E_d is the dispersion, or nonpolar, contribution to the total cohesive energy, E . Hildebrand, in his 1950 work, discusses the effect of temperature on solubility parameters by recalling the expression for the dependence of E on the volume²⁸¹

$$E = -\frac{k}{V^n} \quad (5-26)$$

where k is a constant dependent upon the nature of the particular liquid and n is about 1.5 for normal liquids. Substituting eqn. (5-26) into Hansen's definition for the dispersion solubility parameter, eqn. (5-25),

$$\delta_d^2 = -\frac{k}{V^{n+1}} \quad (5-27)$$

so that

$$\delta_d = -\frac{k^{1/2}}{V^{(n+1)/2}} \quad (5-28)$$

The change in δ_d produced by a change in volume can be calculated by taking the partial derivative of eqn. (5-28) with respect to volume at constant temperature and pressure,

$$\begin{aligned}\left(\frac{\partial \delta_d}{\partial V}\right)_{T,P} &= k^{1/2} \left(\frac{n+1}{2}\right) \left[V^{-\frac{(n+1)}{2}}\right] [V^{-1}] \\ &= \frac{k^{1/2}}{V^{\frac{(n+1)}{2}}} \left(\frac{n+1}{2}\right) [V^{-1}] \\ &= -\delta_d \left(\frac{n+1}{2}\right) \left(\frac{1}{V}\right)\end{aligned}\quad (5-29)$$

and

$$\frac{\partial \delta_d}{\delta_d} = -\left(\frac{n+1}{2}\right) \frac{\partial V}{V} = -\left(\frac{1.5+1}{2}\right) \frac{\partial V}{V} = -1.25 \frac{\partial V}{V} \quad (5-30)$$

Equation (5-30) can now be differentiated for either a change in temperature or pressure, or integrated. The partial derivatives will be discussed first, followed by the integration of eqn. (5-30).

The partial derivative of δ_d with respect to temperature at constant pressure is

$$\left(\frac{1}{\delta_d}\right) \left(\frac{\partial \delta_d}{\partial T}\right)_p = -1.25 \left(\frac{1}{V}\right) \left(\frac{\partial V}{\partial T}\right)_p \quad (5-31)$$

The isobaric coefficient of thermal expansion, α , is defined by

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p \quad (5-32)$$

so that by combining eqn. (5-31) and eqn. (5-32),

$$\boxed{\left(\frac{\partial \delta_d}{\partial T}\right)_P = -1.25 \delta_d \alpha} \quad (5-33)$$

The same type of derivation can be performed to generate an expression for the change in δ_d with respect to pressure at constant temperature:

$$\left(\frac{1}{\delta_d}\right)\left(\frac{\partial \delta_d}{\partial P}\right)_T = -1.25 \left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial P}\right)_T \quad (5-34)$$

The isothermal compressibility, β , is defined by

$$\beta = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T \quad (5-35)$$

so that by substituting eqn. (5-35) into eqn. (5-34),

$$\boxed{\left(\frac{\partial \delta_d}{\partial P}\right)_T = 1.25 \delta_d \beta} \quad (5-36)$$

The integrated form of eqn. (5-30) is obtained by integrating between the limits of an initial reference state δ_{dref} , V_{ref} (at P_{ref} and T_{ref}), to some new δ_d , V (at P and T),

$$\int_{\delta_{dref}}^{\delta_d} \frac{\partial \delta_d}{\delta_d} = -1.25 \int_{V_{ref}}^V \frac{\partial V}{V} \quad (5-37)$$

and

$$\ln \delta_{dref} - \ln \delta_d = -1.25 (\ln V_{ref} - \ln V) \quad (5-38)$$

$$\ln \frac{\delta_{dref}}{\delta_d} = -1.25 \ln \frac{V_{ref}}{V} \quad (5-39)$$

$$\boxed{\frac{\delta_{dref}}{\delta_d} = \left(\frac{V_{ref}}{V} \right)^{-1.25}} \quad (5-40)$$

5.3.2 Temperature and Pressure Effects on HSP's: δ_p

From Section 4.2.3, the polar solubility parameter, δ_p , was defined as;

$$\delta_p^2 = \frac{E_p}{V} \quad (5-41)$$

where E_p is the polar contribution to the total cohesive energy. The first values of δ_p were assigned by Hansen and Skaarup using the Böttcher equation, as described in Section 5.4.2.2.1,

$$\delta_p^2 = \frac{12108}{V^2} \frac{\epsilon - 1}{2\epsilon + n_D^2} (n_D^2 + 2) \mu^2 \quad \left[\frac{\text{cal}}{\text{cm}^3} \right] \quad (5-42)$$

A simplified equation was later developed by Hansen and Beerbower,²⁸²

$$\delta_p = \frac{37.4\mu}{V^{1/2}} \quad \left[\text{MPa}^{1/2} \right] \quad (5-43)$$

where μ is the dipole moment. This equation is utilized for determining the change in δ_p with respect to either temperature at constant pressure or with respect to pressure at constant

temperature. First, the partial derivative of eqn. (5-43) with respect to volume at constant temperature and pressure is determined,

$$\begin{aligned}\left(\frac{\partial \delta_p}{\partial V}\right)_{T,P} &= -\left(\frac{1}{2}\right)V^{-3/2}(37.4\mu) \\ &= -\frac{1}{2V}\left(\frac{37.4\mu}{V^{1/2}}\right) = -\frac{\delta_p}{2V}\end{aligned}\quad (5-44)$$

and

$$\frac{\partial \delta_p}{\delta_p} = -\frac{\partial V}{2V} \quad (5-45)$$

Equation (5-45) can now be differentiated for either a change in temperature or pressure, or integrated. Differentiating δ_p with respect to temperature at constant pressure,

$$\left(\frac{1}{\delta_p}\right)\left(\frac{\partial \delta_p}{\partial T}\right)_P = -\left(\frac{1}{2}\right)\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \quad (5-46)$$

Substituting in the isobaric coefficient for thermal expansion, α ,

$$\boxed{\left(\frac{\partial \delta_p}{\partial T}\right)_P = -\delta_p\left(\frac{\alpha}{2}\right)} \quad (5-47)$$

A similar derivation can be performed to calculate the change in δ_p due to pressure at constant temperature,

$$\left(\frac{1}{\delta_p}\right)\left(\frac{\partial \delta_p}{\partial P}\right)_T = -\left(\frac{1}{2}\right)\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \quad (5-48)$$

and substituting for the isothermal compressibility, β ,

$$\left(\frac{\partial \delta_p}{\partial P} \right)_T = \delta_p \left(\frac{\beta}{2} \right) \quad (5-49)$$

The integrated form of eqn. (5-45) is

$$\int_{\delta_{pref}}^{\delta_p} \frac{\partial \delta_p}{\delta_p} = -0.5 \int_{V_{ref}}^V \frac{\partial V}{V} \quad (5-50)$$

so that by integrating, we have

$$\ln \delta_{pref} - \ln \delta_p = -0.5 (\ln V_{ref} - \ln V) \quad (5-51)$$

$$\ln \frac{\delta_{pref}}{\delta_p} = -0.5 \ln \frac{V_{ref}}{V} \quad (5-52)$$

$$\frac{\delta_{pref}}{\delta_p} = \left(\frac{V_{ref}}{V} \right)^{-0.5} \quad (5-53)$$

5.3.3 Temperature and Pressure Effects on HSP's: δ_h

In Hansen's early work, the hydrogen bonding parameter was almost always found by subtracting the polar and dispersion energies of vaporization from the total energy of vaporization. This is still widely used where the required data are available and reliable. Hansen,²⁸³ however, while noting that "there is no rigorous way of arriving at values of the temperature dependence of the hydrogen bonding solubility parameter", developed an empirical approach for the determination of the temperature dependence of δ_h which

involves experimental heats of vaporization data for hydrogen-bonded substances, which, in turn, are taken from Bondi.²⁸⁴

From Section 4.2.3, the hydrogen bonding solubility parameter, δ_h , was defined as

$$\delta_h^2 = \frac{E_h}{V} \quad (5-54)$$

so that

$$E_h = V\delta_h^2 \quad (5-55)$$

where E_h is the hydrogen bonding contribution to the total cohesive energy. Differentiating eqn. (5-55) with respect to temperature at constant pressure,

$$\begin{aligned} \left(\frac{\partial E_h}{\partial T} \right)_P &= V(2\delta_h) \left(\frac{\partial \delta_h}{\partial T} \right)_P + \delta_h^2 \left(\frac{\partial V}{\partial T} \right)_P \\ 2V\delta_h \left(\frac{\partial \delta_h}{\partial T} \right)_P &= \left(\frac{\partial E_h}{\partial T} \right)_P - \delta_h^2 \left(\frac{\partial V}{\partial T} \right)_P \end{aligned} \quad (5-56)$$

$$\left(\frac{\partial \delta_h}{\partial T} \right)_P = \frac{\left(\frac{\partial E_h}{\partial T} \right)_P - \delta_h^2 \left(\frac{\partial V}{\partial T} \right)_P}{2V\delta_h}$$

Simplifying, rearranging terms and substituting in the isobaric coefficient of thermal expansion, β ,

$$\left(\frac{\partial \delta_h}{\partial T}\right)_p = \left(\frac{1}{2V\delta_h}\right)\left(\frac{\partial E_h}{\partial T}\right)_p - \frac{\delta_h}{2}\left(\frac{1}{V}\frac{\partial V}{\partial T}\right)_p$$

$$\left(\frac{\partial \delta_h}{\partial T}\right)_p = \left(\frac{\delta_h}{2V\delta_h^2}\right)\left(\frac{\partial E_h}{\partial T}\right)_p - \delta_h\left(\frac{\alpha}{2}\right) \quad (5-57)$$

$$\left(\frac{\partial \delta_h}{\partial T}\right)_p = \delta_h \left(\frac{\left(\frac{\partial E_h}{\partial T}\right)_p}{2E_h} - \frac{\alpha}{2} \right)$$

Bondi,²⁸⁵ through exploratory calculations, has shown that the difference between the heat of vaporization of a hydroxylic compound (a compound displaying strong hydrogen bonding) and that of its hydrocarbon (or other nonpolar) homomorph constitutes a good measure of hydrogen bond strength. This work also discusses the decrease in the heat of formation of the hydrogen bond with increasing temperature. Reference curves of $\left(\frac{dE_h}{dT}\right)$ were constructed²⁸⁶ for various functional groups and are shown in Table 5.7, along with experimentally derived values of E_h .²⁸⁷

Table 5-7. Experimentally determined values of E_h and $\left(\frac{dE_h}{dT}\right)$.

Functional Group	Hydrogen-bond parameter, E_h (cal/mole)	dE_h/dT (cal/mole · K)
—OH (aliphatic)	4650 ± 400	-10
—NH ₂ (aliphatic)	1350 ± 200	-4.5
—CN (aliphatic)	500 ± 200	-7.0
—COOH (aliphatic)	2750 ± 250	-2.9

Averaging the rate of change of the hydrogen bond heat of vaporization with temperature (dE_h/dT), and dividing by the average excess heats of vaporization (heat of vaporization of the hydrogen bonding compound minus the heat of vaporization of its nonpolar homomorph) results in the following form of eqn. (5-57):

$$\boxed{\begin{aligned}\left(\frac{\partial \delta_h}{\partial T}\right)_P &= -\delta_h \left(\frac{2.64 \times 10^{-3}}{2} + \frac{\alpha}{2} \right) \\ &= -\delta_h \left(1.32 \times 10^{-3} + \frac{\alpha}{2} \right)\end{aligned}} \quad (5-58)$$

The change in the δ_h with respect to pressure at constant temperature is obtained by utilizing the relationship

$$\frac{\partial \delta_h}{\partial P} = \frac{\partial \delta_h}{\partial T} \cdot \frac{\partial T}{\partial P} \quad (5-59)$$

and, from eqns. (5-32) and (5-35),

$$\frac{\partial T}{\partial P} = -\frac{\beta}{\alpha} \quad (5-60)$$

so that

$$\left(\frac{\partial \delta_h}{\partial P}\right)_T = -\delta_h \left(1.32 \times 10^{-3} + \frac{\alpha}{2} \right) \cdot \left(-\frac{\beta}{\alpha} \right) \quad (5-61)$$

and

$$\boxed{\left(\frac{\partial \delta_h}{\partial P}\right)_T = \delta_h \left(\frac{1.32 \times 10^{-3} \beta}{\alpha} + \frac{\beta}{2} \right)} \quad (5-62)$$

Equation (5-58) can be rearranged to a form that can be easily integrated,

$$\begin{aligned}\left(\frac{\partial \delta_h}{\partial T}\right)_p &= -\delta_h \left(1.32 \times 10^{-3} + \frac{\alpha}{2}\right) \\ &= -\delta_h \left(1.32 \times 10^{-3} + \frac{dV}{2VdT}\right) \\ \frac{d\delta_h}{\delta_h} &= -\left(1.32 \times 10^{-3} dT + \frac{dV}{2V}\right)\end{aligned}\tag{5-63}$$

Upon integration of eqn. (5-63) from $(\delta_{href}, T_{ref}$ and $V_{ref})$ to $(\delta, T$ and $V)$,

$$\int_{\delta_{href}}^{\delta_h} \frac{d\delta_h}{\delta_h} = -\left(1.32 \times 10^{-3} \int_{T_{ref}}^T dT + .5 \int_{V_{ref}}^V \frac{dV}{V}\right)\tag{5-64}$$

$$\ln \frac{\delta_{href}}{\delta_h} = -1.32 \times 10^{-3} (T_{ref} - T) - \ln \left(\frac{V_{ref}}{V}\right)^{0.5}\tag{5-65}$$

$$\boxed{\frac{\delta_{href}}{\delta_h} = \exp \left[-1.32 \times 10^{-3} (T_{ref} - T) - \ln \left(\frac{V_{ref}}{V}\right)^{0.5} \right]}\tag{5-66}$$

The total solubility parameter, incremented for small changes in temperature and pressure, can be calculated from eqns. (5-33), (5-36), (5-47), (5-49), (5-58) and (5-62) using

$$\delta^2 = \left[\delta_d + \left(\frac{\partial \delta_d}{\partial T} \right)_p \Delta T + \left(\frac{\partial \delta_d}{\partial P} \right)_T \Delta P \right]^2 + \left[\delta_p + \left(\frac{\partial \delta_p}{\partial T} \right)_p \Delta T + \left(\frac{\partial \delta_p}{\partial P} \right)_T \Delta P \right]^2 + \left[\delta_h + \left(\frac{\partial \delta_h}{\partial T} \right)_p \Delta T + \left(\frac{\partial \delta_h}{\partial P} \right)_T \Delta P \right]^2$$

(5-67)

or from eqns. (5-40), (5-53) and (5-66) using

$$\delta^2 = \left[\frac{\delta_{dref}}{\left(\frac{V_{ref}}{V} \right)^{-1.25}} \right]^2 + \left[\frac{\delta_{pref}}{\left(\frac{V_{ref}}{V} \right)^{-0.5}} \right]^2 + \left[\frac{\delta_{href}}{\exp \left(-1.32 \times 10^{-3} (T_{ref} - T) - \ln \left(\frac{V_{ref}}{V} \right)^{0.5} \right)} \right]^2$$

(5-68)

The derivative forms are summarized in Table 5.8 and the integrated forms in Table 5.9.

Table 5-8. Equations (derivative form) for the temperature and pressure effects on HSP's.

	Temperature increment	Pressure increment
δ_d	$\left(\frac{\partial \delta_d}{\partial T} \right)_p = -1.25 \delta_d \alpha$	$\left(\frac{\partial \delta_d}{\partial P} \right)_T = 1.25 \delta_d \beta$
δ_p	$\left(\frac{\partial \delta_p}{\partial T} \right)_p = -\delta_p \left(\frac{\alpha}{2} \right)$	$\left(\frac{\partial \delta_p}{\partial P} \right)_T = \delta_p \left(\frac{\beta}{2} \right)$
δ_h	$\left(\frac{\partial \delta_h}{\partial T} \right)_p = -\delta_h \left(1.32 \times 10^{-3} + \frac{\alpha}{2} \right)$	$\left(\frac{\partial \delta_h}{\partial P} \right)_T = \delta_h \left(\frac{1.32 \times 10^{-3} \beta}{\alpha} + \frac{\beta}{2} \right)$

Table 5-9. Equations (integrated form) for the temperature and pressure effects on HSP's.

δ_d	$\frac{\delta_{dref}}{\delta_d} = \left(\frac{V_{ref}}{V} \right)^{-1.25}$
δ_p	$\frac{\delta_{pref}}{\delta_p} = \left(\frac{V_{ref}}{V} \right)^{-0.5}$
δ_h	$\frac{\delta_{href}}{\delta_h} = \exp \left[-1.32 \times 10^{-3} (T_{ref} - T) - \ln \left(\frac{V_{ref}}{V} \right)^5 \right]$

Appendix C includes results of the equations summarized in Table 5-9 for CO₂.

5.4 Cosolvent Solubility Parameters

5.4.1 1-Parameter Models (Hildebrand)

As established for CO₂, total (Hildebrand) solubility parameters can be determined for nonpolar and weakly polar solvents using an appropriate equation of state and equating the calculated internal pressure to the cohesive energy density (see eqn. (4-17)). However, EOS data are often unavailable for compounds used as cosolvents or is available only over a very limited range of T and/or P. In these cases, the total solubility parameter can be found from the isobaric coefficient of thermal expansion, α , and the isothermal compressibility, β , since it can be shown that

$$\left(\frac{\partial E}{\partial V} \right)_T = T \cdot \left(\frac{\alpha}{\beta} \right)_P - P. \quad (5-69)$$

where, as before,

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad \text{and} \quad \beta = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad (5-70)$$

An alternative method for calculating the total (Hildebrand) solubility parameter is based on equating the cohesive energy density to the heat of vaporization.

The molar cohesive energy, E , can be divided into two parts:²⁸⁸ (1) the molar vaporization energy, required to vaporize a mole of the liquid to its saturated vapor (at constant volume), ${}_l\Delta_g E$, and (2) the energy, required to expand the saturated vapor to infinite volume at constant temperature; that is, the energy necessary to completely separate the molecules, ${}_g\Delta_\infty E$, so that

$$E = {}_l\Delta_g E + {}_g\Delta_\infty E \quad (5-71)$$

The molar vaporization energy is related to the molar vaporization enthalpy, ${}_l\Delta_g H$, by²⁸⁹

$${}_l\Delta_g E = {}_l\Delta_g H - PV \quad (5-72)$$

Assuming ideal behavior for the vapor phase, so that $PV = RT$,

$${}_l\Delta_g E = {}_l\Delta_g H - RT \quad (5-73)$$

The isothermal energy of expansion is related to the isothermal heat of expansion, i.e., the enthalpy change on isothermally expanding 1 mole of saturated vapor to zero pressure, ${}_g\Delta_\infty H$, by

$${}_g\Delta_\infty E = {}_g\Delta_\infty H + p_s V \quad (5-74)$$

where p_s is the saturation vapor pressure at temperature T and V is the molar volume of the liquid. The molar cohesive energy can therefore be written as

$$E = {}_l\Delta_g H + {}_g\Delta_\infty H - RT + p_s V \quad (5-75)$$

At pressures below 1 atmosphere ${}_g\Delta_\infty H$ and $p_s V$ are usually negligible,²⁹⁰ so that

$$E = {}_l\Delta_g H - RT \quad (5-76)$$

and the total solubility parameter, $(E/V)^{1/2}$, can therefore be written as

$$\delta = \left(\frac{\Delta H - RT}{V} \right)^{1/2} \quad (5-77)$$

where ${}_l\Delta_g H$ is identified with the molar heat of vaporization, ΔH .

From eqn. (5-77), it can be seen that total solubility parameter values of liquids can be calculated from the molar volume and molar heat of vaporization, determined at temperature T . It is usually possible to find a reliable value for the molar volume, but discrepancies frequently exist between reported values for ΔH , depending on whether the reported value is obtained experimentally, from calorimetric measurements, or by an estimation method. Some of these estimation methods will now be discussed.

The heat of vaporization is the difference between the enthalpy of the saturated vapor and that of the saturated liquid at the same temperature. Most estimation methods for ΔH are based on the Clausius-Clapeyron equation,²⁹¹ where it can be shown that ΔH is related to the slope of the saturated vapor-pressure curve by

$$\frac{dp_s}{dT} = \frac{\Delta H}{T\Delta V} = \frac{\Delta H}{(RT^2 / p_s)\Delta Z} \quad (5-78)$$

Here, p_s is the saturation vapor pressure, and ΔV and ΔZ are the differences in the molar volume and compressibility factor of saturated vapor and saturated liquid, respectively. Other empirical formulas relate ΔH at T to the heat of vaporization at the normal boiling point, T_b . Several variations of this type exist, including those due to Riedel,²⁹²

$$\Delta H_b \left(\frac{J}{mol} \right) = 1.093 RT_c \left[T_{br} \frac{\ln P_c - 1.013}{0.930 - T_{br}} \right] \quad (5-79)$$

Chen,²⁹³

$$\Delta H_b \left(\frac{J}{mol} \right) = RT_c T_{br} \frac{3.978 T_{br} - 3.958 + 1.555 \ln P_c}{1.07 - T_{br}} \quad (5-80)$$

Vetere,²⁹⁴

$$\Delta H_b \left(\frac{J}{mol} \right) = RT_c T_{br} \frac{0.4343 \ln P_c - 0.69431 + 0.89584 T_{br}}{0.37691 - 0.37306 T_{br} + 0.15075 P_c^{-1} T_{br}^{-2}} \quad (5-81)$$

and Hildebrand,²⁹⁵

$$\Delta H_b \left(\frac{cal}{mol} \right) = 17.0 T_b + 0.009 T_b^2 \quad (5-82)$$

In eqns. (5-79) to (5-82), P_c and T_c refer to the critical pressure and temperature, respectively, and T_{br} is the reduced boiling temperature (T_b/T_c). A number of other methods for estimating ΔH have been proposed, however none appear to offer significant advantages over those given above.

A third correlation for the latent heat of vaporization as a function of temperature makes use of the fact that ΔH decreases continuously with temperature along the boiling line and vanishes at the termination of the boiling line, i.e., the critical point. An early functional relationship proposed to express the variation of ΔH with T is the Watson equation²⁹⁶

$$\frac{\Delta H_{v2}}{\Delta H_{v1}} = \left(\frac{1 - T_{r2}}{1 - T_{r1}} \right)^n \quad (5-83)$$

where subscripts 1 and 2 refer to temperatures 1 and 2. A common choice of n is 0.375 or 0.38. Other variations of the Watson relation exist in the literature, with different functional forms for the temperature dependence.

Despite the differences between values obtained from the various estimation methods, the molar vaporization enthalpies (ΔH) and the solubility parameters (δ) obtained from them generally do not differ too widely, and each of the variety of methods usually provides values that are acceptable for many purposes. However this methodology will only be applicable below the critical temperature, as ΔH , as noted earlier, vanishes at T_c .

5.4.2 Calculation of HSP's

The total cohesive energy density can also be subdivided into contributions from various types of molecular interactions. In all cases, however, some approximations or assumptions are made, and the expressions resulting from these assumptions and approximations are not exact even for liquids, let alone polymers. Rather, the

expressions are best considered as useful, empirical relations which have some theoretical foundation but which are chosen for their practical usefulness in particular situations. The most important situation where caution is required is where specific interactions *within* a component exist. The most common of these, and the most problematic, is hydrogen bonding within a pure component.²⁹⁷

Methods to calculate individual HSP's depend to a great extent on what data are available. Commonly, a total solubility parameter is first determined from Hildebrand's original 1-component solubility parameter model, using either eqn. (4-21) or eqn. (5-77). The general approach is then to calculate two of the three parameters, δ_d , δ_p , δ_h , from methods to be described below and to then obtain the third parameter by difference from the total solubility parameter. HSP values calculated this way are available in the literature for a large number of liquid solvents and polymers.^{298,299}

5.4.2.1 Dispersion Solubility Parameter, δ_d

5.4.2.1.1 Homomorph Method

The initial approach to dividing the total solubility parameter into components representing dispersion, polar, and hydrogen bonding interactions was based on the homomorph concept and empirically on the basis of many experimental observations.³⁰⁰ The dispersion component, ΔE_d , was calculated directly from the energy of vaporization of the nonpolar homomorph. Following the additional recommendation that the homomorph should have the same molar volume as well as a similar structure to that of the polar compound, Blanks and Prausnitz³⁰¹ published a homomorphic plot of the energy of vaporization for straightchain hydrocarbons against molar volume at various reduced

temperatures. On the same basis, Weimer and Prausnitz³⁰² prepared homomorph plots of the cohesive pressure against molar volume at various temperatures for normal alkanes, cycloalkanes, and aromatic hydrocarbons. Using the appropriate homomorph, ΔE , used to approximate ΔE_d , or the cohesive energy density (δ_d^2) as a function of molar volume and reduced temperature, is obtained. The dispersion solubility parameter is then

$$\delta_d = \sqrt{\frac{\Delta E_d}{V}} \quad (5-84)$$

5.4.2.1.2 Index of refraction (n_D) Correlation

The main idea in this correlation is that the interaction energy between nonpolar molecules, due to van der Waals-London forces, is dependent on the polarizability (see eqn. (3-1)).³⁰³ The polarizability, in turn, is related to the refractive index, n_D , by the Lorentz-Lorenz equation,

$$\frac{4\pi N}{3V} \alpha = \frac{n_D^2 - 1}{n_D^2 + 2} \quad (5-85)$$

where N is the number of molecules per cubic centimeter (the Loschmidt number) and α is the average polarizability of the molecule. Subsequently, Koenhen and Smolder³⁰⁴ found a nearly linear relationship between δ_d and n_D for 60 nonpolar and polar liquid organic solvents in the region of n_D values ($1.3 < n_D < 1.6$).

$$\begin{aligned} \delta_D &= 9.55n_D - 5.55 \quad (\text{cal/cm}^3)^{1/2} \\ &= 19.5n_D - 11.4 \quad (\text{MPa}^{1/2}) \end{aligned} \quad (5-86)$$

The relation resulted in a correlation coefficient of 0.90 and a standard error of 0.32.

5.4.2.1.3 Group contribution method

This method provides a quick estimate of the dispersion parameter (or polar or hydrogen bonding parameters) based on a summing of the dispersion (or polar or hydrogen bonding) contribution of individual structural units within the molecule,

$$\delta_d = \frac{\sum F_{id}}{V} \quad (5-87)$$

where F_{id} is the molar attraction constant for dispersion forces of a specific functional group i . Molar attraction constants have been derived by Koenhen and Smolders,³⁰⁵ van Krevelen,³⁰⁶ and Hansen and Beerbower.³⁰⁷ A summary of these tables is presented in Barton.³⁰⁸ When using the group contribution method, it is essential to check that the molar attraction constants and cohesion parameter data from different literature sources are based on the same models and assumptions, and are therefore self-consistent.

5.4.2.2 *Polar Solubility Parameter, δ_p*

5.4.2.2.1 Böttcher Equation

Böttcher derived an empirical relation for calculating the contribution of permanent dipoles to the cohesion energy of a liquid or a gas. This energy is given as W in eqn. (5-88).³⁰⁹

$$W = \frac{-4\pi}{3} \frac{dN_A^2}{M} \frac{\epsilon - 1}{2\epsilon + n_D^2} \frac{(n_D^2 + 2)}{3} \mu^2 \quad (\text{calories}) \quad (5-88)$$

Hansen and Skkaarup³¹⁰ equated (W/V) with δ_p to assign polar HSP values:

$$\delta_p = \sqrt{\frac{12108}{V^2} \frac{\epsilon - 1}{2\epsilon + n_D^2} (n_D^2 + 2) \mu^2} \quad \left(\frac{\text{cal}}{\text{cm}^3} \right)^{1/2} \quad (5-89)$$

The use of this equation requires the molar volume (V), dipole moment (μ), refractive index (n_D), and the dielectric constant (ϵ) of the compound.

5.4.2.2.2 Hansen/Beerbower Equation

This equation is a simplified version of the Böttcher equation, eqn. (5-89), and has been used extensively by Hansen.³¹¹

$$\delta_p = 37.4 \frac{\mu}{V^{1/2}} \quad (\text{MPa})^{1/2} \quad (5-90)$$

An extensive listing of dipole moments can be found in McClellan.³¹² It must be noted that $\mu = 0$ (for nonpolar molecules) is not a sufficient basis to assign $\delta_p = 0$.³¹³

5.4.2.2.3 Group Contribution Method

When the dipole moment of a molecule is unknown, group contributions can be used to estimate δ_p :

$$\delta_p = \frac{\sqrt{\sum F_{ip}^2}}{V} \quad (5-91)$$

Molar attraction constants have been derived by Koenhen and Smolders,³¹⁴ van Krevelen,³¹⁵ and Hansen and Beerbower.³¹⁶ A summary of these tables is presented in Barton.³¹⁷

5.4.2.3 Hydrogen Bonding Solubility Parameter, δ_h

5.4.2.3.1 Difference Method

In early tabulations of HSP's, the hydrogen bonding parameter was almost always found by subtracting the sum of the polar and dispersion energies from the total energy of vaporization, so that

$$(\delta_h)^2 = \delta^2 - \delta_d^2 - \delta_p^2 \quad (5-92)$$

This is still widely used where the required data are available and reliable.

5.4.2.3.2 Group Contribution Method

Estimation methods based on group contribution are considered reasonably reliable for most of the required calculations. Hansen and Beerbower,³¹⁸ however, have determined that the group contribution method using molar attraction constants, as in eqn. (5-87) and eqn. (5-91), is not directly applicable to the calculation of δ_h . Instead, they have assumed that hydrogen bonding contributions from structural units within a molecule to the overall molecular hydrogen bonding cohesive energy are additive, leading to

$$\delta_h = \left(\frac{\sum U_h}{V} \right)^{1/2} \quad (5-93)$$

Caution is needed, however, in adding group contributions in the use of a single hydrogen bonding parameter to describe an interaction really requiring both donor and acceptor components. Hydrogen bonding parameter group contributions, based on structural group, have been comprised by Koenhen and Smolders,³¹⁹ van Krevelen,³²⁰ and Hansen and Beerbower.³²¹ A summary of these tables is presented in Barton.³²²

Figure 5-6 gives a summary of the methods for the determination of HSP values.

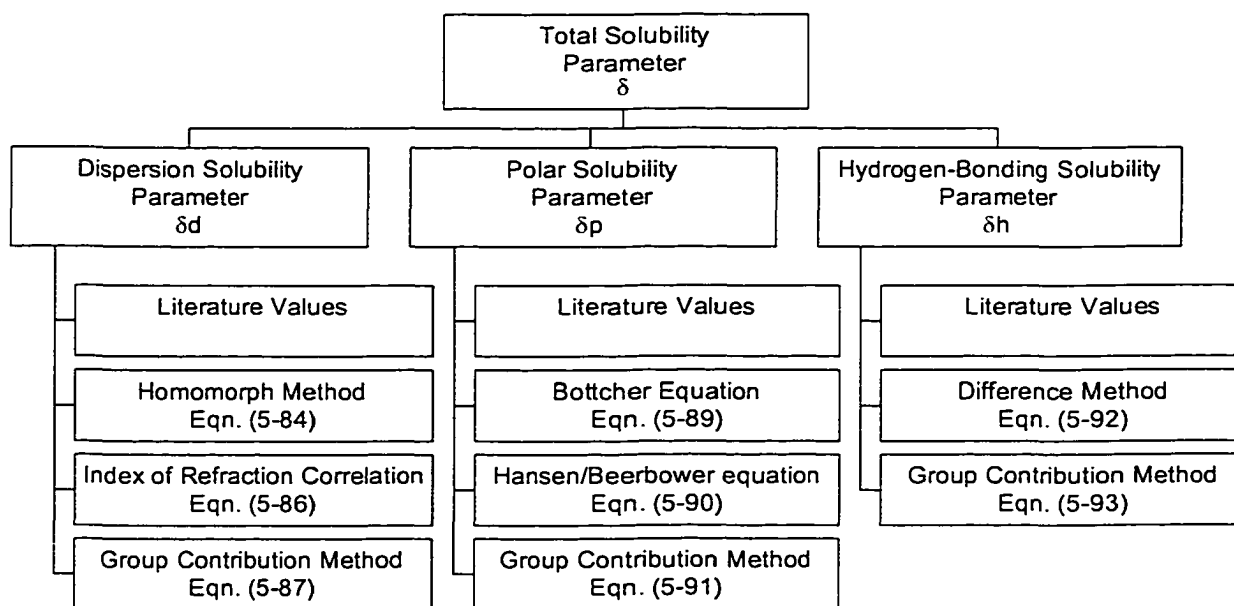


Figure 5-6. Available methods for the calculation of Hansen solubility parameters δ_d , δ_p , δ_h .

5.4.3 Temperature and Pressure Effects

Adjusting cosolvent HSP values for temperature and pressure effects will require obtaining either an EOS for the desired cosolvent, or reliable coefficient of thermal expansion (α) and isothermal compressibility (β) data. Depending on which of the two methods is used, cosolvent HSP values can be adjusted using the derivative equations summarized in Table 5-8, or the integrated equations summarized in Table 5-9.

5.5 Polymer Solubility Parameters

5.5.1 1-Component Models (Hildebrand)

The solubility parameters of polymers can be evaluated directly from the heat of vaporization and eqn. (5-77) only for those polymers that can be vaporized. However, as with the solvent and cosolvent (section 5.1.2 and 5.4.1), polymer solubility parameters can be approximated from calculation of the internal pressure, eqn. (5-12), along with suitable PVT data or EOS,

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_T - P \quad (5-94)$$

It has been observed, however, that the internal pressure of polymers measured above and below the glass transition temperature, T_g , shows unusual behavior.³²³ At temperatures above T_g , where the polymer is in the rubber state, the variation of internal pressure with temperature is qualitatively indistinguishable from the behavior shown by

other organic molecules. However, as the temperature is lowered and T_g is reached, the internal pressure has been observed to drop, falling rapidly with decreasing temperature. Yet in passing through T_g , no sudden change in the magnitude of the internal pressure should be expected.³²⁴ This behavior is illustrated in Figure 5-7, where the internal pressure, P_i , is plotted against T from 20°C to 150°C for polymethylmethacrylate (PMMA).³²⁵

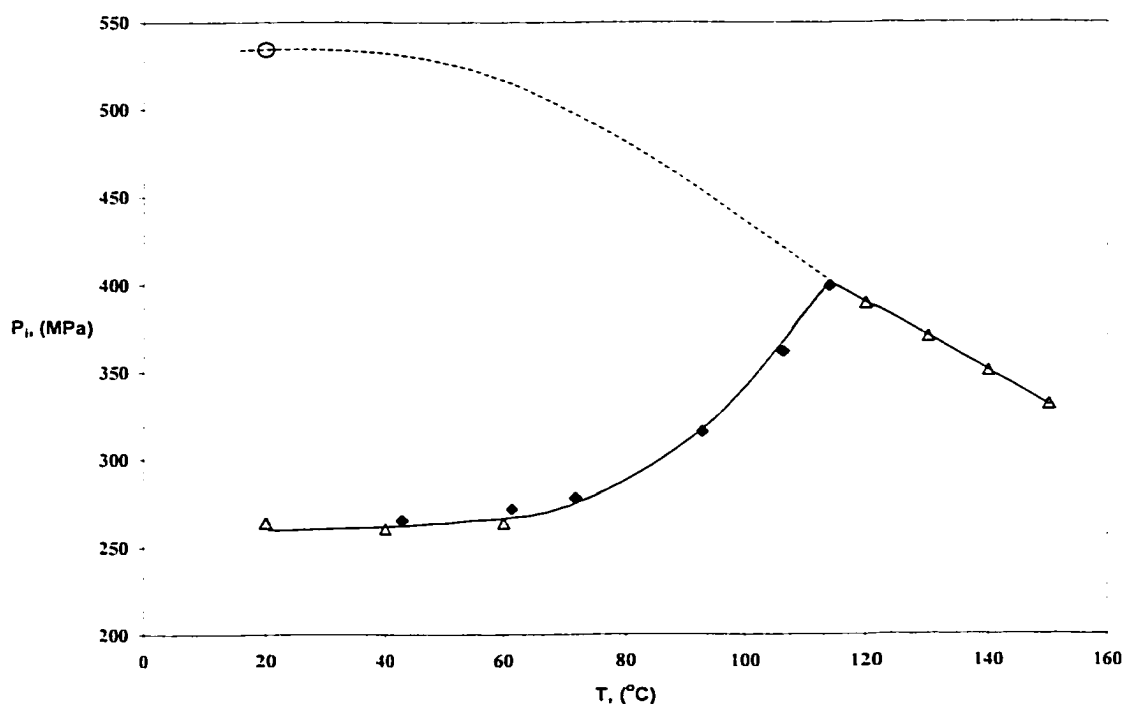


Figure 5-7. The internal pressure of PMMA as a function of temperature. Symbols: ♦ data of Allen, Sims and Wilson,³²⁶ Δ data of Hellwege, Knappe and Lehmann,³²⁷ O calculated from solution data after Hansen³²⁸.

Additionally, internal pressure values have been calculated from eqn. (5-69)

$$\left(\frac{\partial E}{\partial V} \right)_T = T \cdot \left(\frac{\alpha}{\beta} \right)_V - P \quad (5-95)$$

and α and β are determined from polymer PVT data. Representative PVT data for PMMA, poly(vinyl butyral), and PC are shown in Figures 5-8, 5-9, and 5-10.

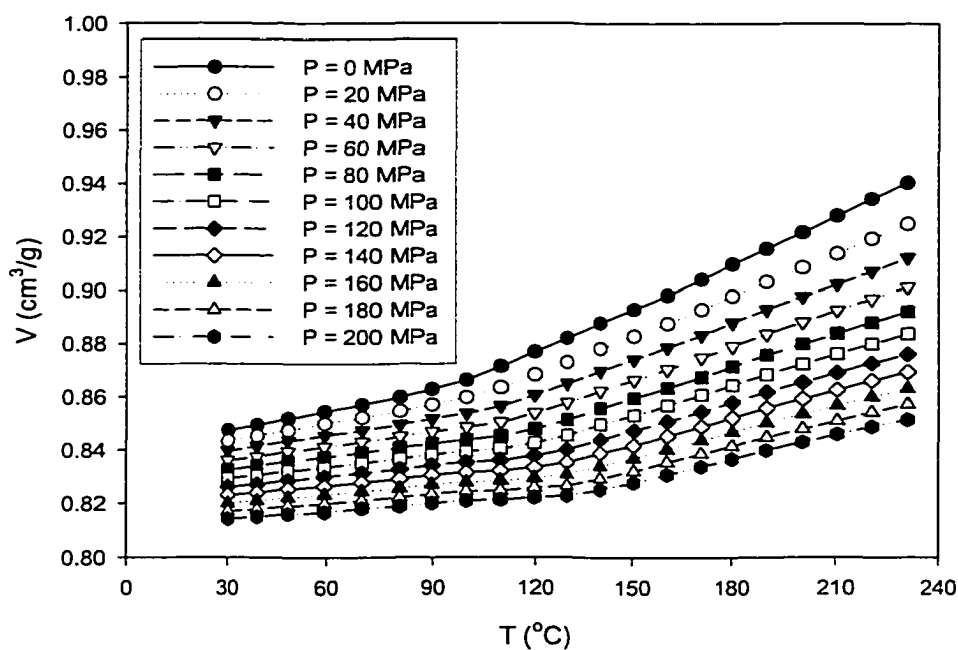


Figure 5-8. Plots of standard PVT for PMMA ($M = 1 \times 10^5$).³²⁹

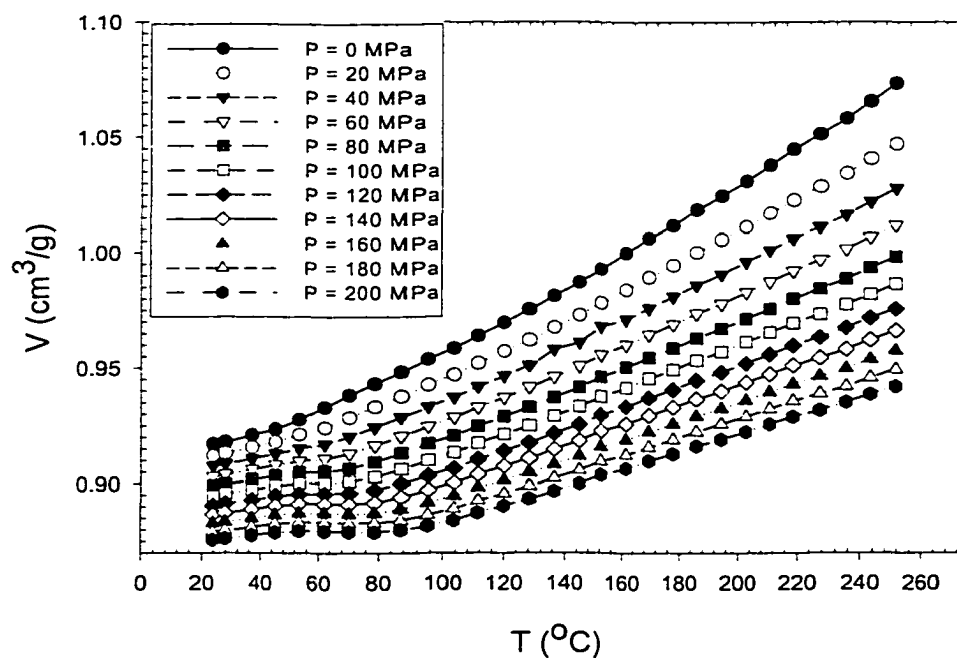


Figure 5-9. Plots of standard PVT Poly(vinyl butyral).³³⁰

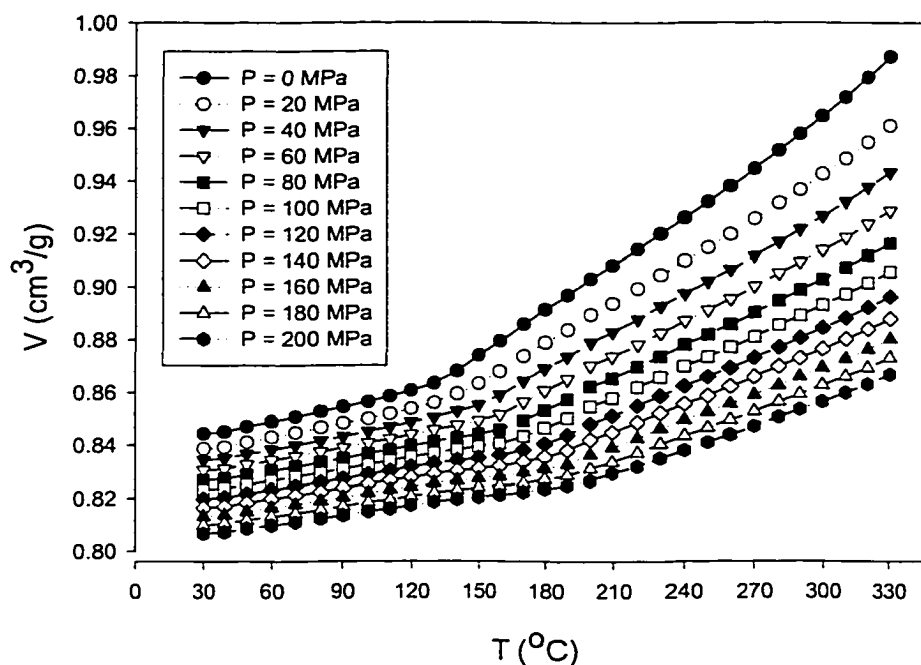


Figure 5-10. Plots of standard PVT for Polycarbonate.³³¹

From an examination of the PVT data plotted in Figure 5-8 through 5-10, noticeable “breaks”, or changes in slope, in the various isobars are observed for each of the polymers. This change in slope represents the polymers glass transition (from rubber to glass on cooling). Therefore, the data well to the left of the break represents PVT data for the polymer’s glass state, while the PVT data to the right of the break, represents data for the polymer’s rubber state. Although not quantified at this time, it is apparent that the isobaric thermal expansion coefficient, α , decreases significantly, whereas the effect on the isothermal compressibility, β , is much less marked in the rubber-glass transition.³³² The lower values of α in the glass versus rubber state will also result in a lower internal pressure, for the glass, as calculated from eqn. (5-95).

In considering the reason for this apparent decrease in internal pressure it is necessary to reconsider the concept of internal pressure, as utilized in this work, as an equilibrium quantity. It is therefore applicable to materials, including polymers, only when local, internal equilibrium can be maintained, i.e., above T_g . Internal pressure, as defined in section 4.1 has no meaning below T_g . It is therefore pointless to talk about the internal pressure (as defined here) of a polymer below T_g , since T_g represents the loss of internal degrees of freedom of the polymer matrix, and, at any temperature below T_g , the polymer is therefore in a nonequilibrium state.

Experimental PVT data, such as shown in Figures 5-8 to 5-10, is available in the literature for some polymers. One excellent source is a compilation by Zoller and Walsh.³³³ In the absence of extended tabulations of measured data, empirical models for the PVT behavior of polymers must be used. The most widely employed equation for representing the PVT data for polymers is the Tait equation.³³⁴ The Tait equation relates the specific volume, $V(P,T)$, in terms of the zero-pressure volume, $V(0,T)$, and the Tait parameter, $B(T)$,

$$V(P,T) = V(0,T) \left(1 - C \ln \left[1 + \frac{P}{B(T)} \right] \right) \quad (5-96)$$

The parameter C is often taken to be independent of temperature and pressure, and a universal value of 0.0894 is commonly assumed. $B(T)$ is parameterized as

$$B(T) = B_o \exp(-B_1 T) \quad (5-97)$$

and the zero-pressure volume $V(0,T)$ is parameterized by

$$V(0,T) = A_0 + A_1T + A_2T^2 \quad (5-98)$$

where B_0 , B_1 , A_0 , A_1 and A_2 are material dependent parameters and T is in degrees Centigrade.

The Tait equation provides a convenient means to compute the of thermal expansion coefficient, α , and isothermal compressibility, β ,

$$\alpha(P,T) = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \alpha(0,T) - PB_1\beta(P,T) \quad (5-99)$$

and

$$\beta(P,T) = \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = \frac{C/(P + B(T))}{1 - C \ln(1 + P/B(T))} \quad (5-100)$$

where

$$\alpha(0,T) = \frac{A_1 + 2A_2T}{A_0 + A_1T + A_2T^2} \quad (5-101)$$

This allows for calculation of the internal pressure, and the solubility parameter, using eqn. (5-95).

Application of the Tait equation, however, is restricted to polymers where the parameters A_i , B_i have been regressed from experimental data, since no methods are currently available to estimate them from chemical structure. Tabulated values are currently available for 56 polymers.³³⁵

A variety of other empirical equations have been proposed to describe the PVT behavior of polymers, although none of these equations have been used as extensively as

the Tait equation. These equations will be briefly mentioned here, along with a reference containing more detailed discussions.

1. Spencer and Gilmore³³⁶ modified the van der Waals equation of state for polymers, employing a constant value for the internal pressure instead of the van der Waals' attractive term $\left(\frac{a}{V^2}\right)$,

$$(P + \pi)(V - \omega) = RT \quad (5-102)$$

where P is the external pressure, π is the internal pressure, V is the volume, and ω is the polymer volume at absolute zero temperature. The Spencer-Gilmore equation is a very simple two-parameter equation, however, it has only been applied with moderate success to a limited number of polymers.³³⁷

2. Weir³³⁸ developed an empirical isobaric equation to describe the PVT relationship of polymers. Along an isobar, the volume is expressed as a polynomial equation in temperature

$$V = V_o \left[(1 + a_1 P + a_2 P^2) + (1 + b_1 P + b_2 P^2) T + (1 + c_1 P + c_2 P^2) T^2 \right] \quad (5-103)$$

where V_o is the specific volume at 21°C, a_i , b_i and c_i are material constants of the polymer. The Weir equation, with its 10 undetermined coefficients, is cumbersome to use. Furthermore, it is also noted to be less accurate than the Tait equation.³³⁹

3. Whitaker and Griskey³⁴⁰ observed that at any given temperature, the correlation between the compressibility factor, i.e. PV/RT , and a reduced temperature, T/T_g , resulted in a family of curves that can be collapsed into a single master curve. Their equation for this corresponding states curve is

$$V = \left[\frac{0.01205}{\rho_o^{0.9421}} \right] P^{n-1} \left(\frac{T}{T_g} \right)^{m+1} R \quad (5-104)$$

where n and m are universal parameters for all polymers that depend on pressure and are given graphically in the original article. Consequently, only the polymer density at 25°C and 1 atm, ρ_o , and the glass transition temperature, T_g , are needed to estimate the temperature and pressure dependent specific volume. Although the Whitaker-Griskey equation has limited predictive capability if ρ_o and T_g of the polymer are known, it does not have the accuracy offered by the other empirical PVT equations.³⁴¹

4. Hartman and Haque³⁴² derived an equation of state by combining the theoretical temperature dependence of thermal pressure from Pastine and Warfield³⁴³ with the zero pressure isobar of the Simha-Somcynsky³⁴⁴ equation of state and an empirical volume dependence of the thermal pressure. The equation, in reduced form, is given by

$$\tilde{P}\tilde{V}^5 = \tilde{T}^{3/2} - \ln \tilde{V} \quad (5-105)$$

where

$$\tilde{P} = \frac{P}{P_o}; \quad \tilde{V} = \frac{V}{V_o}; \quad \tilde{T} = \frac{T}{T_o} \quad (5-106)$$

and P_o , V_o , and T_o are the reducing parameters. P_o is the isothermal bulk modulus extrapolated to zero temperature and pressure, V_o is the polymer liquid volume extrapolated to zero temperature and pressure, and T_o is defined implicitly from the relation $V(P_o, T_o) = V(0, 0)$. The Hartman-Haque equation is a relatively new but promising empirical equation of state with only three parameters and has an accuracy comparable to the Tait equation. Both the Tait and Hartman-Haque equations have been evaluated for a variety of polymers.³⁴⁵

Other correlation methods can also be utilized for determining polymer solubility parameter values. As with solvent and cosolvent, a polymer internal pressure can be used as an approximation of the cohesive energy density and δ^2 . Correlations between internal pressure and cohesive energy density have also been evaluated for polymer systems. A theoretical derivation by Voeks³⁴⁶ resulted in

$$\frac{\left(\frac{\partial E}{\partial V}\right)_T}{\left(\frac{\Delta E}{V}\right)} = n \approx 1.3 \quad (5-107)$$

Where the internal pressure and cohesive energy density are again related by the quantity n (see eqn. 4-18).

Values of internal pressure and cohesive energy density for a number of polymers are compared in Table 5-10,³⁴⁷ which shows eqn. (5-107) to be a valid first approximation.

Table 5-10. Comparison of internal pressure and cohesive energy density of polymers at 20°C.

Polymer	$\left(\frac{\partial E}{\partial V}\right)_T$ (bar)	$\left(\frac{\Delta E}{V}\right)_T$ (bar)	n
Polyethylene	3200	2500/2900	1.3/1.1
Polyisobutylene	3300	2500/2700	1.3/1.2
Polystyrene	4600	3000/3600	1.5/1.3
Polyvinyl acetate	4300	3600/5100	1.2/0.8
Polyethyl acrylate	4400	3500/3700	1.3/1.2
Polymethyl methacrylate	3800	3400/6900	1.1/0.6
Polypropylene oxide	3700	2300/4200	1.6/0.9
Polydimethyl siloxane	2400	2200/2400	1.1/1.0

Another method to estimate total solubility parameters of polymers is based on surface tension. Since surface tension is a direct manifestation of intermolecular forces, it may therefore be expected that a relation exists between surface tension and cohesive energy density. The relationship is³⁴⁸

$$\delta^2 \approx \frac{\gamma^{3/2}}{0.75} \quad (5-108)$$

where γ is in mJ/m² and δ^2 is in J/cm³. Values of surface tension for polymer melts have been determined and are available in the literature. According to Macleod's relation, the surface tension varies with density according to³⁴⁹

$$\gamma = \gamma^o \rho^{\kappa} \quad (5-109)$$

where γ^o and κ are constants, independent of temperature. The κ is known as Macleod's exponent, and usually has a value of 3.0–4.5 for polymers³⁵⁰. Alternatively, the interfacial energy of solid polymers may be calculated from an additive function, known as the parachor, by applying the following equation.

$$\gamma = \left(\frac{P_s}{V} \right)^4 \quad (5-110)$$

where P_s is the parachor parameter and V is the molar volume of the repeat unit. Parachor atomic and structural contribution constants were originally introduced by Sugden³⁵¹ and later modified by Mumford and Phillips,³⁵² and by Quayle.³⁵³ The group contributions to the parachor as presented by different investigators are given in Table 5-11.³⁵⁴

Table 5-11. Atomic and structural contribution to the Parachor.

Unit	Values assigned by $[(\text{cm}^3/\text{mol}) \times (\text{mJ}/\text{m}^2)^{1/4}]$		
	Sugden	Mumford and Phillips	Quayle
CH ₂	39.0	40.0	40.0
C	4.8	9.2	9.0
H	17.1	15.4	15.5
O	20.0	20.0	19.8
O ₂ (in esters)	60.0	60.0	54.8
N	12.5	17.5	17.5
S	48.2	50.0	49.1
F	25.7	25.5	26.1
Cl	54.3	55.0	55.2
Br	68.0	69.0	68.0
I	91.0	90.0	90.3
Double bond	23.2	19.0	16.3-19.1
Triple bond	46.4	38.0	40.6
3-membered ring	16.7	12.5	12.5
4-membered ring	11.6	6.0	6.0
5-membered ring	8.5	3.0	3.0
6-membered ring	6.1	0.8	0.8
7-membered ring		-4.0	4.0

In Table 5-12, polymer solubility parameter values obtained in the literature are compared with values calculated from the polymer surface tension, eqn (5-108) and eqn. (5-110).

Table 5-12. Polymer surface tension and solubility parameters.

Polymer	Surface Tension mJ/m ²		Solubility Parameter MPa ^{1/2}		
	Observed	Calculated from P _s	Eqn. (5-108) Lit. γ	Eqn. (5-110) from P _s	Lit.
Polytetrafluoro ethylene	18.5	26	10.3	13.3	13.1
Poly(dimethyl siloxane)	24	21.5	12.5	11.5	14.9
Polyisobutylene	27	30.5	13.7	15.0	16.3
Polypropylene	29	32.5	14.4	15.7	16.6
Polyethylene	31	31.5	15.2	15.3	16.5
Poly(vinyl acetate)	37	40	17.3	18.4	19.2
Poly(vinyl alcohol)	37	59	17.3	24.6	25.6
Poly(ethylene terephthalate)	41.5	49	18.9	21.4	21.7
Poly(methyl methacrylate)	39	42	18.0	19.0	22.4
Poly(vinyl chloride)	39	42	18.0	19.0	19.4
Polycarbonate	45	42.5	20.1	19.2	20
Poly(vinyl butyral)	38	-	16.6	-	23

Another polymer property that shows a general correlation with cohesive energy is the glass transition temperature, T_g . It is generally observed that there is an approximately linear dependence of T_g on cohesive energy density, so that polymers with high values of T_g tend to have high (Hildebrand) total solubility parameters.³⁵⁵ Although there is no direct mathematical relationship, Table 5-13 illustrates the general trend (with the exception of poly(vinyl alcohol), and poly(vinyl butyral)) in polymer glass transition values and solubility parameters.

Table 5-13. Polymer glass transition temperatures and solubility parameters.

Polymer	T_g (°C)^{356,357}	δ, (MPa)^{1/2} ³⁵⁸
Poly(dimethyl siloxane)	-128	14.9
Polyethylene	-125	16.4
Natural rubber	-72	16.6
Polybutadiene	-25	17.6
Poly(tetrafluoroethylene)	27	13.1
Poly(vinyl acetate)	30	19.3
Poly(vinyl butyral)	51	23.1
Poly(ethyl methacrylate)	66	18.6
Poly(ethylene terephthalate)	69	21.8
Poly(vinyl chloride)	75	19.4
Poly(vinyl alcohol)	85	25.6
Poly(methyl methacrylate)	105	18.8
Polycarbonate	148	20.0

5.5.2 Calculation of Polymer HSP's

Hansen's original solubility parameter work was developed out of studies into film drying and solvent retention, the phenomenon that solvent can be found in many paint and varnish films years after their application. The assumption was that hydrogen bonding between the solvent and polymer molecules was responsible for this retained solvent. Although this assumption was ultimately found to be false, the statement that hydrogen bonding had no significant effect on solvent retention without defining hydrogen bonding was not satisfactory for Hansen. Therefore, in order to better define hydrogen bonding and polar bonding, Hansen initiated a study based on the Hildebrand solubility parameter. This study eventually led to the concept of a three dimensional solubility parameter,³⁵⁹ a concept that has gone on to become an important tool for the study of solubility, swelling, and other physical interactions between polymers and solvents. For this reason, extensive compilations exist of total solubility parameters and

dispersion and polar HSP's for polymers. Also, hydrogen-bonding HSP's have been determined from turbidimetric titrations of solubility in solvents and from swelling of polymers in solvents, where the solvent has been previously characterized for its HSP's.

Because many polymers are amorphous and, therefore, "liquid-like" in some of their properties, their solubility behavior can be treated by many of the methods used for liquids. For this reason, the correlations developed in Section 5.4.2 for cosolvents, are also applicable for polymers.

5.5.2.1 *Dispersion Solubility Parameter, δ_d*

Two of the relations discussed in Section 5.4.2.1 can be utilized for polymers: the index of refraction correlation and the group contribution method.

5.5.2.1.1 Index of refraction (n_D) Correlation

Koenhen and Smolder³⁶⁰ predicted δ_d for several polymers using the index of refraction, n_D ,

$$\begin{aligned} \delta_D &= 9.55n_D - 5.55 \quad (\text{cal/cm}^3)^{1/2} \\ &= 19.5n_D - 11.4 \quad (\text{MPa}^{1/2}) \end{aligned} \quad (5-111)$$

5.5.2.1.2 Group contribution method

As discussed earlier for cosolvent HSP's, this method provides a quick estimate of the dispersion parameter (a similar approach has been developed for the polar and

hydrogen HSP's) based on a summing of the contributions of individual structural units within the molecule to the total dispersion energy

$$\delta_d = \frac{\sum F_{id}}{V} \quad (5-112)$$

where F_{id} is the molar attraction constant for dispersion forces of a specific group i . Molar attraction constants have been derived by Koenhen and Smolders,³⁶¹ van Krevelen,³⁶² and Hansen and Beerbower.³⁶³ A summary of these tables is presented in Barton.³⁶⁴

5.5.2.2 Polar Solubility Parameter, δ_p

Two of the relations discussed in Section 5.4.2.2 can be utilized for polymers: the Hansen/Beerbower equation and the group contribution method.

5.5.2.2.1 Hansen/Beerbower Equation

If the dipole moment of the polymer is known, eqn. (5-113) can be used to predict δ_p . The measured average dipole moments of polymers are generally 70-90% of the dipole moment of the corresponding monomer unit, therefore for polymer μ values not found in the literature, an estimated dipole moment of 80% of the dipole moment of the monomer is recommended,³⁶⁵ so that

$$\delta_p = 37.4 \frac{\mu}{V^{1/2}} \quad (MPa)^{1/2} \quad (5-113)$$

5.5.2.2.2 Group Contribution Method

When the dipole moment of a molecule is unknown, group contributions can be used to estimate the polar solubility parameter.

$$\delta_p = \frac{\sqrt{\sum F_{ip}^2}}{V} \quad (5-114)$$

Molar attraction constants have been derived by Koenhen and Smolders,³⁶⁶ van Krevelen,³⁶⁷ and Hansen and Beerbower.³⁶⁸ A summary of these tables is presented in Barton.³⁶⁹

5.5.2.3 *Hydrogen Bonding Solubility Parameter, δ_h*

5.5.2.3.1 Difference Method

In the earlier tabulations, the hydrogen bonding parameter was almost always found by subtracting the sum of the polar and dispersion energies from the total energy of vaporization, so that

$$(\delta_h)^2 = \delta^2 - \delta_d^2 - \delta_p^2 \quad (5-115)$$

This is still widely used where the required data are available and reliable.

5.5.2.3.2 Group Contribution Method

As with the calculation of δ_h for cosolvents, Hansen and Beerbower have assumed that the contribution of individual molecular subunits to the total hydrogen bonding cohesive energy are additive, leading to

$$\delta_h = \left(\frac{\sum U_h}{V} \right)^{1/2} \quad (5-116)$$

Hydrogen bonding contributions, based on structural group, have been compiled by Koenhen and Smolders,³⁷⁰ van Krevelen,³⁷¹ and Hansen and Beerbower.³⁷² A summary of these tables is presented in Barton.³⁷³

In Figure 5-11 a summary of the methods for determining polymer HSP values is

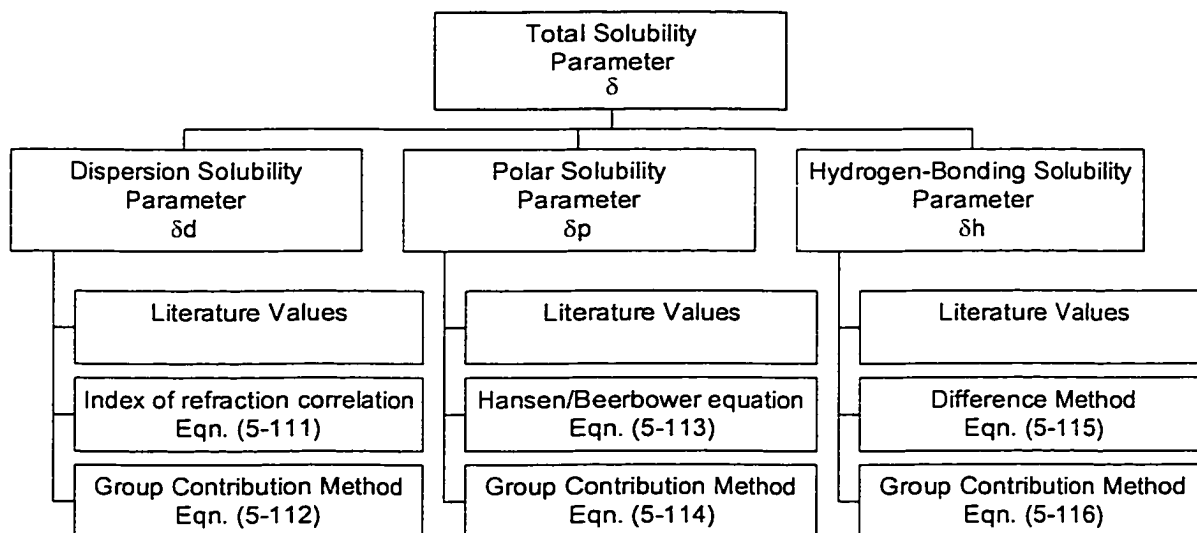


Figure 5-11. Diagram of the components, δ_d , δ_p , δ_h , to the total Hansen solubility parameter, δ , and methods for their determination.

shown.

5.5.3 Temperature and Pressure Effects

Adjusting polymer HSP values for temperature and pressure effects can be approached in several ways. One option is the use of published PVT data for the given polymer and using the equations developed in Section 5.3 and summarized in Table 5-9. Alternatively, the coefficient of thermal expansion and the isothermal compressibility in the rubber state, along with the equations developed in Section 5.3 and summarized in Table 5-8 can be used. Lastly, empirical equations of state (such as the Tait equation) can be used to generate the necessary PVT data or α and β for use in either the derivative or integrated equations. All of these approaches, however, are applicable only to PVT states in the polymer's rubber phase.

6 Binary Interactions

6.1 Solvent/Polymer Interactions

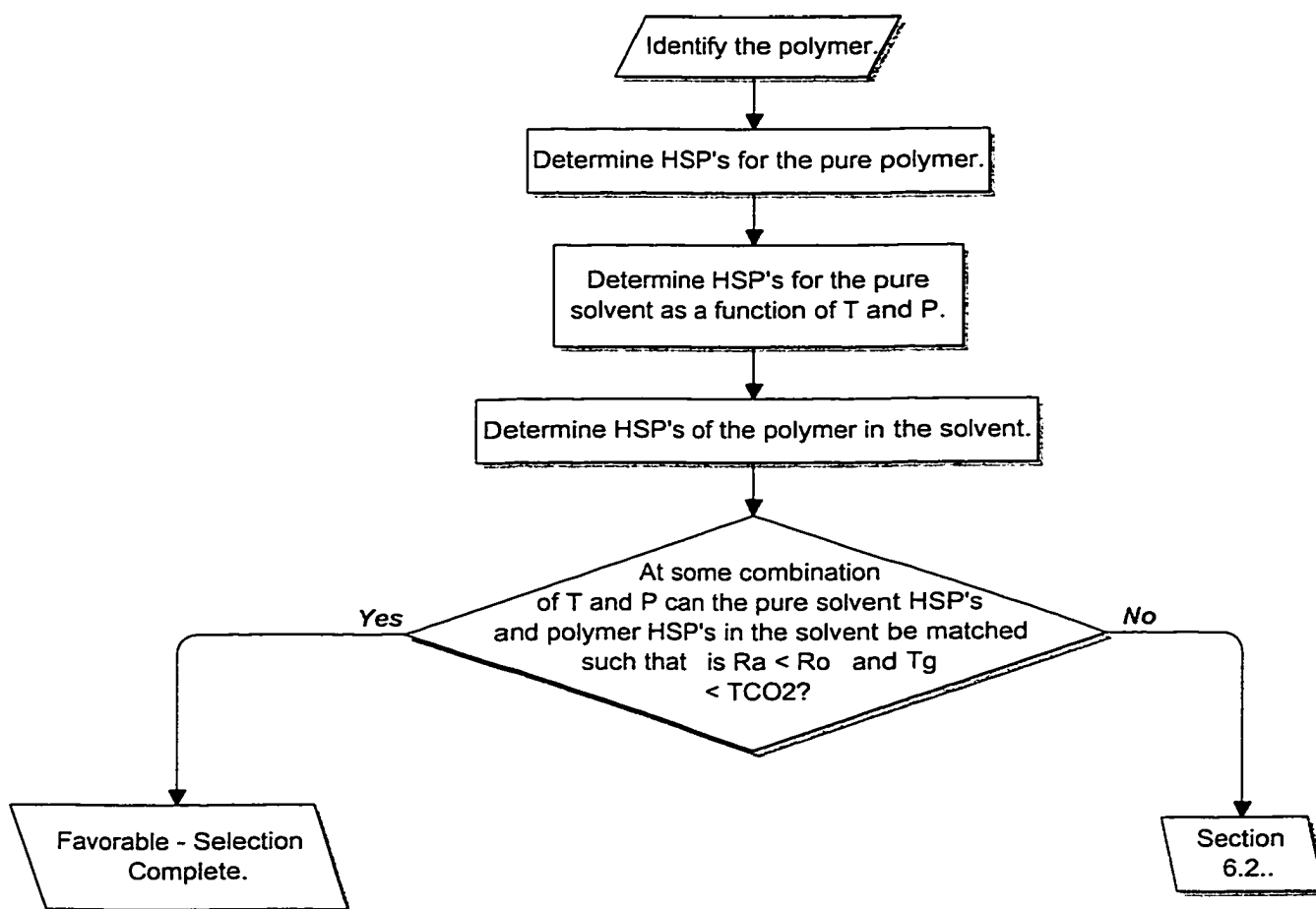


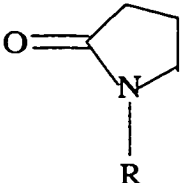
Figure 6-1. Decision tree for the selection of an optimum solvent for a desired polymer interaction.

The removal of polymer coatings with a (supercritical) solvent is dependent on sorption of the solvent into the polymer, and therefore on favorable intermolecular interactions. Predicting and optimizing this sorption means producing conditions giving the best match between the solubility parameters of the solvent (CO₂) and the polymer. This will require knowledge of the chemical and physical characteristics of the polymer.

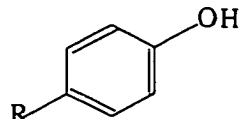
The ability of a polymer to solublize CO₂ depends on its chemical structure. For example, it has been shown that polymers possessing electron-donating (Lewis base) functional groups exhibit specific (attractive) interactions with CO₂.³⁷⁴ In theory, the presence and strength of an acid-base interaction can be predicted from the type, number, and location of functional groups within a given polymer. Many industrial polymers contain pyrrolidone, ether, nitrile, carbonyl, siloxane, or fluorine groups that act as proton acceptors (Lewis bases) in the presence of CO₂, or hydroxyl, phenol, sulfonic acid, or carboxyl groups that act as proton donors (Lewis acids) in a CO₂ environment.³⁷⁵ Table 6-1 illustrates these functional groups.

Table 6-1. Common polymer functional groups and their Lewis acid-base behavior in the presence of CO₂.

Lewis Base Functional Groups

Pyrrolidone	Ether	Nitrile	Carbonyl	Siloxane	Fluorine
	$\begin{array}{c} \text{C} - \text{O} - \text{C} \\ \quad \quad \\ \text{R} \quad \quad \text{R} \end{array}$	$\begin{array}{c} \text{N} \equiv \text{C} - \text{C} \\ \\ \text{R} \end{array}$	$\begin{array}{c} \text{R} \\ \\ \text{C} = \text{O} \\ \\ \text{R} \end{array}$	$\begin{array}{c} \text{Si} - \text{O} \\ \quad \\ \text{R} \quad \text{R} \end{array}$	$\text{R} - \text{F}$

Lewis Acid Functional Groups

Hydroxyl	Phenol	Sulfonic Acid	Carboxyl
$\text{R} - \text{OH}$		$\begin{array}{c} \text{O} \\ \\ \text{R} - \text{S} - \text{OH} \\ \\ \text{O} \end{array}$	$\begin{array}{c} \text{O} \\ \\ \text{R} - \text{C} - \text{OH} \end{array}$

As an example of specific intermolecular interactions, it has been documented that the presence of a carbonyl group in a polymer enhances the solubility of CO₂.^{376,377,378,379,380,381,382,383,384} There is spectroscopic evidence that the interaction of the carbonyl oxygen (acting as a Lewis base) with the carbon atom of CO₂ (acting as a Lewis acid), produces an ordered “complex” in one of the two configurations shown in Figure 6-2.

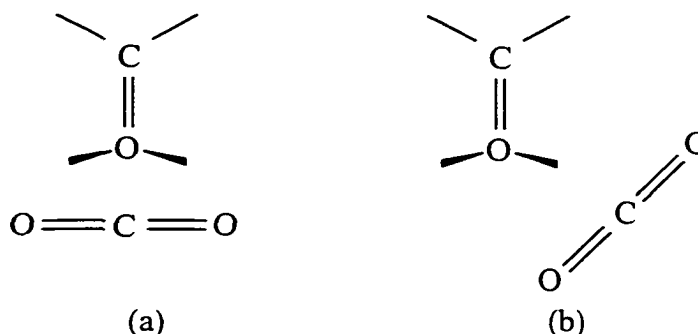


Figure 6-2. Proposed physical configuration produced by Lewis acid-base interaction between CO₂ and polymeric carbonyl functional group.³⁸⁵

The evidence for this type of interaction was found by Kazarian and coworkers³⁸⁶ using Fourier transform infrared spectroscopy. Details of this work can be found in the indicated reference, but the general results support the importance of Lewis base functional groups, and particularly the carbonyl functional group, in the strength of a Lewis acid-base type interaction with CO₂, and the resulting enhancement of CO₂ solubility. Table 6-2 lists the polymers evaluated by Kazarian in the order of decreasing CO₂ interaction strength (based on the change in the CO₂ bending mode frequency). Also included in the table, for comparison, is CO₂ sorption data at comparable temperature and pressure conditions. It is noted in the table whether the sorption data was measured in-situ (at pressure and temperature), or ex-situ (immediately following depressurization). It was noted by Kazarian in this work that the higher sorption of CO₂ with poly(styrene) compared to poly(ethylene) is due a weak acid/base interaction electrostatic interactions of CO₂ with the benzyl group in polystyrene, acting as a weak Lewis base.

Table 6-2. Strength of interaction of CO₂ with polymers containing Lewis base groups, as measured by molecular bending mode frequency, $\Delta\nu_{1/2}$, and measured CO₂ solubility, [CO₂].

Polymer	Monomer Structure	$\Delta\nu_{1/2}$ (cm ⁻¹) ³⁸⁷	[CO ₂] × 10 ³ (moles CO ₂ /cm ³ polymer)
Poly(vinyl acetate)- PVA	$\left[\begin{array}{c} \text{CH} - \text{CH}_2 - \\ \\ \text{O} - \text{C} - \text{CH}_3 \\ \\ \text{O} \end{array} \right]_n$	16	13.1 ³⁸⁸ (in-situ) (25°C, 65.5 bar) 6.16 ³⁸⁹ (in-situ) (47°C, 60 bar)
Poly(ethyl methacrylate) – PEMA	$\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{C} - \text{CH}_2 - \text{CH}_2 \\ \\ \text{C} - \text{O} - \text{CH}_2 \\ \\ \text{O} \quad \text{CH}_3 \end{array} \right]_n$	15	4.09 ³⁹⁰ (in-situ) (35°C, 44.5 bar) 2.50 ³⁹¹ (in-situ) (55°C, 44.5 bar)
Poly(methyl methacrylate) – PMMA	$\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{C} - \text{CH}_2 - \text{CH}_2 \\ \\ \text{C} - \text{O} - \text{CH}_3 \\ \\ \text{O} \end{array} \right]_n$	15	3.86 ³⁹² (in-situ) (35°C, 50 bar) 2.18 ³⁹³ (in-situ) (65°C, 50 bar)
Poly(styrene) – PS	$\left[\begin{array}{c} \text{CH} - \text{CH}_2 - \\ \\ \text{C}_6\text{H}_5 \end{array} \right]_n$	0	2.03 ³⁹⁴ (in-situ) (35°C, 51 bar) 1.48 ³⁹⁵ (in-situ) (50°C, 51 bar)
Poly(ethylene) – PE	$\left[\text{CH}_2 - \text{CH}_2 \right]_n$	0	0.12 ³⁹⁶ (ex-situ) (40°C, 69 bar)

The location of the functional group within a polymer also affects the amount of CO₂ sorption,³⁹⁷ as seen in the example of CO₂ uptake in poly(methyl methacrylate) (PMMA) and glycol modified poly(ethylene terephthalate) (PETG), Figure 6-3. In this study, PMMA showed greater CO₂ solubility than PETG, despite the higher T_g for PMMA (105°C vs 79°C). Because both materials were amorphous, it was hypothesized that the presence of the side-chain ester functionality, as compared to the main-chain ester functionality of PETG allows for greater dissolution of CO₂ in PMMA.³⁹⁸ In the

work of Kirby and McHugh,³⁹⁹ the effects of chain branching were observed to increase solubility in two ways; through an increase in the free volume of the polymer, which makes it easier to absorb solvent, and in a reduction of intermolecular interactions between polymer segments which arise in linear segments due to short-range molecular orientation.

In the case of structurally similar polymers such as PVA and PMMA, Table 6-2, the polymer having the lower glass transition temperature shows greater CO₂ solubility. PVA, with $T_g = 30^\circ\text{C}$, has a significantly higher solubility for CO₂ than PMMA, with

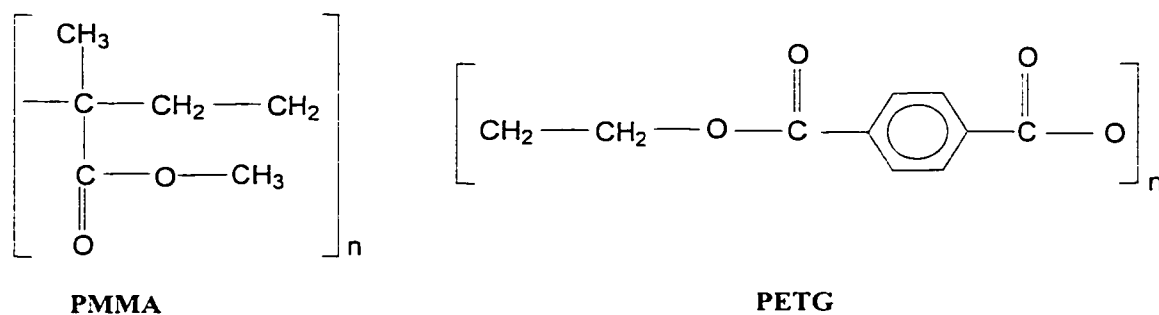


Figure 6-3. Monomer structures of Poly(methyl methacrylate) (PMMA), $T_g = 105^\circ\text{C}$, and Glycol Modified Poly(ethylene terephthalate) (PETG), $T_g = 79^\circ\text{C}$.

$T_g = 105^\circ\text{C}$. Unlike the PMMA and PETG case where the increased solubility can be related to increase free volume, the increased solubility between two (in this case branched) polymers with similar structures can be correlated with a lower cohesive energy density, for which T_g can be used as an indicator, as discussed in Section 5.5.2

There have been many studies on the sorption of CO₂ in polymers, although the temperatures and pressures where these experiments have been conducted are generally below the critical point of CO₂ (31°C, 73.8 bar). Table 6-3 is a compilation of reported CO₂ solubilities in various polymers. Only the maximum CO₂ concentration at the

experimental conditions of temperature and pressure has been listed, although additional solubility data at other conditions of T and P can be found in the noted references. In addition, the monomer structure of each polymer is shown, as well as the ambient condition values of the polymer T_g) and HSP's. The Hansen solubility parameter values given for CO₂ were determined as in Section 5.3, at the temperature and pressure conditions for which the absorbed CO₂ concentration is given.

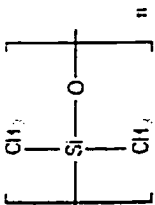
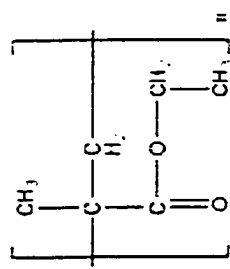
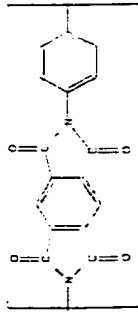
Because the data shown in Table 6-3 were measured using different experimental techniques, and at different conditions of temperature and pressure, direct comparisons are difficult. Furthermore, the polymer processing history, as well as size and geometry of the samples are not included in the comparison. Nevertheless, some general observations from the data in Table 6-3 can be made:

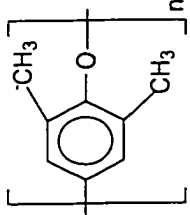
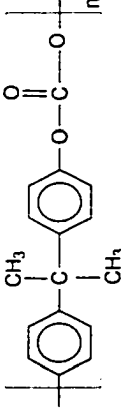
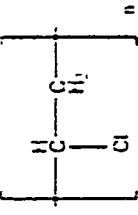
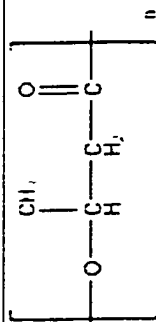
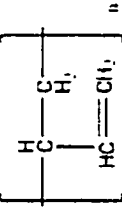
1. In the case of structurally similar polymers, polymers with lower T_g 's favor CO₂ solubility. Poly(vinyl acetate), with a low T_g , solubilizes nearly three times more CO₂ than poly(methyl methacrylate) or poly(ethyl methacrylate) at the same temperature and pressure. Stated another way, all other things being equal, a low T_g indicates low intra-molecular interactions, and therefore lower cohesive energy densities.
2. Silicone containing (Lewis base) polymers, which exhibit weak polymer-polymer interactions, as evidenced by the low HSP values and T_g of poly(dimethyl siloxane), favor CO₂ sorption, indicating that the presence of Lewis base groups, in the absence of interfering intra-molecular interactions within the polymer promote CO₂ sorption.

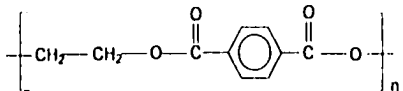
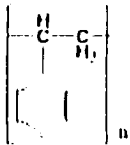
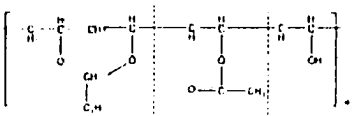
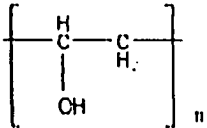
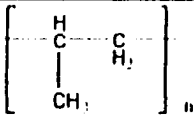
3. Hydrocarbon polymers, such as polybutadiene and polypropylene, show lower uptake of CO₂ per unit of polymer, despite relatively low polymer-polymer interaction (as evidenced by the low HSP values and low T_g for both polymers. This indicates that the absence of Lewis base groups, even without interfering intra-molecular interactions within the polymer, results in low CO₂ solubilities.
4. When Lewis base functional groups are present, their location on a side-chain versus the main-chain favors higher CO₂ solubilities.

Table 6-3. Maximum solubilities of CO₂ in various polymers.

Polymer	Monomer Structure	T _g (°C) (25°C, 1 atm)	Polymer (δ_d , δ_p , δ_h) (MPa) ^{1/2} (25°C, 1 atm)	T (°C)	P (bar)	[CO ₂] × 10 ⁻³ (moles CO ₂ /cm ³ polymer)	CO ₂ (δ_d , δ_p , δ_h) (MPa) ^{1/2}
Poly(vinyl acetate) – PVA	$\left[\begin{array}{c} \text{H} - \text{C} - \text{C} - \\ \quad \\ \text{O} - \text{C} - \text{CH}_3 \\ \\ \text{O} \end{array} \right]_n$	30	$\delta_d = 16.0$ $\delta_p = 6.8$ $\delta_h = 9.8^{400}$	25	51	9.03 ⁴⁰¹	$\delta_d = 1.4$ $\delta_p = 2.0$ $\delta_h = 2.2$
Poly(methyl methacrylate) - PMMA	$\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{C} - \text{CH}_2 - \text{CH}_2 \\ \quad \\ \text{C} - \text{O} - \text{CH}_3 \\ \\ \text{O} \end{array} \right]_n$	105	$\delta_d = 17.6$ $\delta_p = 7.1$ $\delta_h = 5.0^{402}$	32.7	102.5	6.5 ⁴⁰³	$\delta_d = 9.5,$ $\delta_p = 4.2$ $\delta_h = 4.7$
				35	216.2	13.6 ⁴⁰⁴	$\delta_d = 11.5$ $\delta_p = 4.6$ $\delta_h = 5.1$
				50	286.5	12.3 ⁴⁰⁵	$\delta_d = 11.3$ $\delta_p = 4.6$ $\delta_h = 4.9$
				35	50	3.86 ⁴⁰⁶	$\delta_d = 1.0$ $\delta_p = 1.7$ $\delta_h = 1.9$

Polymer	Monomer Structure	T _g (°C) (25°C, 1 atm)	Polymer (δ_d , δ_p , δ_h) (MPa) ^{1/2} (25°C, 1 atm)	T (°C)	P (bar)	[CO ₂] × 10 ⁻³ (moles CO ₂ /cm ³ polymer)	CO ₂ (δ_d , δ_p , δ_h) (MPa) ^{1/2}
Poly(dimethyl siloxane) - PDMS		-128	$\delta_d = 15.5$ $\delta_p = 0$ $\delta_h = 0^{407}$	50	120	8.53 ⁴⁰⁸	$\delta_d = 7.1$ $\delta_p = 3.8$ $\delta_h = 4.1$
				25	50.7	5.45 ⁴⁰⁹	$\delta_d = 1.4$ $\delta_p = 2.0$ $\delta_h = 2.2$
				42	220	34.54 ⁴¹⁰	$\delta_d = 10.9$ $\delta_p = 4.5$ $\delta_h = 4.9$
				35	50	3.85 ⁴¹²	$\delta_d = 1.0$ $\delta_p = 1.7$ $\delta_h = 1.9$
Poly(ethyl methacrylate) – PEMA		66	$\delta_d = 17.8$ $\delta_p = 6.5$ $\delta_h = 4.7^{411}$	55	44.5	2.50 ⁴¹³	$\delta_d = 0.7$ $\delta_p = 1.5$ $\delta_h = 1.6$
				40	96.5	3.63 ⁴¹⁵	$\delta_d = 7.1$ $\delta_p = 3.8$ $\delta_h = 4.1$
Polyimide - PI		227	$\delta_d = 19.6$ $\delta_p = 7.6$ $\delta_h = 9.0^{414}$				

Polymer	Monomer Structure	T _g (°C) (25°C, 1 atm)	Polymer ($\delta_d, \delta_p, \delta_h$) (MPa) ^{1/2} (25°C, 1 atm)	T (°C)	P (bar)	[CO ₂] × 10 ⁻³ (moles CO ₂ /cm ³ polymer)	CO ₂ ($\delta_d, \delta_p, \delta_h$) (MPa) ^{1/2}
Poly(2, 6-dimethyl phenylene oxide) - PPO		216	$\delta_d = 18.0$ $\delta_p = 3.1$ $\delta_h = 8.5$ ⁴¹⁶	35	40.5	2.36 ⁴¹⁷	$\delta_d = 0.8$ $\delta_p = 1.6$ $\delta_h = 1.7$
Polycarbonate - PC		150	$\delta_d = 18.1$ $\delta_p = 5.9$ $\delta_h = 6.9$ ⁴¹⁸	40	96.5	3.27 ⁴¹⁹	$\delta_d = 7.1$ $\delta_p = 3.8$ $\delta_h = 4.1$
				35	271	4.1 ⁴²⁰	$\delta_d = 12.1$ $\delta_p = 4.7$ $\delta_h = 5.2$
Poly(vinyl chloride) - PVC		85	$\delta_d = 18.8$ $\delta_p = 10.0$ $\delta_h = 3.1$ ⁴²¹	35	20.3	0.86 ⁴²² (ex-situ)	$\delta_d = 0.2$ $\delta_p = 1.0$ $\delta_h = 1.1$
				25	63.8	2.49 ⁴²³	$\delta_d = 2.8$ $\delta_p = 2.6$ $\delta_h = 2.9$
Poly(hydroxy butyrate) - PHB			$\delta_d = 16.0$ $\delta_p = 11.9$ $\delta_h = 8.3$ ⁴²⁴	35	60	2.38 ⁴²⁵	$\delta_d = 1.4$ $\delta_p = 2.0$ $\delta_h = 2.2$
Polybutadiene - PB		-25	$\delta_d = 17.5$ $\delta_p = 0$ $\delta_h = 1.0$ ⁴²⁶	25	50.7	2.54 ⁴²⁷	$\delta_d = 1.4$ $\delta_p = 2.0$ $\delta_h = 2.2$

Polymer	Monomer Structure	T _g (°C) (25°C, 1 atm)	Polymer (δ_d , δ_p , δ_h) (MPa) ^{1/2} (25°C, 1 atm)	T (°C)	P (bar)	[CO ₂] × 10 ⁻³ (moles CO ₂ /cm ³ polymer)	CO ₂ (δ_d , δ_p , δ_h) (MPa) ^{1/2}
Poly(ethylene terephthalate) - PET		74	$\delta_d = 19.4$ $\delta_p = 6.2$ $\delta_h = 8.6$ ⁴²⁸	35	60.8	2.19 ⁴²⁹	$\delta_d = 1.4$ $\delta_p = 2.0$ $\delta_h = 2.2$
Polystyrene - PS		100	$\delta_d = 21.3$ $\delta_p = 5.8$ $\delta_h = 4.3$ ⁴³⁰	35	71	2.77 ⁴³¹	$\delta_d = 2.3$ $\delta_p = 2.5$ $\delta_h = 2.7$
				40	165	3.34 ⁴³²	$\delta_d = 10.3$ $\delta_p = 4.4$ $\delta_h = 4.8$
Poly(vinyl butyral) - PVB		55-90	$\delta_d = 17.4$ $\delta_p = 8.8$ $\delta_h = 11.3$ ⁴³³	25	35.5	2.04 ⁴³⁴	$\delta_d = 0.6$ $\delta_p = 1.4$ $\delta_h = 1.5$
Poly(vinyl alcohol) - PVOH		85	$\delta_d = 17.8$ $\delta_p = 9.0$ $\delta_h = 18.0$ ⁴³⁵	47	60	1.61 ⁴³⁶	$\delta_d = 1.2$ $\delta_p = 1.9$ $\delta_h = 2.0$
				35	60	1.01 ⁴³⁷	$\delta_d = 1.4$ $\delta_p = 2.0$ $\delta_h = 2.2$
Polypropylene - PP		-14	$\delta_d = 17.2$ $\delta_p = 0$ $\delta_h = 0$ ⁴³⁸	25	50.7	0.73 ⁴³⁹ (in-situ)	$\delta_d = 1.4$ $\delta_p = 2.0$ $\delta_h = 2.2$

With the exception of the noted value for PVC, all CO₂ sorption values are in-situ.

Factors not considered in the analysis of the CO₂ sorption values in Table 6-3 include the temperature and hydrostatic pressure effects on the polymer HSP values, polymer swelling resulting from CO₂ sorption, and the difference between the density of the CO₂ absorbed within the polymer (i.e., partial molar volume) and the density of the CO₂ in the gas phase.

As discussed in Section 5.5.3, polymer HSP's can be adjusted for temperature and hydrostatic pressure using experimental PVT data, empirical equations of state, or representative coefficients of thermal expansion and compressibility. In addition to these two effects, which occur for all polymers and in all environments, polymer swelling due to CO₂ sorption will result in increased distances between polymer segments, and therefore an increased polymer specific volume. This will lower the cohesive energy density and HSP's of the polymer. To evaluate the magnitude of the increase and/or decrease in polymer HSP's with T, P, and CO₂ sorption, it is proposed that the effects on polymer specific volume are separable and additive, i.e.,

$$V^{T,P} = V_o^{T_0,P_0} + \Delta V^{T-T_0} + \Delta V^{P-P_0} + \Delta V^{CO_2 \text{ sorption}} \quad (6-1)$$

where $V_o^{T_0,P_0}$ is the polymer specific volume at ambient conditions (normally 25°C and 1 atmosphere), ΔV^{T-T_0} is the change in the polymer specific volume due to a change in temperature, ΔV^{P-P_0} is the change in the polymer specific volume due to a change in hydrostatic pressure, and $\Delta V^{CO_2 \text{ sorption}}$ is the increase in polymer specific volume due to the sorption of CO₂ at T and P.

The sorption of CO₂ results in a change in polymer volume only when the polymer is in its rubber state, i.e., when the sorption temperature is above T_g. However, as discussed in Section 2.2.5, the sorption of CO₂ will lower the polymer T_g. It is therefore necessary to be able to predict whether a polymer will be in the glass or rubber state at the sorption conditions. The observed change in T_g with CO₂ sorption,

$\left(\frac{dT_g}{dP}\right)_{Observed}$, incorporates the effect of two separate contributions: an increase in T_g

caused by hydrostatic compression, $\left(\frac{dT_g}{dP}\right)_{Hydrostatic}$, and a decrease in T_g caused by

swelling due to gas sorption, $\left(\frac{dT_g}{dP}\right)_{Swelling}$, i.e.

$$\left(\frac{dT_g}{dP}\right)_{Observed} = \left(\frac{dT_g}{dP}\right)_{Hydrostatic} + \left(\frac{dT_g}{dP}\right)_{Swelling} \quad (6-2)$$

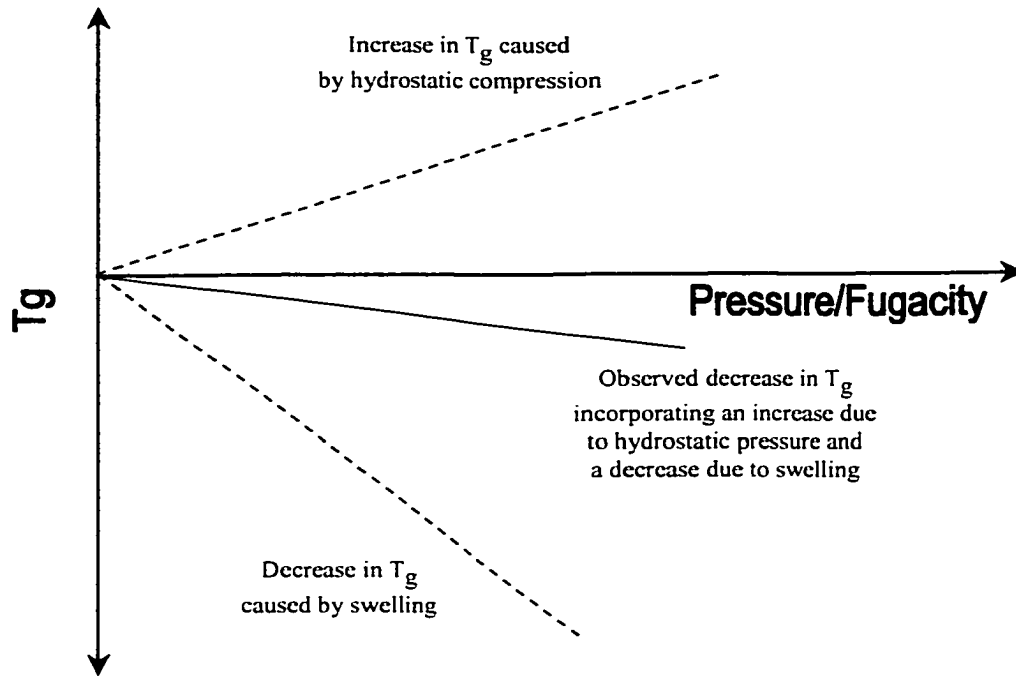


Figure 6-4. Schematic illustration of the observed change in polymer T_g when exposed to pressurized, penetrating gas (at constant temperature). This observed change incorporates two separate effects: An increase in T_g due to hydrostatic compression and a decrease due to swelling. For a non-penetrating fluid, only the increase in T_g will be observed.

The volume fraction of absorbed CO_2 , $[CO_2]$, can be approximated using the dual mode sorption model,^{440,441,442,443}

$$C \left(\frac{\text{cm}^3 \text{ CO}_2}{\text{cm}^3 \text{ polymer}} \right) = C_D + C_H = k_D P + \frac{C'_H b P}{1 + b P} \quad (6-3)$$

where $k_D P$ is the linear sorption term (Henry's law relationship) and $\frac{C'_H b P}{1 + b P}$ the Langmuir sorption term. The Langmuir sorption term corresponds to hole filling in the glass state and does not contribute to overall volume dilation of the polymer. The presence of the Langmuir sorption sites in a polymer is connected with the existence of a nonequilibrium free volume at temperatures below the glass transition temperature in the

polymer matrix.⁴⁴⁴ For $T > T_g$, the volume fraction of absorbed CO_2 can therefore be expressed by the linear sorption term, $k_D P$.

$$C \left(\frac{cm^3 CO_2}{cm^3 polymer} \right) = C_D = k_D P \quad (6-4)$$

This is a Henry's law-type relationship, where k_D is analogous to the Henry's law constant.⁴⁴⁵ This relation is discussed further in Appendix B.

In theory, therefore, the increase in polymer volume due to absorbed CO_2 , $\Delta V^{CO_2 \text{ sorption}}$, can be found by multiplying the volume fraction of absorbed CO_2 , $[CO_2]$ by its partial molar volume at the sorption conditions, $\bar{V}_{CO_2}$, the volume of a mole of ideal gas at $0^\circ C$ and 1 atm and the specific volume of the unswollen polymer, $V_{polymer}^o$ ⁴⁴⁶

$$\Delta V^{CO_2} = [CO_2] \cdot \frac{\bar{V}_{CO_2}}{22415} V_{polymer}^o \quad (6-5)$$

where 22,415 is the volume of 1 mole of ideal gas at $0^\circ C$ and 1 atm.⁴⁴⁷

Combining eqns. (6-2) and (6-5),

$$\Delta V^{CO_2} = k_D P \cdot \left(\frac{\bar{V}_{CO_2}}{22415} \right) \cdot V_{Polymer}^o \quad (6-6)$$

so that

$$\boxed{\frac{\Delta V^{CO_2}}{V_{Polymer}^o} = k_D P \cdot \left(\frac{\bar{V}_{CO_2}}{22415} \right)} \quad (6-7)$$

Equation (6-7) was derived by Fleming and Koros⁴⁴⁸ to determine the volume increase of polymers due to sorption of CO₂, where V_o is the unswollen polymer volume, and the partial molar volume of CO₂ was taken by these authors to be $\bar{V}_{CO_2} = 46 \text{ (cm}^3/\text{mole)}$. This value of $\bar{V}_{CO_2}$ was obtained by averaging the values of CO₂ partial molar volume in six liquid solvents (at 25°C). The list of solvents used by Fleming and Koros to determine their $\bar{V}_{CO_2}$ is reproduced in Table 6-4.

Table 6-4. Partial molar volume of CO₂ in various liquids at 25°C.

Solvent	$\bar{V}_{CO_2} \text{ (cm}^3/\text{mole)}$
Carbon tetrachloride	48.2
Chlorobenzene	44.6
Benzene	47.9
Acetone	44.7
Methyl acetate	44.5
Methanol	43.0
	Avg. $\bar{V}_{CO_2} = 46.0$

An expanded tabulation of CO₂ partial molar volumes in various liquid solvents, as reported in the literature at $p_{CO_2} = 1 \text{ atm}$ and 25°C, is given in Table 6-5.

Table 6-5 Partial Molar Volume of CO₂ in Various Liquids, $p_{CO_2} = 1 \text{ atm}$, $T = 25^\circ\text{C}$.

$\bar{V}_{CO_2}$ (cm ³ /mole)	Solvent	V_{m1} (cm ³ /mole) solvent	δ_d (MPa) ^{1/2}	δ_p (MPa) ^{1/2}	δ_h (MPa) ^{1/2}	δ_T (MPa) ^{1/2}	Ref
33	water	17.54	15.5	16.0	42.3	47.8	449
33.5	<i>n</i> -formyl morpholine	100.82	16.6	11.7	10.0	22.6	450
35	water	17.54	15.5	16.0	42.3	47.8	451
35.6	<i>n</i> -formyl morpholine	100.82	16.6	11.7	10.0	22.6	452
42.2	propylene carbonate	85.08	20.0	18.0	4.1	27.2	453
43	methanol	40.71	15.1	12.3	22.3	29.6	454
44.2	methyl acetate	79.91	15.5	7.2	7.6	18.7	455
44.4	chlorobenzene	102.23	19.0	4.3	2.0	19.6	456
44.4	acetone	73.89	15.5	10.4	7.0	19.9	457
44.7	acetone	73.89	15.5	10.4	7.0	19.9	458

45.9	methylbenzene	106.52	18.0	1.4	2.0	18.2	459
47.6	benzene	89.48	18.4	0.0	2.0	18.5	460
47.9	tetrachloromethane	97.17	17.8	0.0	0.6	17.8	461
48.0	hexadecane	294.08	16.3	0.0	0.0	16.3	462
48.4	tetradecane	261.73	16.2	0.0	0.0	16.2	463
48.9	dodecane	229.64	16.0	0.0	0.0	16.0	464
49.7	decane	195.44	15.7	0.0	0.0	15.7	465
50.8	nonane	179.38	15.7	0.0	0.0	15.7	466
51.3	cyclohexane	108.88	16.8	0.0	0.0	16.8	467
52.0	methylcyclohexane	128.18	16.0	0.0	1.0	16.0	468
52.1	octane	163.42	15.5	0.0	0.0	15.5	469
52.7	heptane	146.93	15.3	0.0	0.0	15.3	470
69	perfluoroheptane	227.3	12.0	0.0	0.0	12	471

A more accurate value for the partial molar volume of CO₂ dissolved in a polymer, over that used by Fleming and Koros, can be obtained by using an EOS of CO₂, eqn. (5-14) and eqn. (5-12), and the internal pressure of the polymer, as discussed in Section 4.1. It is proposed that the condition of equilibrium of an inert gas dissolved in a non-polar polymer can be expressed as

$$T\left(\frac{\partial P}{\partial T}\right)_v^{Solute} - P = T\left(\frac{\partial P}{\partial T}\right)_v^{Solvent} - P \quad (6-8)$$

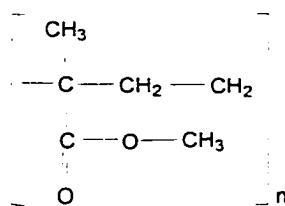
This is a similar approach to that used in Section 5.2.1, where the HSP's of CO₂ were determined by an optimization based on solubility in liquid solvents. The implicit assumption in that approach is that the cohesive energy density of the CO₂ and the liquid solvent in which CO₂ was most soluble are equal.

The internal pressure of the polymer of interest, $T\left(\frac{\partial P}{\partial T}\right)_v - P$, can be calculated using the techniques outline in Section 5.5.1: Using measured PVT data, empirical PVT

equations of state, total solubility parameter, $(n \cdot \delta_{Total}^2)$, or the appropriate values of thermal expansion coefficient and compressibility. The EOS of CO₂ is then used to calculate the value CO₂ specific volume, at the temperature of interest, which gives the same value of polymer internal pressure. Of all the CO₂ solubility studies listed in Table 6-3, only one value of $\bar{V}_{CO_2}$ is reported. Fleming and Koros⁴⁷² give a value of $\bar{V}_{CO_2} = 46.1 \left(\text{cm}^3 / \text{mole} \right)$ for CO₂ dissolved in poly(dimethyl siloxane) at T = 35°C and up to a CO₂ mass fraction of 14%. This value was obtained using complementary sorption and dilation data, from which a plot of the total specific volume of the penetrant-laden PMDS as a function of CO₂ mass fraction was generated. The partial specific volumes of the polymer and penetrant (CO₂) were then determined graphically from the tangential slope of the total specific volume versus mass fraction plot. For the same conditions of T and P, and using $T \left(\frac{\partial P}{\partial T} \right)_r - P = 2400 \text{ (bar)}$ eqn. (6-8) gives a value of $\bar{V}_{CO_2} = 41.5 \left(\text{cm}^3 / \text{mole} \right)$.

The proposed method of calculating $\bar{V}_{CO_2}$ by equating the internal pressures of solute and solvent is most accurate for the case of an inert gas dissolved in a non-polar polymer, such as polyethylene, i.e., when solute-solvent interactions are absent. While CO₂ does interact with many polymers, it is suggested that this proposed method does offer the opportunity to incorporate thermodynamic information of the gas and polymer into the value of $\bar{V}_{CO_2}$.

6.1.1 CO₂/PMMA Interactions



Hansen solubility parameter values for PMMA, Figure 6-5, have been determined experimentally by Hansen,⁴⁷³ and Van Dyk et al.,⁴⁷⁴ and calculated by Shaw⁴⁷⁵ and Koenhen and Smolders.⁴⁷⁶ As with many commercial polymers, the composition, and therefore the HSP's, will vary between particular manufacturers, and in the case of PMMA a range of HSP values have been determined,

$$\delta_d = 19.4 - 15.6 \text{ MPa}^{1/2}$$

$$\delta_p = 10.5 - 5.7 \text{ MPa}^{1/2}$$

$$\delta_h = 7.8 - 4.7 \text{ MPa}^{1/2}$$

$$\delta_d = \delta_{dref} = 17.6 \text{ MPa}^{1/2}$$

$$\delta_d = \delta_{pref} = 7.1 \text{ MPa}^{1/2}$$

$$\delta_d = \delta_{href} = 5.0 \text{ MPa}^{1/2}$$

The interaction radius, R_o (as defined in Section 5.2.1), determined on the basis of PMMA dissolution behavior in a range of liquid solvents is $R_o^{liq} = 8.6 \text{ MPa}^{1/2}$.⁴⁷⁷

Experimental PVT data for PMMA⁴⁷⁸ was presented graphically in Figure 5-8. From the PVT data above T_g , indicated by the change in slope of the isobars, the specific volume in the rubber state at ambient conditions, V_{rubber} , is estimated to be $0.8242 \left(\text{cm}^3/\text{g} \right)$, Figure 6.6. This will be taken to be the reference volume of the polymer, V_{ref} at $T_{ref} = 25^\circ\text{C}$ and $P_{ref} = 1 \text{ bar}$. From Figure 6.6, the specific volume in the glass state at ambient conditions is $V_{glass} = 0.8460 \left(\text{cm}^3/\text{g} \right)$.

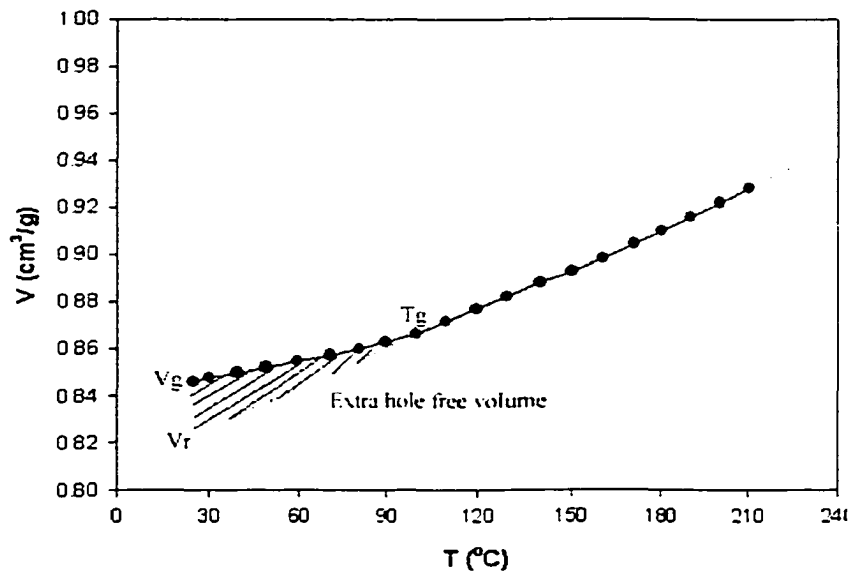


Figure 6-6. Projected specific volume of PMMA at ambient conditions. The crosshatched region represents the extra volume due to the frozen in "holes" in the glass phase.

Using the remaining specific volume data for PMMA for $T > T_g$, the change in PMMA volume due to temperature and hydrostatic pressure effects can be determined. As with the specific volume at ambient conditions, V_{rubber} , the specific volume at other

temperatures and pressures below T_g , can be extrapolated from the PVT data above T_g .

The change in PMMA specific volume, as a result of temperature and hydrostatic pressure changes are shown in Table 6-6.

Table 6-6. Change in PMMA specific volume (cm^3/g) as a result of changes in T and P , from PVT data.⁴⁷⁹

T (°C)	Pressure (bar)			
	0	100	200	400
25	0.0000	-0.0038	-0.0049	-0.0075
30.2	0.0031	-0.0012	-0.0023	-0.0049
39.3	0.0086	0.0033	0.0022	-0.0004
48.7	0.0142	0.0080	0.0069	0.0043
59.5	0.0207	0.0135	0.0124	0.0098
70.4	0.0272	0.0189	0.0178	0.0152
80.6	0.0334	0.0240	0.0229	0.0203
89.7	0.0388	0.0285	0.0275	0.0249
99.8	0.0423	0.0336	0.0325	0.0299
109.8	0.0474	0.0386	0.0375	0.0349
119.8	0.0528	0.0477	0.0425	0.0399
129.6	0.0580	0.0535	0.0489	0.0409
140.1	0.0638	0.0590	0.0542	0.0458
150.5	0.0688	0.0638	0.0588	0.0500

For comparison, this calculation was repeated using the Tait equation, eqns. (5-96), (5-97), and (5-98), and the Tait parameters $A_0 = 0.8254 \left(\text{cm}^3/\text{g} \right)$, $A_1 = 2.8383 \times 10^{-4} \left(\text{cm}^3/\text{g} \cdot ^\circ\text{C} \right)$, $A_2 = 7.792 \times 10^{-7} \left(\text{cm}^3/\text{g} \cdot ^\circ\text{C}^2 \right)$, $B_0 = 321.59 \text{ (MPa)}$, $B_1 = 4.146 \times 10^{-3} \left(1/^\circ\text{C} \right)$, and $C = 0.0894$,⁴⁸⁰ as given in Section 5.5.

Table 6-7. Change in PMMA specific volume (cm³/g) as a function of changes in T and P, derived from the Tait equation.

T (°C)	Pressure (bar)			
	0	100	200	400
25	0.0000	-0.0025	-0.0050	-0.0096
30.2	0.0017	-0.0009	-0.0034	-0.0081
39.3	0.0033	0.0007	-0.0019	-0.0067
48.7	0.0048	0.0021	-0.0005	-0.0055
59.5	0.0121	0.0091	0.0063	0.0009
70.4	0.0163	0.0132	0.0102	0.0046
80.6	0.0204	0.0171	0.0140	0.0081
89.7	0.0241	0.0208	0.0175	0.0114
99.8	0.0285	0.0250	0.0216	0.0152
109.8	0.0330	0.0293	0.0257	0.0191
119.8	0.0376	0.0337	0.0300	0.0231
129.6	0.0423	0.0382	0.0344	0.0272
140.1	0.0475	0.0432	0.0392	0.0317
150.5	0.0528	0.0483	0.0441	0.0363

As can be seen from the values in Table 6-6 and Table 6-7, the change in specific volume calculated using the Tait equation are less than that observed from the measured PVT data, but the trend is quite similar.

HSP values for PMMA can also be calculated at different temperatures and pressures using the changes in specific volume given in Table 6-6, and the equations summarized in Table 5-8,

$$\delta_d = \frac{\delta_{dref}}{\left(\frac{V_{ref}}{V^{T,P}} \right)^{-1.25}} \quad (6-9)$$

$$\delta_p = \frac{\delta_{pref}}{\left(\frac{V_{ref}}{V^{T,P}}\right)^{-0.5}} \quad (6-10)$$

$$\delta_h = \frac{\delta_{href}}{\exp\left[-1.32 \times 10^{-3}(T_{ref} - T) - \ln\left(\frac{V_{ref}}{V^{T,P}}\right)^{0.5}\right]} \quad (6-11)$$

Table 6-8. PMMA HSP values ($\text{MPa}^{1/2}$), at T and P , calculated using eqns. (6-9)-(6-11).

T (°C)	Pressure, (bar)											
	0			100			200			400		
	δ_d	δ_p	δ_h	δ_d	δ_p	δ_h	δ_d	δ_p	δ_h	δ_d	δ_p	δ_h
25	17.60	7.10	5.00	17.70	7.12	5.01	17.73	7.12	5.01	17.79	7.13	5.02
30.2	17.52	7.09	4.96	17.63	7.11	4.97	17.66	7.11	4.97	17.72	7.12	4.98
39.3	17.37	7.06	4.88	17.51	7.09	4.90	17.54	7.09	4.90	17.59	7.10	4.91
48.7	17.23	7.04	4.80	17.39	7.07	4.82	17.42	7.07	4.83	17.47	7.08	4.83
59.5	17.06	7.01	4.72	17.25	7.04	4.74	17.28	7.05	4.74	17.33	7.06	4.75
70.4	16.90	6.99	4.63	17.11	7.02	4.66	17.14	7.02	4.66	17.19	7.03	4.66
80.6	16.75	6.96	4.55	16.98	7.00	4.58	17.01	7.00	4.58	17.06	7.01	4.59
89.7	16.62	6.94	4.49	16.87	6.98	4.51	16.89	6.98	4.52	16.94	6.99	4.52
99.8	16.53	6.92	4.42	16.74	6.96	4.44	16.77	6.96	4.44	16.82	6.97	4.45
109.8	16.41	6.90	4.35	16.62	6.94	4.37	16.65	6.94	4.37	16.70	6.95	4.38
119.8	16.29	6.88	4.28	16.41	6.90	4.29	16.53	6.92	4.30	16.67	6.95	4.32
129.6	16.17	6.86	4.21	16.27	6.88	4.22	16.38	6.90	4.23	16.57	6.93	4.25
140.1	16.03	6.84	4.14	16.14	6.86	4.15	16.25	6.88	4.16	16.45	6.91	4.18
150.5	15.92	6.82	4.07	16.03	6.84	4.08	16.15	6.86	4.09	16.35	6.89	4.11

The remaining adjustment to the HSP's of PMMA will be based of the volume change due to CO_2 sorption. From Figure 6-5, PMMA contains a side-chain carbonyl functional group which allows for an acid-base interaction when exposed to CO_2 , and from Table 6-3, it can be seen that CO_2 is, in fact, very soluble in PMMA. In Table 6-9, literature values of CO_2 sorption in PMMA, at a variety of temperatures and pressures has been compiled.

Table 6-9. Literature values of CO₂ sorption in PMMA.

T (°C)	P (bar)	[CO ₂] $\left(\text{cm}^3 \text{STP} / \text{cm}^3 \text{ polymer} \right)$	Ref	T (°C)	P (bar)	[CO ₂] $\left(\text{cm}^3 \text{STP} / \text{cm}^3 \text{ polymer} \right)$	Ref
35	13.8	28.04	481	65	30.40	30.94	482
35	27.6	49.71	"	65	37.50	38.08	"
35	41.4	69.74	"	65	49.60	51.17	"
35	55.2	89.21	"	65	54.70	56.53	"
35	68.9	113.29	"	85	8.80	7.14	"
35	82.7	133.82	"	85	20.30	14.28	"
35	103.4	157.19	"	85	30.40	23.80	"
40	13.5	48.86	483	85	39.20	29.75	"
40	27.4	68.68	"	85	49.30	39.27	"
40	41.0	84.26	"	68	28.70	43.19	484
40	54.9	101.96	"	68	41.50	58.77	"
40	67.7	119.66	"	68	56.40	75.05	"
40	82.0	152.94	"	68	81.30	110.46	"
40	95.5	170.64	"	68	95.60	118.95	"
35	8.80	17.85	485	68	112.80	125.32	"
35	20.30	39.87	"	68	134.80	143.73	"
35	30.40	56.53	"	68	152.00	167.10	"
35	39.20	77.35	"	68	172.00	185.51	"
35	49.30	95.20	"	68	192.00	194.71	"
65	8.80	10.71	"	68	217.90	216.66	"
65	22.30	23.80	"	68	253.00	233.66	"

In order to estimate the change in the PMMA specific volume due to CO₂ sorption, it is necessary to evaluate whether the PMMA has been plasticized by the absorbed CO₂, that is, whether T_g of the swollen polymer is above or below the sorption temperature, and therefore whether the dilation can be predicted with the Henry's law relationship, eqn. (6-13). For this evaluation, the experimental data of T_g depression as a function of absorbed CO₂ published by Wissinger *et al.*,⁴⁸⁶ and Chiou *et al.* is used,⁴⁸⁷ Figure 6-7.

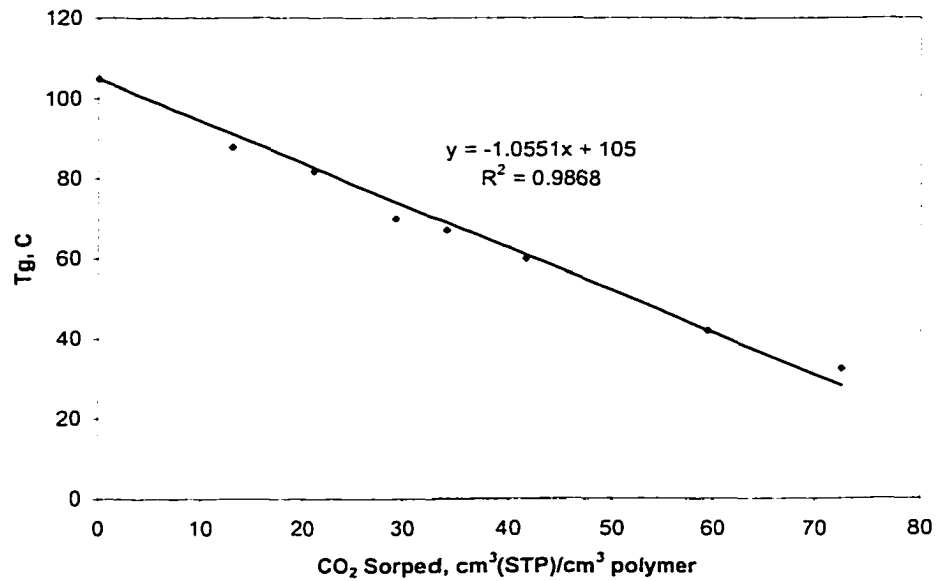


Figure 6-7. *T_g depression in PMMA due to CO₂ sorption.*

From figure 6-7, the depression in T_g as a function of the volume concentration of sorbed CO₂, [CO₂], can be expressed by a linear relation,

$$T_g (^{\circ}C) = -1.055 \cdot \left[CO_2 \left(\frac{cm^3 \text{ STP}}{cm^3 \text{ polymer}} \right) \right] + 105 \quad (6-12)$$

the experimental PMMA sorption data given in Table 6-9 was evaluated, using this linear relation, to determine where the transition from the glass to rubber state occurs, i.e., which values of T are above T_g at each value of P . This transition has been indicated for the respective data sets in Table 6-9 by the bold, italic type. Using the sorption data in Table 6-9, where the polymer is in the rubber phase, a correlation was developed, eqn. (6-13), for the sorption of CO_2 versus temperature as a function of pressure, shown in Figure 6-8.

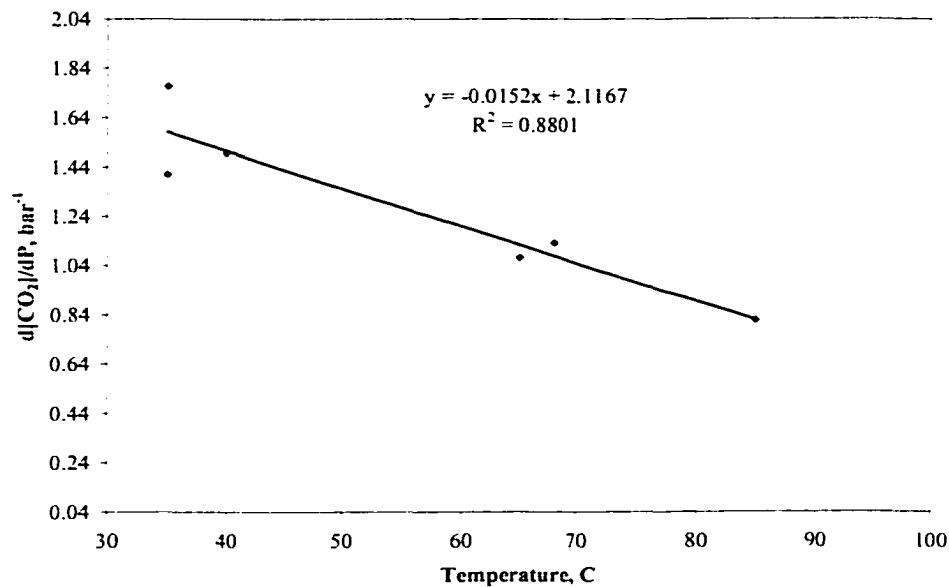


Figure 6-8. CO_2 sorption, $[\text{CO}_2]$, in PMMA as a function of pressure versus temperature.

With this relationship,

$$[\text{CO}_2] \left(\frac{\text{cm}^3 \text{ STP}}{\text{cm}^3 \text{ polymer}} \right) = (-0.0152 \cdot T(^{\circ}\text{C}) + 2.1167) P (\text{bar}) \quad (6-13)$$

and using eqn. (6-7), the following correlation can be made for the volume dilation of PMMA swelled by CO_2

$$\frac{\Delta V^{CO_2}}{V_{Polymer}^0} = k_D P \cdot \left(\frac{\bar{V}_{CO_2}}{22415} \right) = [CO_2] \left(\frac{\bar{V}_{CO_2}}{22415} \right) \quad (6-14)$$

The partial molar volumes of CO₂ dissolved in PMMA are calculated using the method outlined in the previous section, eqn. (6-8). The results for the temperature and pressure range of interest, are presented in Table 6-10.

Table 6-10. Calculated CO₂ partial molar volumes in PMMA.

T, (°C)	P, (bar)	Internal Pressure, PMMA (bar)	$\bar{V}_{CO_2}$ (cm ³ /mol)
35	100	3833.8	39.6
35	200	3845.5	39.4
50	100	3767.5	40.2
50	200	3779.1	39.8
100	100	3530.6	42.6
100	200	3541.9	42.2
Average			40.6

Therefore,

$$\frac{\Delta V^{CO_2}}{V_{Polymer}^0} = (-0.017T + 2.164)P \left(\frac{\bar{V}^{CO_2}}{22415} \right) \quad (6-15)$$

where a value of $\bar{V}_{CO_2} = 40.6$ (cm³/mole) is used, as determined in Table 6-10.

Equation (6-15) has been used to calculate the volume change of PMMA due to CO₂ sorption, and the results are given in Table 6-11. Values above 35°C and 39 bar have been approximated, where the earliest transition occurred in the experimental data and up to 200 bar due to unknown hydrostatic pressure effects above the experimental values in Table 6-11.

Table 6-11. Change in PMMA specific volume (cm^3/mole) due to of CO_2 swelling.

T ($^{\circ}\text{C}$)	Pressure (bar)	
	100	200
25	—	—
30.2	—	—
39.3	0.2231	0.4461
48.7	0.1992	0.3985
59.5	0.1719	0.3437
70.4	0.1442	0.2885
80.6	0.1184	0.2367
89.7	0.0953	0.1906
99.8	0.0697	0.1394
109.8	0.0443	0.0887
119.8	0.0190	0.0380

With the data in Table 6-11, the solubility parameters of PMMA can be adjusted for T, P, and CO_2 swelling, with the results given in Table 6-12.

Table 6-12. PMMA HSP's ($\text{MPa}^{1/2}$) adjusted for the effects of T, P, and dilation due to CO_2 sorption.

	Pressure (bar)								
	0			100			200		
T ($^{\circ}\text{C}$)	δ_d	δ_p	δ_h	δ_d	δ_p	δ_h	δ_d	δ_p	δ_h
25	17.60	7.10	5.00	17.70	7.12	5.01	17.73	7.12	5.01
30.2	17.52	7.09	4.96	17.63	7.11	4.97	17.66	7.11	4.97
39.3	17.37	7.06	4.88	12.99	6.29	4.35	10.23	5.71	3.95
48.7	17.23	7.04	4.80	13.30	6.35	4.33	10.67	5.81	3.97
59.5	17.06	7.01	4.72	13.66	6.42	4.32	11.24	5.93	3.99
70.4	16.90	6.99	4.63	14.04	6.49	4.30	11.86	6.06	4.02
80.6	16.75	6.96	4.55	14.42	6.56	4.29	12.50	6.19	4.05
89.7	16.62	6.94	4.49	14.77	6.62	4.28	13.12	6.31	4.08
99.8	16.53	6.92	4.42	15.18	6.69	4.27	13.89	6.46	4.12
109.8	16.41	6.90	4.35	15.61	6.77	4.26	14.73	6.61	4.16
119.8	16.29	6.88	4.28	15.97	6.83	4.24	15.66	6.78	4.21

From Table 6-12, the effect of swelling due to CO_2 sorption has a significant impact on the PMMA solubility parameters, and especially the dispersion parameter, δ_d , which, as discussed in Section 3-1, varies rapidly with intermolecular distance. The

calculated HSP initially decrease with temperature along an isobar, but then begin to increase with temperature. This is due to the combination of lower CO₂ density and the effect of hydrostatic pressure on the free volume of the polymer, as discussed in Section 6.1.

6.1.2 CO₂/PC Interactions

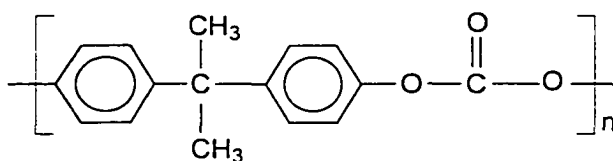


Figure 6-9. Structural repeat unit of Polycarbonate.

Total solubility parameter values for polycarbonate (PC) are available from several sources. The total solubility parameters and the associated reference are given below,

$$\begin{aligned}\delta_T &= 21 \text{ MPa}^{1/2} \text{ }^{488} \\ \delta_T &= 19.6 \text{ MPa}^{1/2} \text{ }^{489} \\ \delta_T &= 19 - 22 \text{ MPa}^{1/2} \text{ }^{490} \\ \delta_T &= 19.4 - 21.7 \text{ MPa}^{1/2} \text{ }^{491}\end{aligned}$$

HSP's, for PC have been determined experimentally by Hansen,⁴⁹² and these values will be used for this analysis,

$$\begin{aligned}\delta_d &= 18.1 \text{ MPa}^{1/2} \\ \delta_p &= 5.9 \text{ MPa}^{1/2} \\ \delta_h &= 6.9 \text{ MPa}^{1/2}\end{aligned}$$

The interaction radius, R_o (as defined in Section 5.2.1), determined on the basis of PC dissolution behavior in a range of liquid solvents is $R_o^{liq} = 5.5 \text{ MPa}^{1/2}$.⁴⁹³

Experimental PVT data for PC⁴⁹⁴ was presented graphically in Figure 5-10. From the PVT data above T_g , indicated by the change in slope of the isobars, the specific volume in the rubber state at ambient conditions, V_{rubber} , is estimated to be $0.7947 \left(\frac{cm^3}{g} \right)$, Figure 6-10, and will be used as the reference volume, V_{ref} , at $T_{ref} = 25^\circ C$ and $P_{ref} = 1$ bar. The glass state specific volume at ambient conditions is $V_{glass} = 0.8418 \left(\frac{cm^3}{g} \right)$.

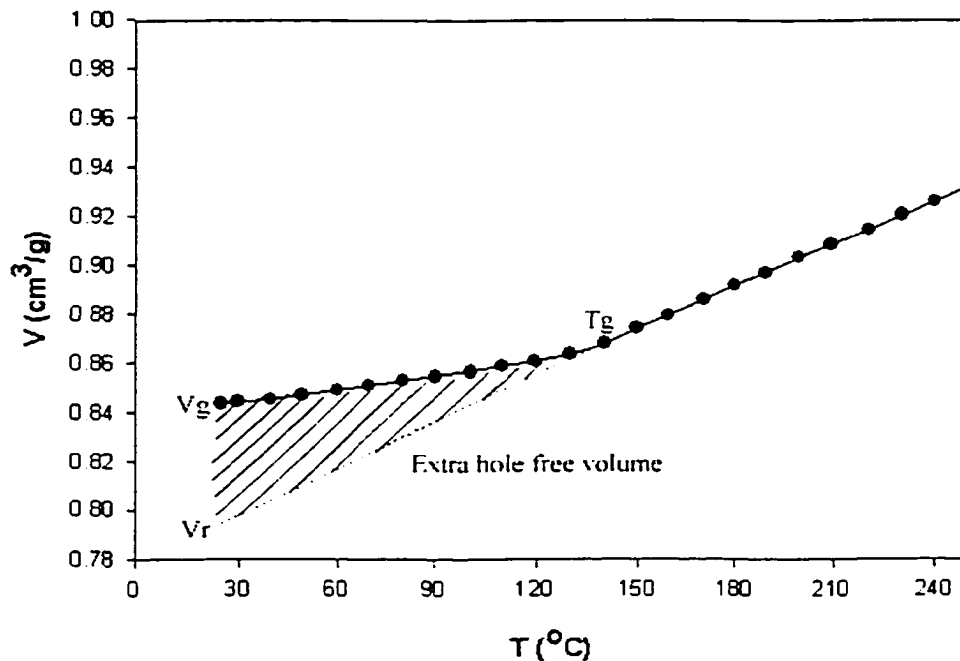


Figure 6-10. Projected specific volume of PC at ambient conditions.

The experimental specific volume data for $T > T_g$, can be used to determine the change in PC volume due to temperature and hydrostatic pressure effects. As with the rubber-state specific volume at ambient conditions, V_{rubber} , the specific volume at other temperatures and pressures below T_g can be extrapolated from the PVT data above T_g .

The calculated change in PC specific volume, as a result of temperature and hydrostatic pressure changes are given in Table 6-13

Table 6-13. Change in PC specific volume $\left(\text{cm}^3/\text{g}\right)$ as a result of changes in T and P , derived from the experimental PVT data.⁴⁹⁵

T (°C)	Pressure (bar)			
	0	100	200	400
25	0.0000	0.0035	-0.0005	-0.0011
30	0.0030	0.0091	0.0020	0.0014
39.3	0.0086	0.0149	0.0066	0.0061
49	0.0144	0.0155	0.0115	0.0109
59.9	0.0209	0.0214	0.0170	0.0164
70.2	0.0271	0.0276	0.0221	0.0215
80.7	0.0334	0.0339	0.0274	0.0268
90.4	0.0392	0.0397	0.0322	0.0316
101	0.0456	0.0461	0.0375	0.0369
110.6	0.0514	0.0519	0.0423	0.0417
119.8	0.0569	0.0574	0.0469	0.0463
130	0.0630	0.0635	0.0520	0.0514
140.1	0.0691	0.0696	0.0571	0.0565
149.8	0.0794	0.0754	0.0619	0.0613
159.4	0.0848	0.0845	0.0667	0.0661
170.3	0.0912	0.0852	0.0791	0.0716
179.7	0.0969	0.0906	0.0843	0.0744
189.3	0.1024	0.0959	0.0893	0.0790

This calculation was repeated using the Tait equation, eqn. (5-96), (5-97), and (5-98), and the Tait parameters⁴⁹⁶ $A_0 = 0.7917 \left(\text{cm}^3/\text{g}\right)$, $A_1 = 4.4201 \times 10^{-4} \left(\text{cm}^3/\text{g} \cdot ^\circ\text{C}\right)$, $A_2 = 2.8583 \times 10^{-7} \left(\text{cm}^3/\text{g} \cdot ^\circ\text{C}^2\right)$, $B_0 = 312.7 \text{ (MPa)}$, $B_1 = 3.9728 \times 10^{-3} \left(1/^\circ\text{C}\right)$, and $C = 0.0894$, as discussed in Section 5.5.

Table 6-14. *Change in PC specific volume (cm³/g) as a function of change in T and P, derived from the Tait equation.*

	Pressure (bar)			
T (°C)	0	100	200	400
25	0.0000	-0.0025	-0.0049	-0.0095
30	0.0023	-0.0003	-0.0027	-0.0074
39.3	0.0066	0.0039	0.0014	-0.0035
49	0.0111	0.0083	0.0057	0.0006
59.9	0.0116	0.0088	0.0061	0.0010
70.2	0.0163	0.0134	0.0106	0.0053
80.7	0.0212	0.0182	0.0152	0.0097
90.4	0.0263	0.0231	0.0200	0.0143
101	0.0311	0.0277	0.0245	0.0185
110.6	0.0363	0.0328	0.0295	0.0232
119.8	0.0412	0.0375	0.0340	0.0275
130	0.0458	0.0420	0.0384	0.0316
140.1	0.0511	0.0471	0.0433	0.0362
149.8	0.0563	0.0521	0.0482	0.0408
159.4	0.0614	0.0570	0.0529	0.0453
170.3	0.0665	0.0619	0.0576	0.0497
179.7	0.0723	0.0676	0.0631	0.0548
189.3	0.0774	0.0725	0.0678	0.0592

As was found for PMMA, the changes in PC specific volume calculated with the Tait equation are less than the measured PVT data, but the trend is preserved.

HSP values for PC, as a function of T and hydrostatic pressure, can also be calculated using the changes in specific volume, along with the equations summarized in Table 5-9. The results are given in Table 6-15.

Table 6-15. PC HSP values ($\text{MPa}^{1/2}$), at T and P , calculated using eqns. (6-9)-(6-11).

	Pressure (bar)											
	0			100			200			400		
$T (^{\circ}\text{C})$	δ_d	δ_p	δ_h	δ_d	δ_p	δ_h	δ_d	δ_p	δ_h	δ_d	δ_p	δ_h
25	18.10	5.90	6.90	18.09	5.90	6.94	18.11	5.90	7.07	18.13	5.90	7.07
30	18.01	5.89	6.84	18.00	5.89	6.93	18.04	5.89	7.06	18.06	5.89	7.06
39.3	17.86	5.87	6.73	17.84	5.87	6.91	17.91	5.88	7.04	17.93	5.88	7.04
49	17.70	5.85	6.63	17.68	5.85	6.88	17.78	5.86	7.02	17.79	5.86	7.02
59.9	17.52	5.82	6.50	17.51	5.82	6.86	17.63	5.84	7.00	17.65	5.84	6.99
70.2	17.36	5.80	6.39	17.34	5.80	6.83	17.49	5.82	6.98	17.51	5.82	6.97
80.7	17.19	5.78	6.28	17.18	5.78	6.81	17.35	5.80	6.95	17.37	5.80	6.95
90.4	17.04	5.76	6.18	17.03	5.76	6.79	17.22	5.78	6.93	17.24	5.79	6.93
101	16.88	5.74	6.07	16.87	5.74	6.76	17.09	5.77	6.91	17.10	5.77	6.91
110.6	16.74	5.72	5.97	16.72	5.72	6.74	16.96	5.75	6.89	16.98	5.75	6.89
119.8	16.60	5.70	5.88	16.59	5.70	6.72	16.85	5.73	6.88	16.86	5.74	6.87
130	16.45	5.68	5.78	16.44	5.68	6.70	16.72	5.72	6.86	16.74	5.72	6.85
140.1	16.31	5.66	5.69	16.30	5.66	6.68	16.60	5.70	6.84	16.61	5.70	6.83
149.8	16.07	5.63	5.58	16.16	5.64	6.66	16.48	5.68	6.82	16.49	5.68	6.81
159.4	15.95	5.61	5.49	15.95	5.61	6.62	16.37	5.67	6.80	16.38	5.67	6.79
170.3	15.80	5.59	5.39	15.94	5.61	6.62	16.08	5.63	6.75	16.25	5.65	6.77
179.7	15.68	5.57	5.31	15.82	5.59	6.60	15.96	5.61	6.73	16.18	5.64	6.76
189.3	15.56	5.55	5.23	15.70	5.57	6.58	15.84	5.59	6.72	16.08	5.63	6.74

The remaining adjustment to the PC solubility parameter values will be based on the volume change due to CO_2 sorption. As can be seen from Figure 6-8, PC contains a main-chain carbonyl functional group, which allows for an acid-base interaction when exposed to CO_2 , and from Table 6-3, it can be seen that CO_2 is slightly soluble in PC. Table 6-16 is a compilation of literature values of CO_2 solubility in PC.

Table 6-16. Literature values of CO₂ solubility in PC.

T (°C)	P (bar)	[CO ₂] $\left(\frac{\text{cm}^3 \text{ STP}}{\text{cm}^3 \text{ polymer}}\right)$	Re f	T (°C)	P (bar)	[CO ₂] $\left(\frac{\text{cm}^3 \text{ STP}}{\text{cm}^3 \text{ polymer}}\right)$	Ref	T (°C)	P (bar)	[CO ₂] $\left(\frac{\text{cm}^3 \text{ STP}}{\text{cm}^3 \text{ polymer}}\right)$	Re f
35	10.8	15.6	497	35	13.1	12.50	498	75	4.75	4.50	499
35	25.3	32.88	"	35	26.3	37.50	"	75	6	5.00	"
35	41.6	48	"	35	42.1	46.70	"	75	7.3	6.50	"
35	59	61.56	"	35	50	50.00	"	75	9	6.75	"
35	76	70.8	"	35	71	58.30	"	75	10	8.25	"
35	95	73.2	"	35	97.4	77.50	"	75	11.8	8.50	"
35	13.8	26.26	500	35	128.9	81.70	"	75	13	9.50	"
35	20.7	34.50	"	35	171.1	85.00	"	75	14.5	10.00	"
35	27.6	40.50	"	35	215.8	86.70	"	75	16	11.00	"
35	34.5	49.50	"	55	1.84	4.55	501	75	18	11.50	"
35	41.4	54.00	"	55	2.76	6.36	"	100	4.75	2.50	"
35	48.3	60.00	"	55	4.6	8.20	"	100	6	3.40	"
35	55.2	66.00	"	55	8.3	11.80	"	100	7.3	4.00	"
35	62.1	73.50	"	55	12.9	15.50	"	100	9	4.70	"
40	13.5	36.00	502	55	20.3	20.90	"	100	10	5.50	"
40	27.4	51.00	"	55	30.4	26.40	"	100	11.8	6.00	"
40	41	51.00	"	55	37.3	30.00	"	100	13	6.50	"
40	54.9	66.00	"	55	44.2	31.80	"	100	14.5	7.00	"
40	67.7	63.00	"	55	49.7	34.50	"	100	16	7.50	"
40	82	60.00	"					100	18	8.00	"
40	95.5	81.00	"								

Estimating the change in PC specific volume resulting from CO₂ swelling again requires finding a relationship between T_g and concentration of sorbed CO₂. Sorption data above T_g can then be evaluated with the Henry's law relationship to generate changes in polymer specific volume. For this evaluation, reported T_g depression data for PC as a function of sorbed CO₂,⁵⁰³ is plotted in Figure 6-11.

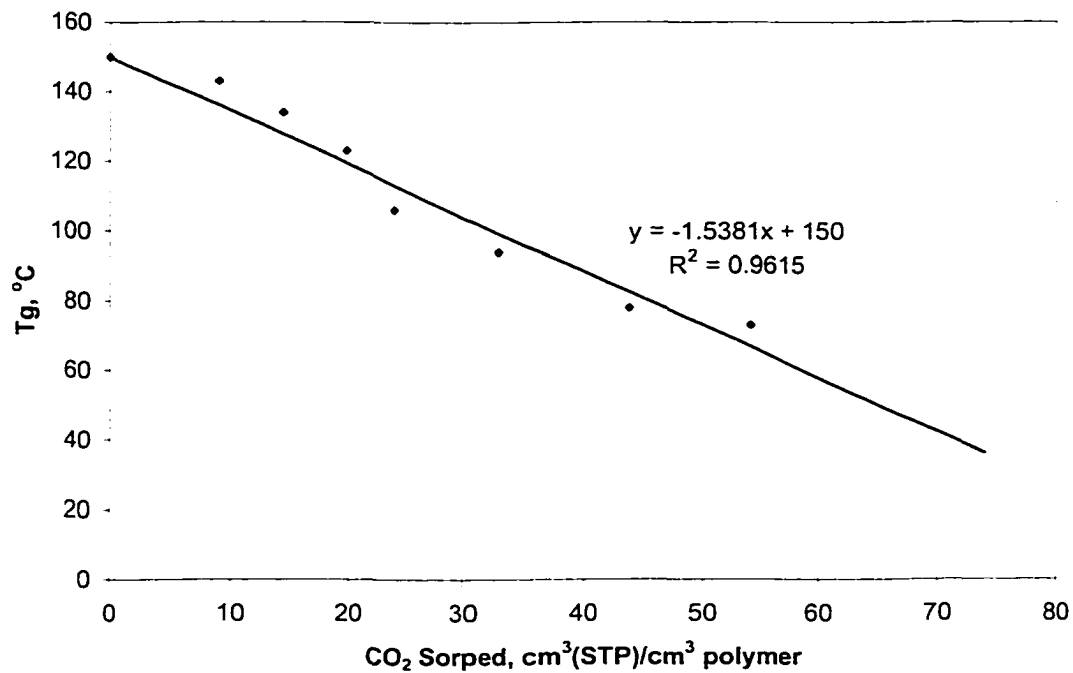


Figure 6-11. *T_g depression in PC due to CO₂ sorption.*

As shown in Figure 6-11, the T_g depression due to CO₂ sorption can be expressed by a linear relation,

$$T_g(^{\circ}C) = -1.5381 \cdot \left[CO_2 \left(\frac{cm^3 \text{ STP}}{cm^3 \text{ polymer}} \right) \right] + 150 \quad (6-16)$$

The experimental PC sorption data in Table 6-16 was evaluated, using this linear relation, to determine the conditions of T and P for the glass to rubber transition. This transition

has been indicated for the respective data sets in Table 6-17 with bold, italic type. In contrast to the tabulated, experimental PMMA data, Table 6-X, only two glass to rubber transitions are predicted to occur in the tabulated PC data. This is explained by the higher (ambient condition) glass transition temperature for PC, and the lower CO₂ solubility, as compared to PMMA, as well as the fact that only one PC sorption study was performed at sufficiently high pressures. As a result, an alternative approach will be used to estimate the CO₂ sorption effect on the PC HSP's.

Von Schnitzler *et al.*,⁵⁰⁴ has measured PC volume swelling at temperatures ranging from 40 to 120°C and at 100 and 300 bar. Their data are plotted in Figure 6-12.

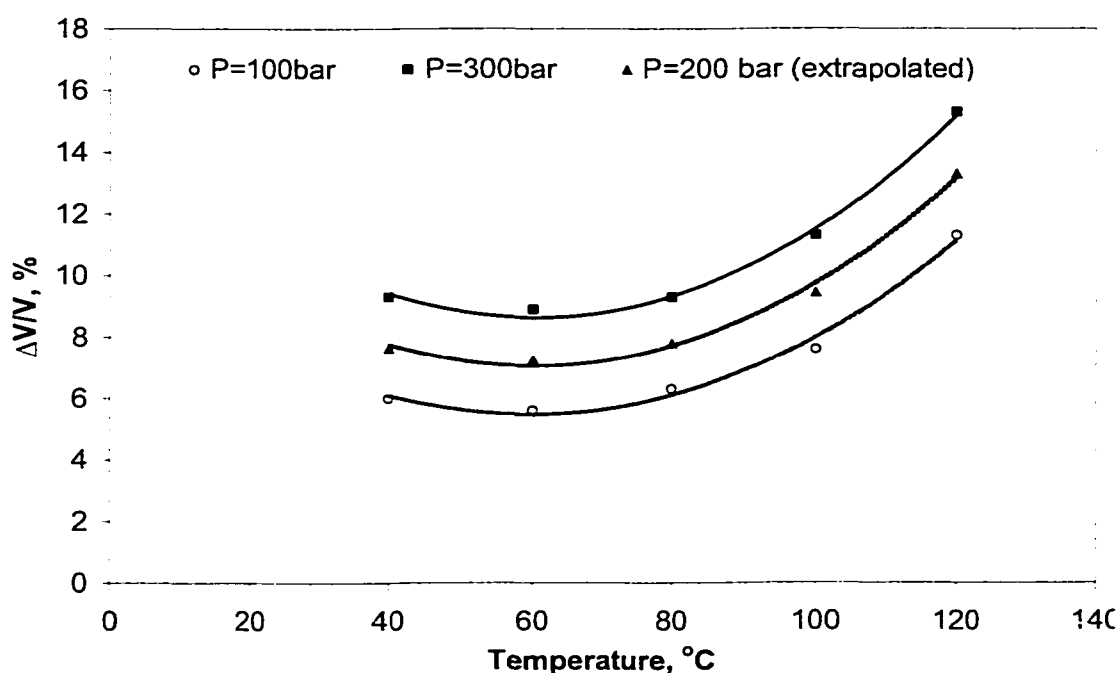


Figure 6-12. *Experimental measurements of PC swelling due to CO₂ sorption (lines drawn based on fit with experimental data).*

From Figure 6-12, it appears that the PC swelling behavior is approximately linear above 80°C along each of the isobars, and the swelling behavior is expressed as

$$\text{(At 100 bar)} \quad \frac{\Delta V^{CO_2}}{V_{Polymer}^0} = 0.0013T - 0.041 \quad (6-17)$$

$$\text{(At 200 bar)} \quad \frac{\Delta V^{CO_2}}{V_{Polymer}^0} = 0.00138T - 0.0357 \quad (6-18)$$

$$\text{(At 300 bar)} \quad \frac{\Delta V^{CO_2}}{V_{Polymer}^0} = 0.0015T - 0.00333 \quad (6-19)$$

The CO₂ sorption which corresponds to these swelling isobars can be determined with eqn. (6-7) and the CO₂ partial molar volume in PC. As with PMMA, the CO₂ partial molar volumes in PC are calculated using the assumption stated in eqn. (6-8), PC PVT data, and the CO₂ EOS (eqn. 5-14). Results, for the temperature and pressure range of interest here, are presented in Table 6-17.

Table 6-17. *Calculated partial molar volumes of CO₂ dissolved in PC.*

T (°C)	P (bar)	Internal Pressure, PC (bar)	$\bar{V}_{CO_2}$ (cm ³ /mol)
50	100	3936.3	39.6
50	200	3972.1	39.1
100	100	3545.7	42.6
100	200	3713.3	41.5
Average			40.7

Rearranging eqn. (6-7), the CO₂ sorption can be now be calculated using,

$$[CO_2] = \frac{\Delta V^{CO_2}}{V_{Polymer}^0} \cdot \left(\frac{22415}{\bar{V}_{CO_2}} \right) \quad (6-20)$$

where an average value of 40.7 (cm³/mol) is used for $\bar{V}_{CO_2}$, Table 6-17. The swelling data in Figure 6-12, for T ≥ 80°C, are shown in Table 6-18, along with the CO₂ volume

fraction calculated from eqn. (6-20), and the glass transition temperature from eqn. (6-16) with the $[CO_2]$ result of eqn. (6-20).

Table 6-18. *Calculated CO_2 sorption and T_g depression for PC.*

T (°C)	P (bar)	$\Delta V/V$	$[CO_2]$ $\left(\frac{cm^3 STP}{cm^3 polymer} \right)$	T_g (°C)
80	100	0.063	34.7	96.6
100	100	0.076	41.9	85.6
120	100	0.113	62.2	54.3
80	300	0.093	51.2	71.2
100	300	0.113	62.2	54.3
120	300	0.153	84.3	20.4

The results of Table 6-18 appear reasonable based on the data shown in Figure 6-12. At 300 bar and 80°C, the swelling behavior appears to transition to a linear behavior and from Table 6-18, the predicted CO_2 sorption indicates a transition temperature of 71.2°C. At 100 bar and 80°C, the polymer has softened and by 100°C is predicted to have passed through a depressed transition temperature.

The change in PC specific volume due to CO_2 sorption is shown in Table 6-19. Equations (6-17) and (6-18) were used to calculate the PC volume changes at temperatures greater than or equal to 80°C, and for the temperature range 40°C to 79°C,

$\left(\frac{\Delta V^{CO_2}}{V_{Polymer}^o} \right)$ is estimated to be 0.056 at 100 bar and 0.073 at 200 bar, based on the data in Figure 6-12.

Table 6-19. Change in PC specific volume, (cm^3/mol) , as a result of CO_2 swelling.

T (°C)	Pressure (bar)		
	100	200	300
25			
30			
39.3	0.0445	0.0580	0.0707
49	0.0445	0.0580	0.0707
59.9	0.0445	0.0580	0.0707
70.2	0.0445	0.0580	0.0707
80.7	0.0476	0.0580	0.0721
90.4	0.0572	0.0704	0.0837
101	0.0677	0.0820	0.0963
110.6	0.0773	0.0925	0.1077
119.8	0.0864	0.1026	0.1187
130	0.0966	0.1137	0.1309
140.1	0.1066	0.1247	0.1429
149.8	0.1162	0.1353	0.1545
159.4	0.1258	0.1458	0.1659

The PC HSP's can now be adjusted for the effects of T, P, and CO_2 dilation, with the results given in Table 6-20.

Table 6-20. PC HSP values ($\text{MPa}^{1/2}$) adjusted for T, P, and CO_2 swelling.

T (°C)	Pressure (bar)											
	0			100			200			300		
	δ_d	δ_p	δ_h	δ_d	δ_p	δ_h	δ_d	δ_p	δ_h	δ_d	δ_p	δ_h
25	18.10	5.90	6.90	18.11	5.90	6.90	18.11	5.90	7.07	18.13	5.90	7.07
30	18.01	5.89	6.84	18.03	5.89	6.84	18.04	5.89	7.06	18.06	5.89	7.06
39.3	17.86	5.87	6.73	16.03	5.62	6.45	16.41	5.67	6.80	16.13	5.63	6.75
49	17.70	5.85	6.63	15.91	5.60	6.35	16.30	5.66	6.78	16.02	5.62	6.73
59.9	17.52	5.82	6.50	15.77	5.58	6.24	16.17	5.64	6.76	15.89	5.60	6.71
70.2	17.36	5.80	6.39	15.65	5.57	6.13	16.05	5.62	6.74	15.78	5.58	6.69
80.7	17.19	5.78	6.28	15.32	5.52	6.00	15.66	5.57	6.67	15.63	5.56	6.67
90.4	17.04	5.76	6.18	14.90	5.46	5.86	15.30	5.52	6.61	15.28	5.51	6.61
101	16.88	5.74	6.07	14.48	5.40	5.71	14.98	5.47	6.56	14.91	5.46	6.54
110.6	16.74	5.72	5.97	14.11	5.34	5.58	14.68	5.43	6.51	14.59	5.41	6.49
119.8	16.60	5.70	5.88	13.85	5.30	5.47	14.59	5.41	6.49	14.30	5.37	6.43
130	16.45	5.68	5.78	13.49	5.24	5.34	14.28	5.37	6.44	13.98	5.32	6.38
140.1	16.31	5.66	5.69	13.14	5.19	5.21	13.99	5.32	6.39	13.68	5.28	6.32
149.8	16.07	5.63	5.58	12.79	5.13	5.09	13.72	5.28	6.34	13.40	5.23	6.27

Once again, the sorption of CO₂ and resultant swelling of the PC results in a decrease in the polymer's HSP values, with the largest decrease observed in the dispersion parameter, δ_d . Unlike PMMA, however, the HSP values for PC continue to decrease with increasing temperature, indicating a continuous uptake of CO₂.

6.1.3 CO₂/PVB Interactions

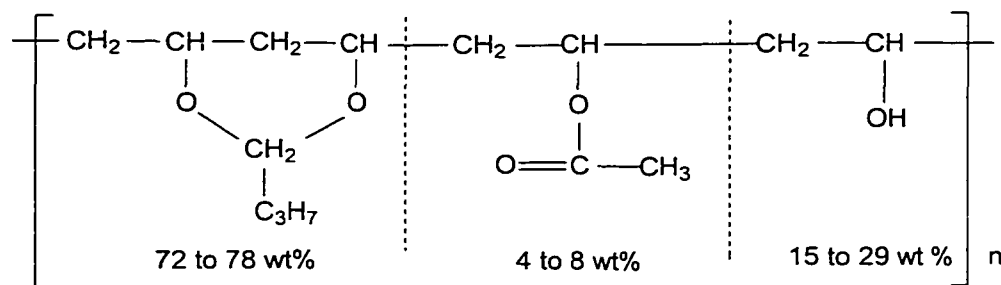


Figure 6-13. Monomer structure of PVB showing the typical range of composition.

Poly(vinyl butyral), Figure 6-13, is a polymer manufactured from poly(vinyl alcohol) by polymerizing butyl aldehyde. In the chemical reaction, 100% butyralization does not take place, resulting in a considerable amount of residual hydroxyl (vinyl alcohol), from 15 to 29 wt.%, in the PVB. There is also a small amount of residual acetyl (4 to 8 wt. %). As a result, the properties of this polymer will vary based upon the overall polymer composition. In solution or in the solid form this polymer tends to hydrogen bond internally, so solubility is dependent on an appreciable acid-base interaction with basic solvents.

HSP solubility parameter values are available from a variety of sources. Two sets of HSP values for Butvar® B76-poly(vinyl butyral) (11-13 wt.% hydroxyl), manufactured by Shawinigan Resins Company have been reported,

$$\begin{array}{l} \text{Set 1}^{505} \\ \delta_d = 17.4 \text{ MPa}^{1/2} \\ \delta_p = 8.8 \text{ MPa}^{1/2} \\ \delta_h = 11.3 \text{ MPa}^{1/2} \end{array}$$

$$\begin{array}{l} \text{Set 2}^{506} \\ \delta_d = 18.6 \text{ MPa}^{1/2} \\ \delta_p = 4.4 \text{ MPa}^{1/2} \\ \delta_h = 13.1 \text{ MPa}^{1/2} \end{array}$$

Using the group contribution method, Sincock and David⁵⁰⁷ determined HSP values, assuming a 28 wt.% hydroxyl content and 72 wt.% vinyl butyral,

$$\begin{array}{l} \delta_d = 15.7 \text{ MPa}^{1/2} \\ \delta_p = 8.2 \text{ MPa}^{1/2} \\ \delta_h = 11.4 \text{ MPa}^{1/2} \end{array}$$

HSP values calculated with the PVB weight percents specified in the Sekisui Materials Safety Data Sheet for the poly(vinyl butyral) product S-Lec B (72 wt.% vinyl butyral, 4 wt.% acetyl, and 24 wt.% hydroxyl) are

$$\begin{array}{l} \delta_d = 15.3 \text{ MPa}^{1/2} \\ \delta_p = 6.6 \text{ MPa}^{1/2} \\ \delta_h = 9.4 \text{ MPa}^{1/2} \end{array}$$

An averaged set of HSP's and an interaction radius as determined by Hansen,⁵⁰⁸ will be used:

$$\begin{array}{l} \delta_d = \delta_{dref} = 16.8 \text{ MPa}^{1/2} \\ \delta_d = \delta_{pref} = 7.0 \text{ MPa}^{1/2} \\ \delta_d = \delta_{href} = 11.3 \text{ MPa}^{1/2} \end{array}$$

The interaction radius, R_o (as defined in Section 5.2.1), determined on the basis of PVB dissolution behavior in a range of liquid solvents is $R_o^{liq} = 9.8 \text{ MPa}^{1/2}$.⁵⁰⁹

Experimental PVT data for PVB⁵¹⁰ are presented graphically in Figure 5-9. From these data, noticeable 'dips' can be observed along the isobars at higher pressures. This

is a feature occasionally observed in polymer PVT data, and is due to nonequilibrium states belonging to different glasses formed under different conditions during the measurement cycle. The glasses formed in this region are generally formed at pressures higher than the formation pressure of the “initial” glass, and therefore may have a higher density than the initial glass. This leads to the pronounced ‘dips’ (densifications) in the plotted isobars.⁵¹¹ From the PVT data above T_g , indicated by the change in slope of the isobars, the specific volume in the rubber state at ambient conditions, V_{rubber} , is estimated to be $0.9074 \left(\frac{cm^3}{g} \right)$, Figure 6-14, and will be taken as the reference volume, V_{ref} , at $T_{ref} = 25^\circ C$ and $P_{ref} = 1$ bar. The glass state specific volume at ambient conditions is $V_{glass} = 0.9171 \left(\frac{cm^3}{g} \right)$.

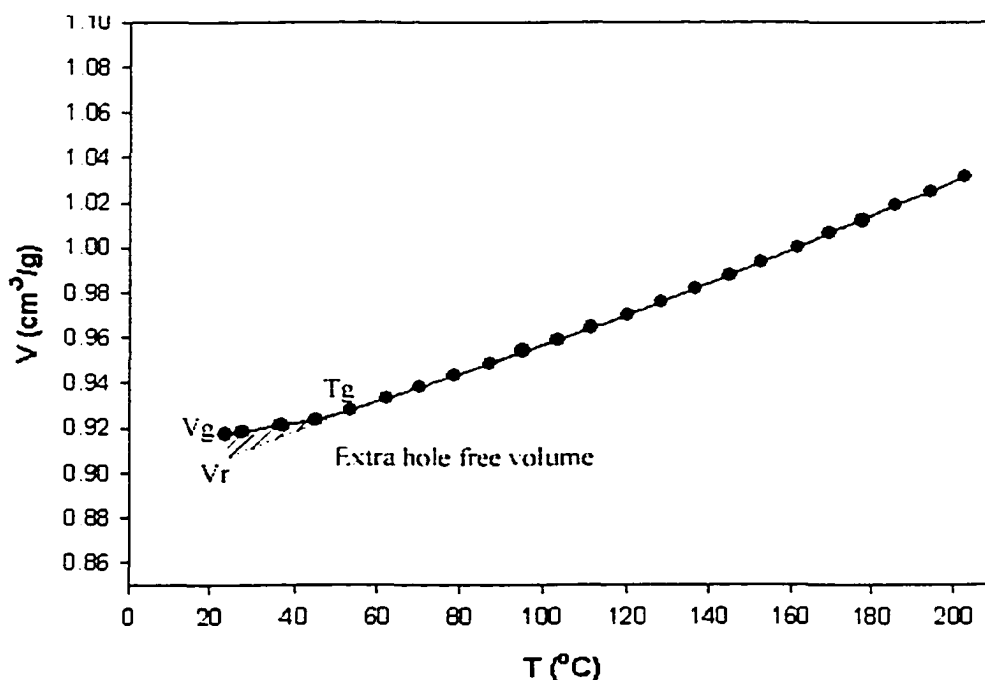


Figure 6-14. Extrapolation of the specific volume of PVB in the rubber state to ambient conditions.

With the remaining specific volume data for PVB above T_g , the change in PVB volume due to temperature and hydrostatic pressure effects can be determined, and the results are given in Table 6-21.

Table 6-21. Change in PVB specific volume (cm^3/g) as a result of T and P changes, derived from PVT data.

T ($^{\circ}\text{C}$)	Pressure (bar)			
	0	100	200	300
25	0.0000	-0.0036	-0.0073	-0.0114
27.8	0.0020	-0.0016	-0.0056	-0.0097
36.9	0.0083	0.0047	-0.0002	-0.0043
45.1	0.0141	0.0105	0.0048	0.0007
53.4	0.0204	0.0163	0.0097	0.0056
62	0.0256	0.0212	0.0168	0.0108
70.2	0.0309	0.0261	0.0212	0.0157
78.6	0.0359	0.0309	0.0259	0.0215
87.1	0.0410	0.0357	0.0304	0.0258
95.2	0.0464	0.0409	0.0353	0.0306
103.4	0.0513	0.0456	0.0398	0.0349
111.3	0.0567	0.0507	0.0447	0.0396
119.9	0.0624	0.0562	0.0499	0.0446
128.2	0.0681	0.0615	0.0548	0.0493
136.4	0.0739	0.0671	0.0602	0.0545
144.8	0.0799	0.0728	0.0656	0.0597
152.3	0.0855	0.0782	0.0709	0.0648
161.3	0.0926	0.0847	0.0767	0.0703

No Tait parameters have been published for PVB so that a comparison between the volume changes determined from experimental PVT data and calculated using the Tait equation cannot be made.

HSP values for PVB are calculated at different temperatures and pressures using the calculated changes in specific volume and the equations summarized in Table 5-9 are given in Table 6-22.

Table 6-22. PVB HSP values ($\text{MPa}^{1/2}$), at T and P , calculated using eqns. (6-9)-(6-11).

	Pressure (bar)											
	0			100			200			300		
$T (^{\circ}\text{C})$	δ_d	δ_p	δ_h	δ_d	δ_p	δ_h	δ_d	δ_p	δ_h	δ_d	δ_p	δ_h
25	16.8	7.0	11.3	16.9	7.0	11.5	17.0	7.0	11.5	17.1	7.0	11.6
27.8	16.8	7.0	11.2	16.8	7.0	11.5	16.9	7.0	11.5	17.0	7.0	11.6
36.9	16.6	7.0	11.1	16.7	7.0	11.5	16.8	7.0	11.5	16.9	7.0	11.5
45.1	16.5	6.9	10.9	16.6	7.0	11.4	16.7	7.0	11.5	16.8	7.0	11.5
53.4	16.3	6.9	10.8	16.4	6.9	11.4	16.6	7.0	11.4	16.7	7.0	11.5
62	16.2	6.9	10.6	16.3	6.9	11.4	16.4	6.9	11.4	16.6	7.0	11.4
70.2	16.1	6.9	10.5	16.2	6.9	11.4	16.3	6.9	11.4	16.4	6.9	11.4
78.6	16.0	6.9	10.3	16.1	6.9	11.3	16.2	6.9	11.3	16.3	6.9	11.4
87.1	15.9	6.8	10.2	16.0	6.9	11.3	16.1	6.9	11.3	16.2	6.9	11.3
95.2	15.8	6.8	10.0	15.9	6.8	11.3	16.0	6.9	11.3	16.1	6.9	11.3
103.4	15.7	6.8	9.9	15.8	6.8	11.2	15.9	6.9	11.3	16.0	6.9	11.3
111.3	15.6	6.8	9.8	15.7	6.8	11.2	15.8	6.8	11.2	15.9	6.9	11.3
119.9	15.5	6.8	9.6	15.6	6.8	11.2	15.7	6.8	11.2	15.8	6.8	11.2
128.2	15.3	6.8	9.5	15.5	6.8	11.2	15.6	6.8	11.2	15.7	6.8	11.2
136.4	15.2	6.7	9.4	15.4	6.8	11.1	15.5	6.8	11.1	15.6	6.8	11.2
144.8	15.1	6.7	9.2	15.3	6.7	11.1	15.4	6.8	11.1	15.5	6.8	11.1
152.3	15.0	6.7	9.1	15.2	6.7	11.1	15.3	6.7	11.1	15.4	6.8	11.1
161.3	14.9	6.7	9.0	15.0	6.7	11.0	15.2	6.7	11.1	15.3	6.7	11.1

Unlike PMMA and PC, little data are available in the literature regarding the sorption of CO_2 by PVB. At the time of this work, only one sorption study had been identified in the literature, conducted at $T = 25^{\circ}\text{C}$ and pressures up to 40 bar,⁵¹³ well below the critical point of CO_2 (31.1°C and 73.8 bar). These data, reproduced in Table 6-23.

Table 6-23. Literature values of CO_2 sorption in PVB.

$T (^{\circ}\text{C})$	P (bar)	$[\text{CO}_2]$ $\left(\frac{\text{cm}^3 \text{ STP}}{\text{cm}^3 \text{ polymer}} \right)$	Ref
25	0	0.00	512
25	5.8	8.70	“
25	10.9	15.20	“
25	20.3	26.90	“
25	30.4	38.70	“
25	35.5	45.70	“

This lack of CO₂ sorption, from which PVB swelling would be determined, does not allow for a calculation of PVB HSP values due to CO₂ sorption. However, it can be observed from the HSP values calculated for PVB as a function of T and P, Table 6-22, little change is noted in the polar or hydrogen bonding values. And while it was observed with PMMA and PC that swelling of these polymers with CO₂ lowers the HSP dispersion value significantly, lesser effects were observed for the polar and hydrogen bonding parameters. This tendency, makes it unlikely that swelling of PVB at the temperatures and pressures of the experiments (to be reviewed in Chapter 8) will lower the polar and hydrogen bonding PVB HSP values to a range comparable with pure CO₂ or, indeed, a CO₂-rich solvent. Also, of the three polymers involved in the current applications, PVB is likely to behave as a Lewis acid in the presence of CO₂ (also a Lewis acid), as a result of the large amount of hydroxyl in the polymer, Figure 6-13. Further, as can be seen from the HSP values, the high value of the hydrogen bonding component indicates some degree of intra-molecular hydrogen bonding (or self association), possibly between the hydrogen of the hydroxyl groups and the carbonyl oxygen in the acetyl groups.

The ambient conditions T_g of PVB varies from 51 to 90°C depending on the hydroxyl content and as can be seen in Figure 6-15, the T_g of PVB can be depressed as a result of CO₂ sorption, which can be expressed by

$$T_g(^{\circ}C) = -0.7975 \cdot \left[CO_2 \left(\frac{cm^3 \text{ STP}}{cm^3 \text{ polymer}} \right) \right] + 51 \quad (6-21)$$

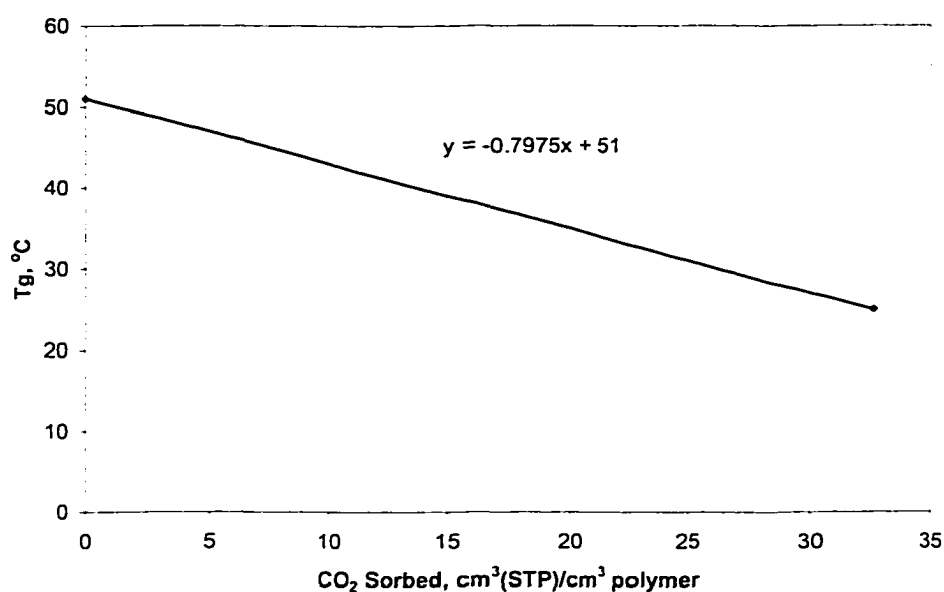


Figure 6-15. *T_g depression in PVB due to CO₂ sorption.*

From the 25°C CO₂ sorption data listed in Table 6-23, the PVB begins its transition from a glass state to a rubber state with the sorption of 32.6 cm³(STP)/cm³ polymer. As indicated by the bold, italic type, the PVB is assumed to be plasticized in a CO₂ environment at 25°C and 30.4 bar.

The partial molar volumes of CO₂ dissolved in PVB are calculated using eqn. 6-8, and are given in Table 6-24.

Table 6-24. *Calculated partial molar volumes of CO₂ dissolved in PVB.*

T (°C)	P (bar)	Internal Pressure, PC (bar)	$\bar{V}_{CO_2}$ (cm ³ /mol)
50	100	4473.2	37.9
50	200	4528.4	37.5
100	100	4214.8	40.1
100	200	4260.1	39.6
Average			38.8

In comparing PVB to PMMA and PC, it can also be seen from Table 6-24, that the internal pressure of PVB for comparable temperatures and pressures are higher than PMMA or PC. This result is also depicted in the higher HSP values of PVB in comparison to PMMA and PC.

6.2 Cosolvent/Polymer Interactions

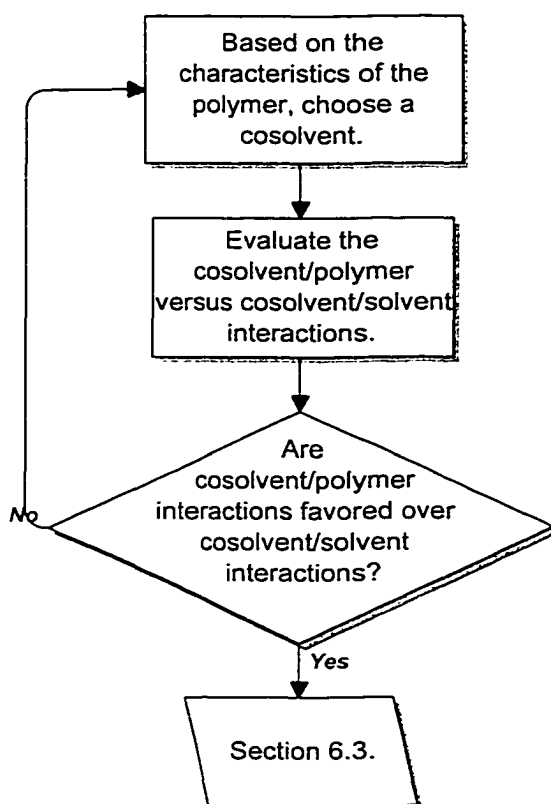


Figure 6-16. *Cosolvent/polymer decision tree.*

The addition of a small amount of cosolvent, in addition to altering the chemical nature of the solvent (CO_2), has also been reported to enhance the swelling of polymers subjected to modified supercritical CO_2 .^{514,515,516} In research recently published by West

et al.,⁵¹⁷ poly(dimethyl siloxane) was swollen by a CO₂/acetone mixture by almost 600%. At the same conditions of temperature and pressure, this is a nearly 5-fold increase over the swelling caused by pure CO₂. The authors of this work attribute the enhanced swelling effect to strong interactions of the cosolvent with the polymer. Further, the less volatile cosolvent may partition preferentially into the polymer phase, especially if favorable interactions between the polymer and cosolvent, such as hydrogen bonding or Lewis acid/base formations exist, and may block active sites, thus precluding polymer/polymer interactions.⁵¹⁸ Work in quantifying and studying the partitioning of cosolvents between supercritical CO₂ and polymer phases is currently ongoing using in situ Fourier transform IR and UV-vis spectroscopy. This methodology has allowed not only the quantification of partitioning, but also the ability to identify the type of interactions playing a role in the partitioning. The increased sorption of methanol in PMDS was attributed to hydrogen bonding between the methanol hydroxyl functional groups and the basic sites of PMDS with this technique.⁵¹⁹ Others researchers using mass spectrometry tracer pulse chromatography reported a C₁₈ bonded phase in contact with 2 mol% methanol modified CO₂ was composed of up to 25 mol% methanol near the critical mixture region, and that at all conditions of temperature and pressure the concentration of methanol in the C₁₈ bonded phase always exceeded the concentration in the supercritical fluid phase.⁵²⁰

6.3 Solvent/Cosolvent Interactions

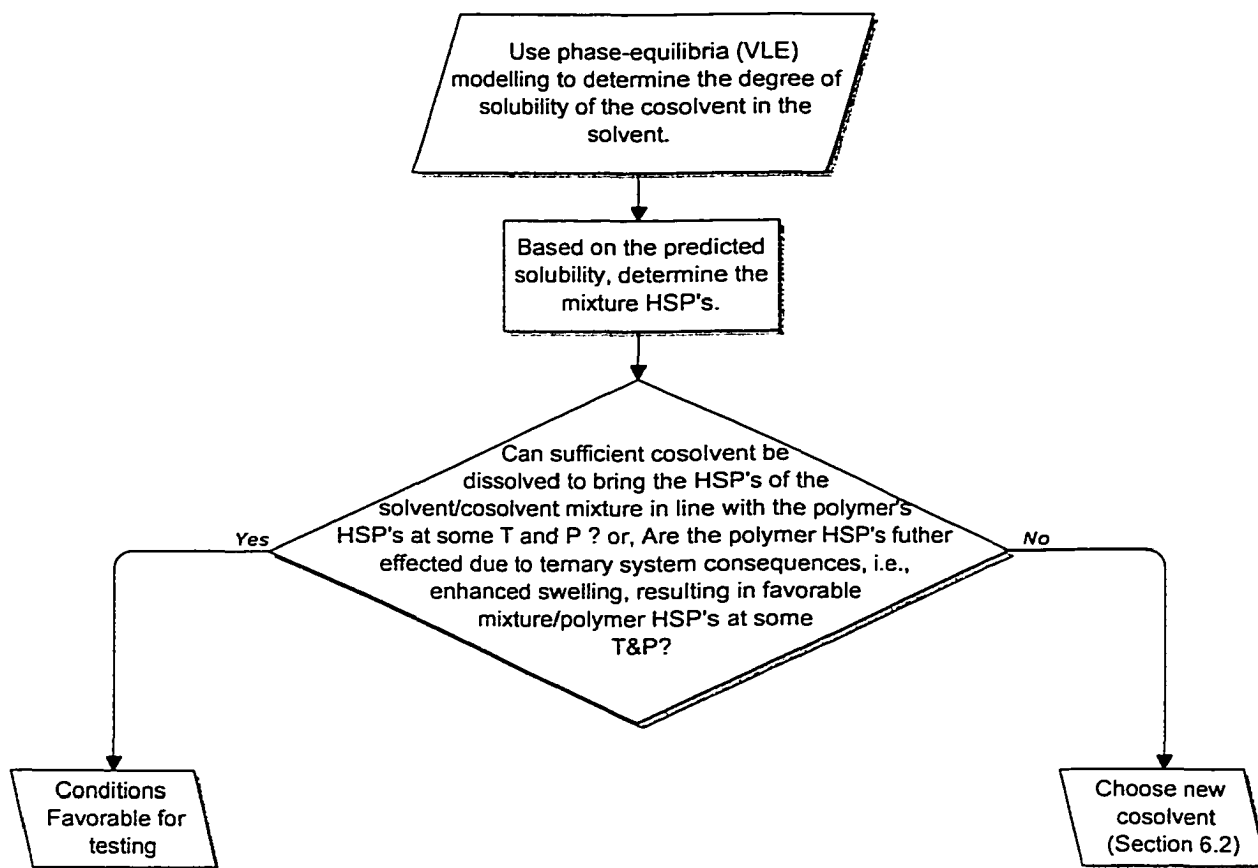


Figure 6-17. *Solvent/cosolvent decision tree.*

As previously mentioned, to enhance CO₂ solubility and disrupt polymer/polymer interactions, a second compound or modifier, may be added to supercritical CO₂ as a cosolvent. The addition of a small amount of cosolvent can also significantly enhance solute solubility if specific interactions exist between the cosolvent and solute. Electrostatic interactions between the cosolvent and solute may include all of the *van der Waals* interactions mentioned previously. When using a polar cosolvent for polar solutes, specific chemical interactions like hydrogen bonding or charge transfer complex

formation can also lead to large cosolvent effects.⁵²¹ However, it must be remembered when selecting a cosolvent that the solvent can compete with the solute for the cosolvent. This is because CO₂ has two carbonyl oxygens that will accept hydrogen bonds and generally the supercritical solvent is in excess in the solution so that if the solvent can compete for specific interaction sites, as the CO₂ can, it will hydrogen bond to the cosolvent before the cosolvent can affect solute solubility levels.⁵²² Such interactions tie up hydrogen-bonding sites that might otherwise be available for interactions between the polymer and cosolvent. This competition between solvent/cosolvent and cosolvent/solute interactions must therefore be considered when choosing a cosolvent, particularly when the solvent has donor-acceptor properties.

Solubility parameter values for a number of compounds, which could be used as cosolvents, are tabulated in various references, or can be determined using the methods outlined in Section 5.4. Once the solubility parameters for the solvent (CO₂) and cosolvent have been assigned, a solubility parameter for the solvent-cosolvent mixture can be calculated using a volume average

$$\delta_m = \frac{\phi_1}{\phi_1 + \phi_2} \delta_1 + \frac{\phi_2}{\phi_1 + \phi_2} \delta_2 \quad (6-22)$$

where δ_1 and δ_2 refer to the solvent and cosolvent solubility parameters respectively, and ϕ_1 , ϕ_2 refer to the respective volume or mole fractions.^{523,524,525,526,527,528}

Determination of the volume fraction of solvent and cosolvent is accomplished through a calculation of the vapor-liquid equilibrium for the solvent (CO₂) - cosolvent system of interest. In this work, a cubic EOS, with temperature-independent mixing rules

is used. Chapter 7 illustrates the use of this EOS to model the VLE for the CO₂-propylene carbonate system, where new phase equilibria data are presented. These new data extends the range of pressures into the supercritical fluid region of CO₂.

7 Vapor-Liquid Equilibrium Modeling

7.1 EOS Modeling of VLE Data

(Cubic) equations of state (EOS), i.e., relations third order in molar volume between pressure, molar volume, and absolute temperature, are widely used for phase equilibrium calculations for pure fluids. The extension of equations of state from pure fluids to the prediction of phase behavior of mixtures is done using mixing and combining rules. However, the use of a single equation of state to predict the composition of both pure compounds and mixtures, in both the vapor and liquid phases, as a function of temperature and pressure, is an elusive goal. Many authors have proposed variations to the semi empirical relationship first derived by van der Waals, eqn. (4-12). One of the most successful modifications was that made by Redlich and Kwong⁵²⁹ (RK),

$$P = \frac{RT}{v-b} - \frac{a}{T^{0.5}v(v+b)}. \quad (7-1)$$

The RK equation of state has been used with good success to calculate volumetric and thermal properties of pure compounds, but its application to multicomponent vapor-liquid equilibrium (VLE) calculations often gives poor results. This has been attributed partly to the equation's lack of accuracy in expressing the influence of temperature. Soave⁵³⁰ modified the RK equation, replacing the $a/T^{0.5}$ term with a more general temperature dependent term, $a(T)$. This equation is known as the Soave -Redlich-Kwong (SRK) equation of state,

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)}, \quad (7-2)$$

where

$$a(T) = \alpha(T) \cdot 0.42747 \frac{R^2 T_c^2}{P_c} \quad (7-3)$$

$$\alpha(T) = \left[1 + \kappa (1 - T_r^{0.5}) \right]^2 \quad (7-4)$$

$$\kappa = 0.48508 + 1.55171\omega - 0.15613\omega^2 \quad (7-5)$$

$$b = 0.086644 \frac{RT_c}{P_c} \quad (7-6)$$

In eqns. (7-3) through (7-6), T_c , and P_c are the critical temperature and critical pressure, respectively, of the pure components, ω is the pure component acentric factor, and $T_r = T/T_c$. The SRK EOS can be written in terms of the compressibility factor, Z ,

$$Z = \frac{Pv}{RT} \quad (7-7)$$

so that

$$Z = \frac{v}{v-b} - \frac{a(T)}{RT(v+b)} \quad (7-8)$$

Kwak and Mansoori⁵³¹ suggested the replacement of the temperature dependent term $a(T)$ based on statistical-mechanical arguments and the fact that the van der Waals

mixing rules are for constants of an equation of state and not for any thermodynamic state functions that may appear in an equation of state. In order to separate thermodynamic variables from constants in the SRK equation of state, Kwak and Mansoori substitute eqns. (7-3) and (7-4) into eqn. (7-8) to obtain,

$$Z = \frac{v}{v-b} - \frac{(1 + \kappa(1 - T_r^{0.5}))^2 \left(0.42747 \frac{R^2 T_c^2}{P_c} \right)}{RT(v+b)}. \quad (7-9)$$

Expanding and rearranging terms in eqn. (7-9) gives

$$Z = \frac{v}{v-b} - \frac{1}{RT(v+b)} \left[\begin{aligned} &\left(0.42747 \frac{R^2 T_c^2}{P_c} \right) + \left(2\kappa 0.42747 \frac{R^2 T_c^2}{P_c} \right) \\ &- \left(2\kappa \left(\frac{T}{T_c} \right)^{0.5} 0.42747 \frac{R^2 T_c^2}{P_c} \right) - \left(2\kappa^2 \left(\frac{T}{T_c} \right)^{0.5} 0.42747 \frac{R^2 T_c^2}{P_c} \right) \\ &+ \left(\kappa^2 0.42747 \frac{R^2 T_c^2}{P_c} \right) + \left(\kappa^2 \left(\frac{T}{T_c} \right) 0.42747 \frac{R^2 T_c^2}{P_c} \right) \end{aligned} \right] \quad (7-10)$$

$$Z = \frac{v}{v-b} - \frac{1}{(v+b)} \left[\begin{aligned} &\frac{0.42747 \frac{R^2 T_c^2}{P_c}}{RT} (1 + \kappa)^2 + 0.42747 \frac{R^2 T_c^2}{P_c} \left(\frac{\kappa^2}{RT_c} \right) \\ &- 2 \left(\frac{0.42747 \frac{R^2 T_c^2}{P_c} (\kappa(1 + \kappa))}{RT_c^{0.5} T^{0.5}} \right) \end{aligned} \right] \quad (7-11)$$

As proposed by Kwak and Mansoori, two new terms c and d are introduced, where

$$c = 0.42747 \frac{R^2 T_c^2}{P_c} (1 + \kappa)^2 \quad (7-12)$$

and

$$d = 0.42747 \frac{R^2 T_c^2}{P_c} \left(\frac{\kappa^2}{RT_c} \right) \quad (7-13)$$

so that

$$Z = \frac{v}{v-b} - \frac{\frac{c}{RT} + d - 2\sqrt{\frac{cd}{RT}}}{v+b} \quad (7-14)$$

and

$$\boxed{P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)}} \quad (7-15)$$

where $a(T) = c + dRT - 2\sqrt{cdRT}$.

In this form, there are now three independent constants in the SRK equation of state: b , c , and d . These constants for the mixture are then evaluated with new mixing rules, also proposed by Kwak and Mansoori, which follow the form originally proposed by van der Waals,

$$\begin{aligned}
b &= \sum_i^n \sum_j^n x_i x_j b_{ij} , \\
c &= \sum_i^n \sum_j^n x_i x_j c_{ij} , \\
d &= \sum_i^n \sum_j^n x_i x_j d_{ij} .
\end{aligned} \tag{7-16}$$

The unlike-interaction parameters b_{ij} , c_{ij} , and d_{ij} , are determined using pure component properties and fitting parameters, k_{ij} , m_{ij} , and l_{ij} ,

$$\begin{aligned}
b_{ij} &= (1 - k_{ij}) \left[(b_{ii}^{1/3} + b_{jj}^{1/3}) / 2 \right]^3 \\
c_{ij} &= (1 - l_{ij}) (c_{ii} c_{jj})^{1/2} \\
d_{ij} &= (1 - m_{ij}) \left[(d_{ii}^{1/3} + d_{jj}^{1/3}) / 2 \right]^3
\end{aligned} \tag{7-17}$$

Equation (7-14) is the cubic EOS used in this work to model solvent-cosolvent vapor-liquid equilibria. In order to use eqn. (7-14) to calculate the pressure and temperature associated with a specific system volume, we need a further relationship between the volume fractions of solvent and cosolvent in the liquid and vapor phases. Various modeling procedures have been proposed in the literature to predict the phase behavior of vapor-liquid systems at high pressures. Regardless of the modeling procedure, however, the following thermodynamic relationship must be satisfied for two phases in thermodynamic equilibrium,⁵³²

$$f_i^V(T, P, y_i) = f_i^L(T, P, x_i) \tag{7-18}$$

where f_i^V is the fugacity of component i in the vapor phase, f_i^L is the fugacity of component i in the liquid phase, y_i is the mole fraction of component i in the vapor phase, and x_i is the mole fraction of component i in the liquid phase. The number of equations implied by eqn. (7-18) is equal to the number of components that appear in both the vapor and liquid phases. The fugacity of component i in each phase can now be written as

$$\begin{aligned} f_i^V(T, P, y_i) &= y_i \phi_i^V P \\ f_i^L(T, P, x_i) &= x_i \phi_i^L P \end{aligned} \quad (7-19)$$

where ϕ_i^V is the fugacity coefficient of component i in the vapor phase, P is the system pressure, T is the system temperature, and ϕ_i^L is the fugacity coefficient of component i in the liquid phase. Fugacity coefficients for the vapor and liquid phases are calculated from the exact thermodynamic relationships,⁵³³

$$RT \ln \phi_i^V = \int_{V^*}^{\infty} \left[\left(\frac{\partial P}{\partial n_i} \right)_{T, V, n_j} - \frac{RT}{V} \right] dV - RT \ln Z_V \quad (7-20)$$

and

$$RT \ln \phi_i^L = \int_{V^L}^{\infty} \left[\left(\frac{\partial P}{\partial n_i} \right)_{T, V, n_j} - \frac{RT}{V} \right] dV - RT \ln Z_L \quad (7-21)$$

where Z_V and Z_L are the mixture compressibility factors in the vapor and liquid phases, respectively.

The solution of eqn. (7-20) will be identical to that of eqn. (7-21), therefore only the solution of the vapor phase fugacity coefficient will be shown. Recalling eqn. (7-15) and substituting the quantity V/n for v (specific volume), where V is the total system volume

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V(V + nb)} \quad (7-22)$$

We next determine the partial derivative of P with respect to n , at constant T , V , and $n_{j \neq i}$.

$$\begin{aligned} \left(\frac{\partial P}{\partial n_i} \right)_{T, V, n_{j \neq i}} &= \frac{RT}{V - nb} + \frac{nRT}{(V - nb)^2} \frac{\partial(nb)}{\partial n_i} - \frac{1}{V(V + nb)} \frac{\partial(n^2 a)}{\partial n_i} \\ &\quad + \frac{n^2 a}{V(V + nb)^2} \frac{\partial(nb)}{\partial n_i} \end{aligned} \quad (7-23)$$

Substituting eqn. (7-23) into eqn. (7-20) or (7-21) and integrating,

$$\begin{aligned} RT \ln \phi_i &= \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i} \right)_{T, V, n_{j \neq i}} - \frac{RT}{V} \right] dV - RT \ln Z, \\ &= RT \left[\ln(V - nb) \right]_V^\infty - \frac{\partial(nb)}{\partial n_i} \left[\frac{nRT}{V - nb} \right]_V^\infty + \frac{1}{nb} \frac{\partial(n^2 a)}{\partial n} \left[\ln \left(\frac{V + nb}{V} \right) \right]_V^\infty \\ &\quad + n^2 a \frac{\partial(nb)}{\partial n_i} \left[\left[\frac{1}{nb(V + nb)} - \frac{1}{(nb)^2} \ln \left(\frac{V + nb}{V} \right) \right] \right]_V^\infty - RT \left[\ln V \right]_V^\infty - RT \ln Z \end{aligned} \quad (7-24)$$

Evaluating the limits of integration and substituting vn for V ,

$$RT \ln \phi_i = -RT \ln \left(\frac{v-b}{v} \right) + \frac{RT}{v-b} \frac{\partial(nb)}{\partial n_i} - \frac{1}{nb} \ln \left(\frac{v+b}{v} \right) \frac{\partial(n^2 a)}{\partial n_i} \quad (7-25)$$

$$- \frac{a}{b} \left[\frac{1}{v+b} - \frac{1}{b} \ln \left(\frac{v+b}{v} \right) \right] \frac{\partial(nb)}{\partial n_i} - RT \ln Z$$

Simplifying, and dividing through by RT ,

$$\ln \phi_i = -\ln \left(Z \left(1 - \frac{b}{v} \right) \right) - \frac{1}{nbRT} \ln \left(1 + \frac{b}{v} \right) \frac{\partial(n^2 a)}{\partial n_i} \quad (7-26)$$

$$+ \left[\frac{1}{v-b} - \frac{a}{bRT(v+b)} + \frac{a}{b^2 RT} \ln \left(1 + \frac{b}{v} \right) \right] \frac{\partial(nb)}{\partial n_i}$$

The last term in eqn. (7-26) can be rewritten as

$$\left[\frac{1}{v-b} - \frac{a}{bRT(v+b)} \right] \frac{\partial(nb)}{\partial n_i} = \frac{1}{b} \left(\frac{b}{v-b} - \frac{a}{RT(v+b)} \right) \frac{\partial(nb)}{\partial n_i} \quad (7-27)$$

$$= \frac{1}{b} \left(\frac{v}{v-b} - \frac{a}{RT(v+b)} - \frac{v}{v-b} + \frac{b}{v-b} \right) \frac{\partial(nb)}{\partial n_i}$$

Substituting eqn. (7-8) into eqn. (7-27),

$$\frac{1}{b} \left(\frac{v}{v-b} - \frac{a}{RT(v+b)} - \frac{v}{v-b} + \frac{b}{v-b} \right) \frac{\partial(nb)}{\partial n_i} = \frac{1}{b} (Z-1) \frac{\partial(nb)}{\partial n_i} \quad (7-28)$$

and substituting eqn. (7-28) into eqn. (7-26),

$$\ln \phi_i = \frac{1}{b} (Z-1) \frac{\partial(nb)}{\partial n_i} - \ln \left[Z \left(1 - \frac{b}{v} \right) \right] + \frac{a}{bRT} \left[\frac{1}{b} \frac{\partial(nb)}{\partial n_i} - \frac{1}{an} \frac{\partial(n^2 a)}{\partial n_i} \right] \ln \left(1 + \frac{b}{v} \right) \quad (7-29)$$

It is now necessary to compute the remaining derivatives in eqn. (7-29), $\left(\frac{\partial(nb)}{\partial n_i}\right)$ and

$\left(\frac{\partial(n^2 a)}{\partial n_i}\right)$. Recalling the definitions given in eqn. (7-15) and eqn. (7-16),

$$\begin{aligned}\frac{\partial(nb)}{\partial n_i} &= \frac{\partial}{\partial n_i} \sum_i^n \sum_j^n x_i x_j b_{ij} = \frac{\partial}{\partial n_i} \left[\frac{1}{n} \sum_i^n \sum_j^n n_i n_j b_{ij} \right] \\ &= -\frac{1}{n^2} \sum_i \sum_j n_i n_j b_{ij} + \frac{1}{n} 2n \sum_j x_j b_{ij}\end{aligned}\quad (7-30)$$

$$\frac{\partial(nb)}{\partial n_i} = -b + 2 \sum_j x_j b_{ij}$$

$$\frac{\partial(n^2 a)}{\partial n_i} \quad (7-31)$$

$$\frac{\partial(n^2 a)}{\partial n_i} = \frac{\partial(n^2 c)}{\partial n_i} + RT \frac{\partial(n^2 d)}{\partial n_i} - 2\sqrt{RT} \frac{\partial[(n^2 c n^2 d)^{1/2}]}{\partial n_i}$$

where, as before $a = c + dRT - 2\sqrt{cdRT}$. Similarly for the derivatives $\left(\frac{\partial(n^2 c)}{\partial n_i}\right)$,

$$\left(\frac{\partial(n^2 d)}{\partial n_i}\right), \text{ and } \left(\frac{\partial(\sqrt{n^2 c n^2 d})}{\partial n_i}\right),$$

$$\frac{\partial(n^2 c)}{\partial n_i} = \frac{\partial}{\partial n_i} n^2 \sum_i^n \sum_j^n x_i x_j c_{ij} = \frac{\partial}{\partial n_i} \sum_i^n \sum_j^n n_i n_j c_{ij} = 2 \sum_j^n n_j c_{ij} = 2n \sum_j x_j c_{ij} \quad (7-32)$$

$$\frac{\partial(n^2 d)}{\partial n_i} = 2n \sum_j^n x_j d_{ij}, \quad (7-33)$$

$$\begin{aligned} \frac{\partial}{\partial n_i} \left[\sqrt{n^2 c} \sqrt{n^2 d} \right] &= \frac{\sqrt{n^2 d}}{2\sqrt{n^2 c}} \frac{\partial(n^2 c)}{\partial n_i} + \frac{\sqrt{n^2 c}}{2\sqrt{n^2 d}} \frac{\partial(n^2 d)}{\partial n_i} \\ &= \frac{1}{2} \sqrt{\frac{d}{c}} \left(2n \sum_j^n x_j c_{ij} \right) + \frac{1}{2} \sqrt{\frac{c}{d}} \left(2n \sum_j^n x_j d_{ij} \right) = n \sqrt{\frac{d}{c}} \left(\sum_j^n x_j c_{ij} \right) + n \sqrt{\frac{c}{d}} \left(\sum_j^n x_j d_{ij} \right) \end{aligned} \quad (7-34)$$

Substituting eqns. (7-32) to (7-34) back into eqn. (7-31) and simplifying,

$$\frac{\partial(n^2 a)}{\partial n_i} = 2n \left[\sum_j^n x_j c_{ij} + RT \sum_j^n x_j d_{ij} - \sqrt{RT} \left(\sqrt{\frac{d}{c}} \sum_j^n x_j c_{ij} + \sqrt{\frac{c}{d}} \sum_j^n x_j d_{ij} \right) \right] \quad (7-35)$$

Substituting eqns. (7-35) and (7-30) into eqn. (7-29),

$$\begin{aligned} \ln \phi_i &= \frac{1}{b} (Z - 1) \left(-b + 2 \sum_j^n x_j b_{ij} \right) - \ln \left[Z \left(1 - \frac{b}{v} \right) \right] + \frac{a}{bRT} \left[\frac{1}{b} \left(-b + 2 \sum_j^n x_j b_{ij} \right) \ln \left(1 + \frac{b}{v} \right) \right] \\ &\quad - \frac{a}{bRT} \left[\frac{1}{an} 2n \left(\sum_j^n x_j c_{ij} + RT \sum_j^n x_j d_{ij} - \sqrt{RT} \left(\sqrt{\frac{d}{c}} \sum_j^n x_j c_{ij} + \sqrt{\frac{c}{d}} \sum_j^n x_j d_{ij} \right) \right) \right] \ln \left(1 + \frac{b}{v} \right) \end{aligned} \quad (7-36)$$

Finally, making the substitutions, $v = \frac{ZRT}{P}$ and $B = \frac{bP}{RT}$, eqn. (7-36) simplifies to

$$\ln \phi_i = \left[\left(\frac{2}{b} \sum_j x_j b_{ij} \right) - 1 \right] \left[Z - 1 + \frac{a}{bRT} \ln \left(1 + \frac{B}{Z} \right) \right] - \ln(Z - B) - \frac{2}{bRT} \ln \left(1 + \frac{B}{Z} \right) \left[\sum_j x_j c_{ij} + RT \sum_j x_j d_{ij} - \sqrt{RT} \left(\sqrt{\frac{d}{c}} \sum_j x_j c_{ij} + \sqrt{\frac{c}{d}} \sum_j x_j d_{ij} \right) \right]$$

(7-37)

Equation (7-37) is applicable to both the vapor and liquid phase fugacity coefficients with the appropriate vapor or liquid phase values used. Equations for b , c , and d are as defined earlier (again these equations are solved separately for the vapor phase and a liquid phase). Calculation of the compressibility factor, Z , is from the polynomial form of the SRK equation,

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0 \quad (7-38)$$

where

$$A = \frac{aP}{R^2 T^2} \quad (7-39)$$

$$B = \frac{bP}{RT}.$$

and $a = c + dRT - 2\sqrt{cdRT}$.

Solving eqn. (7-38) results in three roots. The largest positive root corresponds to the fugacity coefficient of the vapor phase, while the smallest positive root corresponds to the fugacity coefficient of the liquid phase.⁵³⁴ The intermediate root is discarded.

$$y_i \phi_i^V P = x_i \phi_i^L P, \quad (7-40)$$

$$\therefore y_{i,calc} = \frac{x_{i,exp} \phi_i^L}{\phi_i^V}, \quad \text{and} \quad x_{i,calc} = \frac{y_{i,exp} \phi_i^V}{\phi_i^L}.$$

7.2 Example: CO₂-Propylene Carbonate System

Propylene carbonate is a polar solvent used at the Supercritical; Fluids Facility as a co-solvent for polymer removal.^{535,536} The use of the SRK EOS will be illustrated by modeling some newly acquired vapor-liquid equilibrium (VLE) data. The new isothermal vapor-liquid equilibrium data was measured at 298.15 K, 308.15 K, 333.15 K and 373.15 K over a pressure range from 41 to 206.8 bars.⁵³⁷ The results are listed in Table 7-1, where x_2 and y_2 are the mole fractions of carbon dioxide in the liquid phase and vapor phase, respectively.

Table 7-1. Experimental vapor-liquid equilibrium data for propylene carbonate (1) - carbon dioxide (2) mixtures.

T (K)	P (bar)	x_2	y_2	T (K)	P (bar)	x_2	y_2
298.15	41.37	0.4373	0.99999	333.15	137.90	0.6161	0.99394
298.15	61.24	0.7091	0.99989	333.15	172.37	0.6737	0.98522
308.15	55.16	0.4788	0.99995	333.15	206.84	0.7318	0.97279
308.15	82.74	0.6774	0.99381	373.15	55.16	0.2122	0.99953
308.15	110.32	0.7234	0.98665	373.15	82.74	0.2989	0.99917
308.15	137.90	0.7608	0.98281	373.15	110.32	0.3720	0.99852
333.15	55.16	0.3313	0.99990	373.15	137.90	0.4366	0.99776
333.15	82.74	0.4577	0.99958	373.15	172.37	0.5043	0.99542
333.15	110.32	0.5558	0.99855	373.15	206.84	0.5559	0.99152

The experimental phase equilibrium data obtained were modeled using the SRK EOS as described in Section 7.1. The critical constants, T_c , P_c , and acentric factor, ω , of the pure components, for use in eqns. (7-3) through (7-6), are summarized in Table 7-2.

Table 7-2. Critical properties and acentric factors of pure components.

Component	T _c (K)	P _c (bar)	ω
Propylene Carbonate ⁵³⁸	625.15	57.05	.707 ⁵³⁹
Carbon Dioxide ⁵⁴⁰	304.1	73.8	.239

The experimental data in Table 7-1 was fit using an objection function, eqn. (7-41), which minimizes the difference between the experimental CO₂-propylene carbonate vapor and liquid mole fractions and the same mole fractions calculated as described in Section 7.1.

$$\min(S) = \sum (y_{\text{exp}} - y_{\text{calc}})^2 + \sum (x_{\text{exp}} - x_{\text{calc}})^2 \quad (7-41)$$

The values obtained for the three binary fitting parameters, eqn. (7-17), are

$$\begin{aligned} k_{ij} &= -0.041 \\ l_{ij} &= -0.115 \\ m_{ij} &= -0.063 \end{aligned}$$

The results of the modeling correlation are shown in Figure 7-1. The solid lines represent the isotherms calculated using the interaction parameters k_{ij} , l_{ij} , and m_{ij} obtained from the correlation. It can be seen that the agreement is quite good for both the liquid and vapor phases, especially at the higher temperatures.

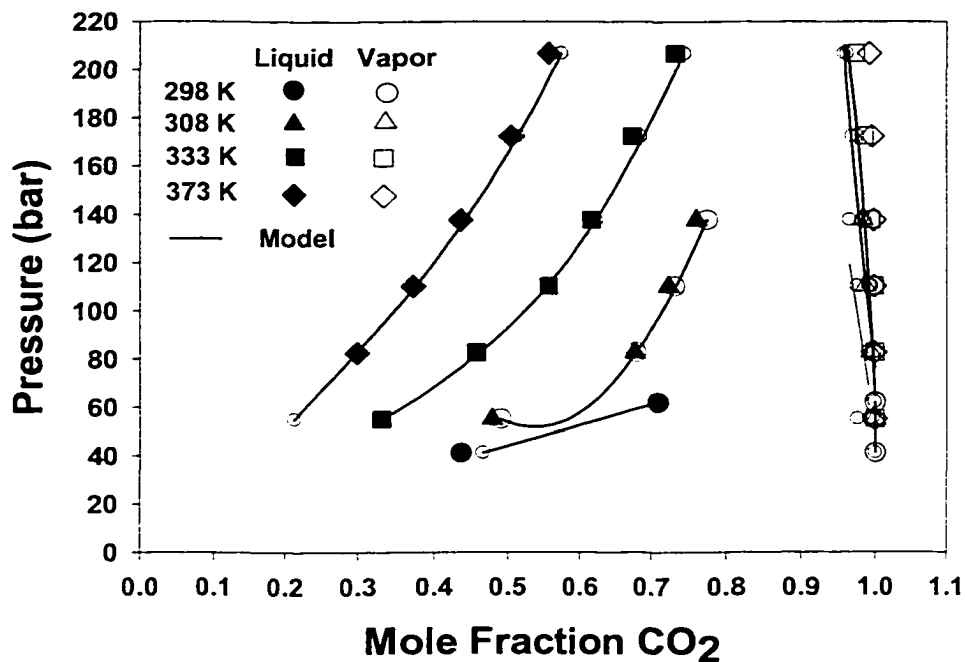


Figure 7-1. Experimental data and results of VLE modeling of the propylene carbonate-CO₂ system.

Figure 7-2 shows that the high-pressure experimental range in this work and in existing literature. It is seen that the experimental data has been extended into the pressure range useful for supercritical CO₂ processing. All the propylene carbonate/CO₂ VLE data^{541,542} (this work, as well indicated references) were modeled using the previously calculated interaction parameters k_{ij} , l_{ij} , and m_{ij} , and results of the liquid equilibrium correlation are represented by the solid lines in Figure 7-2. Again, good agreement is seen between the experimental and calculated values.

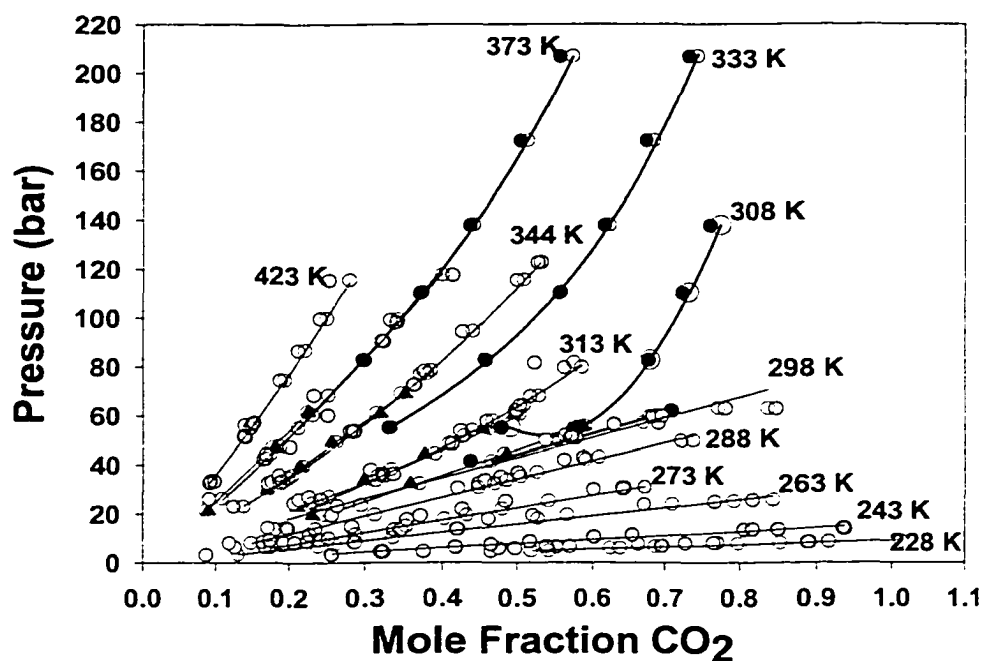


Figure 7-2. Comparison of high-pressure propylene carbonate- CO_2 VLE. This work $\bullet$; reference 543 $\blacktriangle$; reference 544 $\circ$.

A similar modeling procedure was performed for existing vapor-liquid equilibrium data for carbon dioxide-ester binary systems. As in the previous analysis, the correlation utilized three interaction parameters and minimized the difference between the experimental and calculated CO_2 -ester mole fractions. These parameter values and the source of the experimental CO_2 /ester VLE data are shown in Table 7-3.

Table 7-3. Results of VLE modeling of carbon dioxide(2) + ester(1) binary systems.

Component 1	Chemical Formula P_v^a	No. points	T (°C)	P (bar)	Ref.	k_{ij}	l_{ij}	m_{ij}	Sum of squares, $\Sigma\Delta x$, and AAD**
methyl acetate	$\text{CH}_3\text{COOCH}_3$ ($P_v = 0.29$ bar)	22	298.15 - 313.15	6.5 - 80	545	-0.204	-0.025	0.176	0.0011 0.0065
ethyl acetate	$\text{CH}_3\text{CH}_2\text{COOCH}_3$ ($P_v = 0.12$ bar)	42	303.15 - 323.15	20 - 90	546	-0.371	-0.216	0.015	0.0112 0.0138
propyl acetate	$\text{CH}_3(\text{CH}_2)_2\text{COOCH}_3$ ($P_v = 0.05$ bar)	56	303.15 - 323.15	20 - 92	547	-0.338	-0.130	0.150	0.0093 0.0108
ethyl propanoate	$\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3$ ($P_v = 0.05$ bar)	74	303.15 - 323.15	17 - 92	548	-0.245	-0.096	0.121	0.0093 0.0086
methyl myristate	$\text{CH}_3(\text{CH}_2)_{12}\text{COOCH}_3$ ($P_v = 0.004$ bar)	17	313.15 - 343.15	72 - 160	549	-0.393	-0.066	0.343	0.0003 0.0042
methyl palmitate	$\text{CH}_3(\text{CH}_2)_{14}\text{COOCH}_3$ ($P_v = 0.002$ bar)	25	313.15 - 343.15	62 - 183	"	-0.453	0.056	0.530	0.0002 0.0023
methyl oleate	$\text{CH}_3(\text{CH}_2)_7(\text{CH})_2(\text{CH}_2)_7\text{COOCH}_3$ ($P_v = 0.0004$ bar)	25	313.15 - 343.15	72 - 200	"	-0.455	0.062	0.557	0.0010 0.0033
methyl stearate	$\text{CH}_3(\text{CH}_2)_{16}\text{COOCH}_3$ ($P_v = 0.0005$ bar)	22	313.15 - 343.15	60 - 198	"	-0.472	-0.040	0.451	0.0007 0.0045
propylene carbonate	$\text{CH CH}_3\text{CH}_2\text{OCOO}$ ($P_v = 0.00006$ bar)	18	298.15 - 373.15	41 - 207	b	-0.041	-0.115	-0.063	0.0021 0.0081

^a Vapor pressure at atmospheric conditions, bars.

^b This work

8 Comparison of Theoretical Model with Experiments

8.1 Equipment

8.1.1 Photoresist Removal from Silicon Wafers

Polymer coating removal experiments were conducted on two different components: (1) silicon wafers (see Section 1.1), and (2) anodized aluminum photoconductor drums (see Section 1.2). All experiments were performed at the Supercritical Fluids Facility at the Los Alamos National Laboratory, utilizing two experimental setups. Experiments on the removal of photoresist from silicon wafers were carried out in a commercial 10 liter high-pressure vessel. This vessel is part of a computer controlled, closed-loop system, having real-time temperature and pressure control and a variable-speed internal impeller. The system operates in a dynamic mode with a flow rate of 2.7 liter/hr. Temperature control is maintained through a “process logic control” feedback loop with inputs from one thermocouple at the top of the pressure vessel and one thermocouple in the vessel bottom ($\pm 2^{\circ}\text{C}$). Equipment maximum temperature and pressure limitations are 90°C and 3000 psi, respectively. Figure 8-1(a) shows a view of the vessel, at the far right-hand side of the cabinets, along with the associated gas handling equipment and computers. Figure 8-1(b) is a view inside the vessel. An 8” silicon wafer can be seen mounted in the vessel, along with a high-pressure color CCD camera.

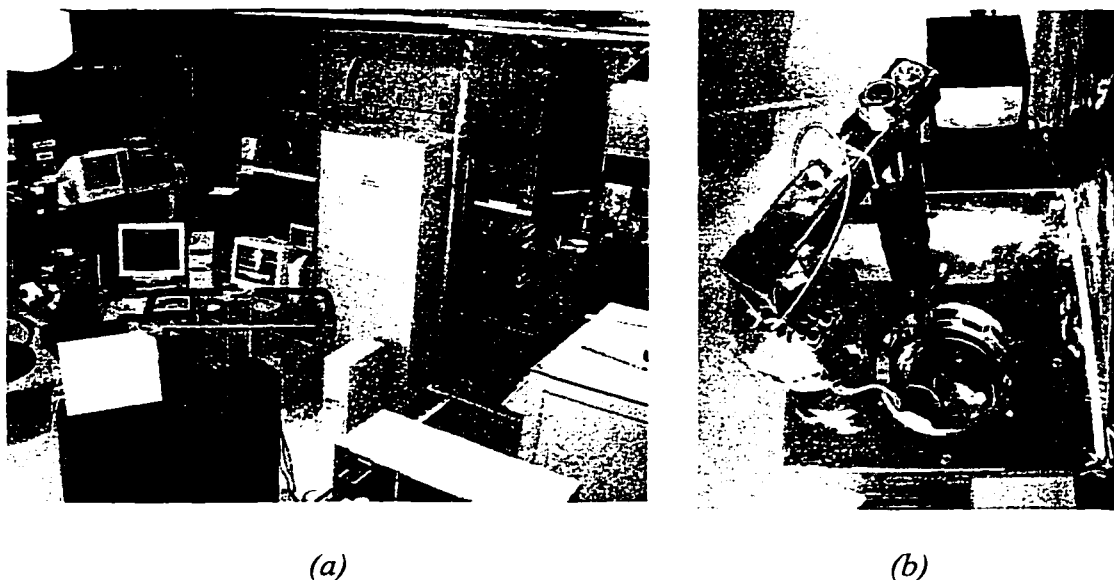


Figure 8-1. (a) View of the Los Alamos National Laboratory Supercritical Fluids Facility, showing the automated, 10-liter pressure system. (b) View inside the 10-liter high-pressure reaction vessel.

Experiments on many photoresist polymers have been conducted at the Supercritical Fluids Facility, using various combinations of T, P, and cosolvents. However, only the PMMA photoresist was sufficiently characterized in terms of composition to allow a comparison between experimental results and the predictions of the HSP model. The remaining photoresist polymers were either of unknown initial composition, or had been subjected to treatments such as ion implantation or plasma etching, again resulting in an unknown overall composition.

8.1.2 Polymer Removal from Photoconductor Drums

Experiments on the removal of polymer coatings from the aluminum photoconductor drums were conducted in a purpose-built, 105 ml bench-top high-pressure vessel. A schematic illustration of this equipment is shown in Figure 8-2(a) and (b).

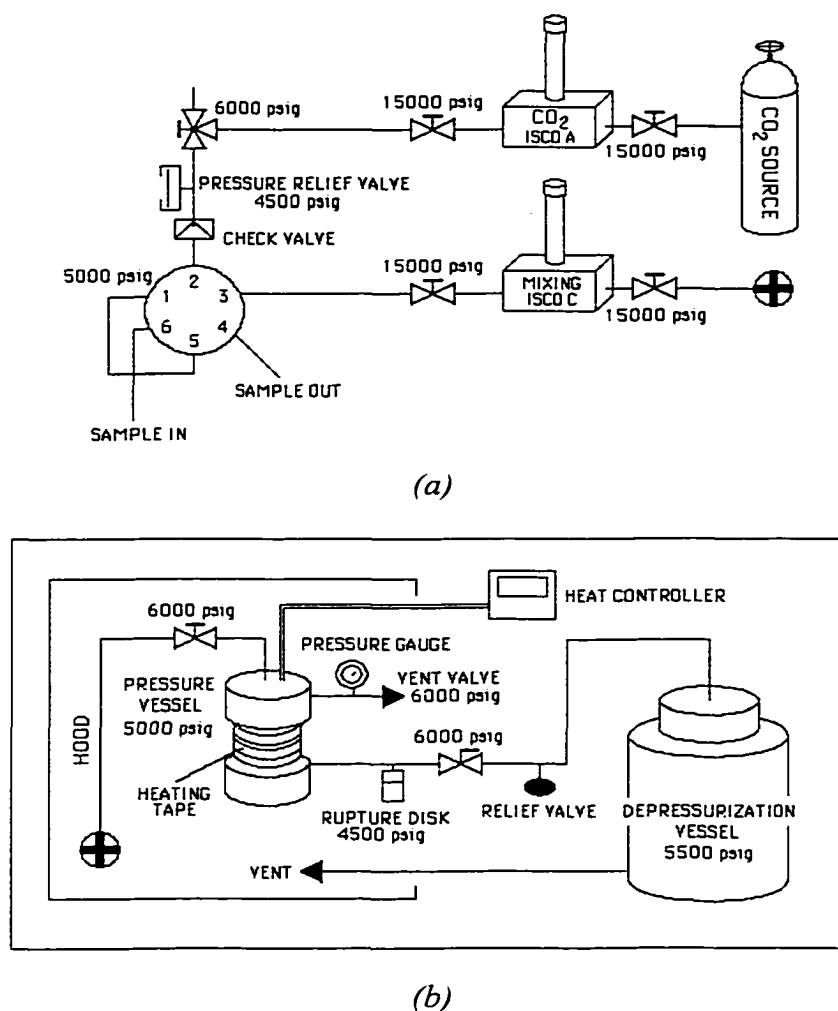


Figure 8-2. Schematic illustration of the 105 ml bench top supercritical fluid system used for the photoconductor drum experiments. (a) CO₂ source, pumps, and cosolvent injection/mixing system. (b) High pressure cleaning vessel, temperature controls, and depressurization vessel.

Unlike the 10-liter vessel system, the bench top system was suitable only for static (non-continuous flow) experiments. However, the bench top system does allow for easy changing of cosolvents, minimum cosolvent usage (based on volume fraction), and rapid depressurization. The rate of depressurization was recognized to be an important variable early in the experimental testing. The swelling of a polymer with CO₂ results in a decrease in polymer/polymer molecular interactions, as described in Chapter 6, and a reduced polymer solubility parameter. Additional disruption of polymer/polymer

intramolecular interactions can also occur through specific interactions with the solubilized CO₂ and/or cosolvent. Upon depressurization, the solubilized CO₂ begins to expand as the vessel pressure decreases. This expansion of the gas, and the reduced hydrostatic pressure exerted on the polymer, often results in a temporarily-enhanced polymer swelling effect. Before the polymer/polymer interactions can be reestablished, stress cracks, bubbles or complete debonding of the polymer film can occur as the CO₂ rapidly desorbs. Rapid depressurization rates were not possible using the 10-liter vessel, although upgrades to the system are currently underway.

The pressure in the 105 ml vessel was controlled with two ISCO high-pressure syringe pumps, each with its own controller. The first pump, 'ISCO A' in Figure 8-2(a), pressurized and supplied pure CO₂ to pump 'ISCO C', which was used as a vessel for the mixing the CO₂ and cosolvent. Intermediate to pump 'ISCO C' is an injection valve, located to allow the CO₂ to deliver a measured amount of cosolvent to the mixing vessel and pump. The number of cosolvent injections was determined based on the desired overall mixture composition, with the injection loop supplying a maximum of 2.5 ml of cosolvent per injection. The cosolvent concentration typically varied from 2 to 3.8 vol.%. The volume of each syringe pump is 266 ml.

The vessel was heated to the desired processing temperature with an external heat tape. The vessel temperature was monitored with an external thermocouple, and adjusted to maintain the desired temperature during the experiment. Precise temperature control was not possible with this setup, but observed fluctuations were less than $\pm 7^{\circ}\text{C}$. Equipment maximum temperature and pressure limitations are 100°C and 3000 psi, respectively

8.2 Results

8.2.1 Photoresist Removal from Silicon Wafers

Silicon wafers, 3" in diameter, coated with approximately 12-14 μm of PMMA photoresist were supplied by Agilent Technologies. The resist was identified by Agilent as a positive acting photoresist (as described in Section 1.1), which had been baked at 160°C. Two removal experiments were conducted, with the treatment conditions shown in Table 8-1.

Table 8-1. *Experimental conditions of the PMMA photoresist removal experiments.*

Resist	T (°C)	P (psi)	cosolvent	vol. %	Time (min)
PMMA	50	3000	butylene carbonate	1.9	10
PMMA	60	3000	propylene carbonate	0.6	20

Butylene carbonate and propylene carbonate, Figures 8-3 and 8-4, are organic cyclic esters supplied by Hunstman Corporation. Both cosolvents contain carbonyl functional groups, which are expected to act as Lewis bases in CO_2 .

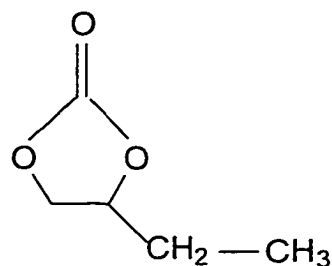


Figure 8-3. *Butylene carbonate, HSP values⁵⁵⁰: $\delta_d = 17.0 \text{ MPa}^{1/2}$, $\delta_p = 6.1 \text{ MPa}^{1/2}$, and $\delta_h = 9.8 \text{ MPa}^{1/2}$.*

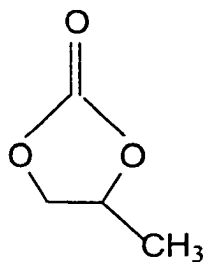


Figure 8-4. Propylene carbonate, HSP values⁵⁵¹: $\delta_d = 20.0 \text{ MPa}^{1/2}$, $\delta_p = 18.0 \text{ MPa}^{1/2}$, and $\delta_h = 4.1 \text{ MPa}^{1/2}$.

An as-received, photoresist-coated silicon wafer is shown in Figure 8-5(a), while Figure 8-5(b) shows a similar wafer after the successful removal of the polymer coating using CO₂/propylene carbonate at the conditions noted in Table 8-1.

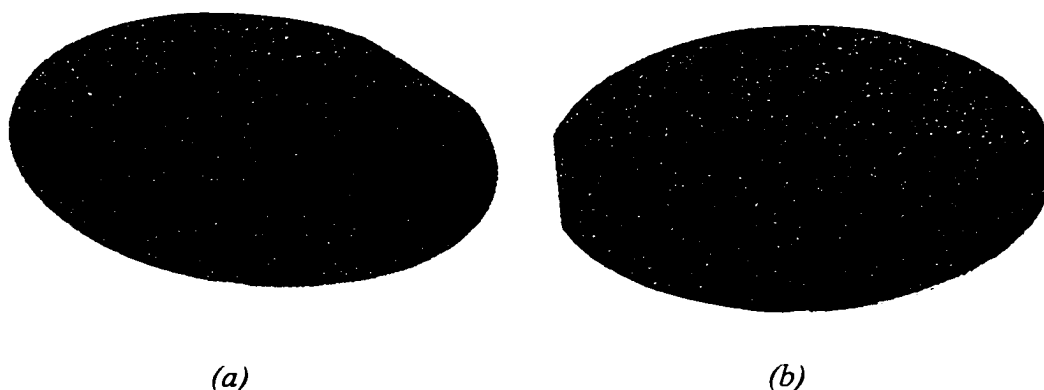


Figure 8-5. (a) Silicon wafer coated with PMMA photoresist, (b) Silicon wafer stripped of photoresist coating.

Figure 8-6 (a) and (b), shows higher magnification optical images of the edges of an untreated, Figure 1-6(a), and treated, Figure 1-6(b), silicon wafer. The left-hand image clearly shows the boundary of the polymer coating.

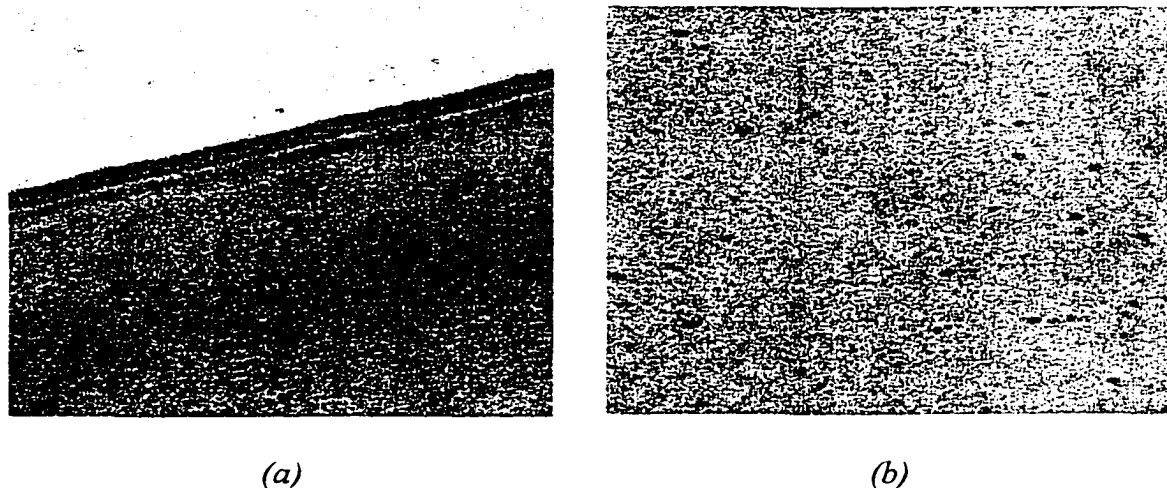


Figure 8-6. (a) As received silicon wafer coated with PMMA photoresist. (b) Silicon wafer stripped of photoresist coating after treatment with CO₂/propylene carbonate (0.6 % v/v) at $T = 60^{\circ}\text{C}$ and $P = 3000\text{ psi}$.

Table 8-2 gives the HSP values of the CO₂/cosolvent mixture, calculated using eqn. (6-22), as well as HSP values of the PMMA, and the value of Ra , calculated using eqn. (5-20) in Section 5.2.1. Recall that Ra is the distance (expressed as a radius) from the HSP value of PMMA at T and P , to the HSP value of the CO₂/cosolvent mixture at T and P . For clarity, eqn. (5-20) is given again as eqn. 8-1, with the calculation of Ra for the first treatment condition shown in Table 8-1.

$$\begin{aligned}
 (Ra)^2 &= 4(\delta_{d2} - \delta_{d1})^2 + (\delta_{p2} - \delta_{p1})^2 + (\delta_{h2} - \delta_{h1})^2 \\
 (Ra)^2 &= 4(10.7 - 10.3)^2 + (5.8 - 4.4)^2 + (4.0 - 4.8)^2 \\
 (Ra)^2 &= 3.24 \\
 Ra &= 1.8
 \end{aligned}
 \tag{8-1}$$

Table 8-2. HSP values of the solvent mixture and PMMA and Ra at the treatment conditions.

T (°C)	P (psi)	Solvent Mixture HSP's (MPa ^{1/2})			PMMA HSP's (MPa ^{1/2})			Ra (MPa ^{1/2})
		δ_d	δ_p	δ_h	δ_d	δ_p	δ_h	
50	3000	10.3	4.4	4.8	10.7	5.8	4.0	1.8
60	3000	9.3	4.3	4.5	11.2	5.9	4.0	4.3

For the two treatment conditions shown in Table 8-1, the PMMA is predicted to be significantly plasticized, with T_g estimated to be -125°C , using eqn. (6-12). In addition, the distance between the HSP values of the solvent mixture and of the PMMA, identified by Ra (see Table 8-2), is below the reported PMMA interaction radius of $8.6 \text{ MPa}^{1/2}$.⁵⁵² The PMMA interaction radius noted in the literature, $R_o^{liq} = 8.6 \text{ MPa}^{1/2}$, was determined on the basis of the dissolution behavior of PMMA in a range of liquid solvents. An interaction radius based on the swelling behavior of PMMA in a SCF is unknown. However, because of the enhanced diffusion of SCFs, an interaction radius larger than that noted for liquid solvents is anticipated. Therefore, the reported liquid interaction radius, R_o^{liq} , will be assumed to be a minimum radius for SCF's, R_o^{SCF} .

Because the T_g of PMMA is significantly depressed at both of the treatment conditions noted in Table 8-1, favorable swelling conditions exist (i.e. CO_2 sorption and polymer swelling increase with increasing pressure). In addition, for both treatment conditions the Ra value (see Table 8-2) is less than the R_o^{liq} value noted for dissolution of PMMA in liquid solvents. Therefore, based on the fact that $T_{CO_2} > T_g^{CO_2}$ and $Ra < R_o^{liq}$, the model framework predicts favorable conditions for the promotion of coating removal by polymer swelling for both of the experimental treatments in Table 8-1. These predictions are in agreement with the experimental results, where successful removal of the PMMA photoresist from the silicon wafers was achieved.

Figure 8-7 shows, in schematic form, the model predictions of the HSP values for PMMA and CO_2 /butylene carbonate mixture, and CO_2 /propylene carbonate mixture.

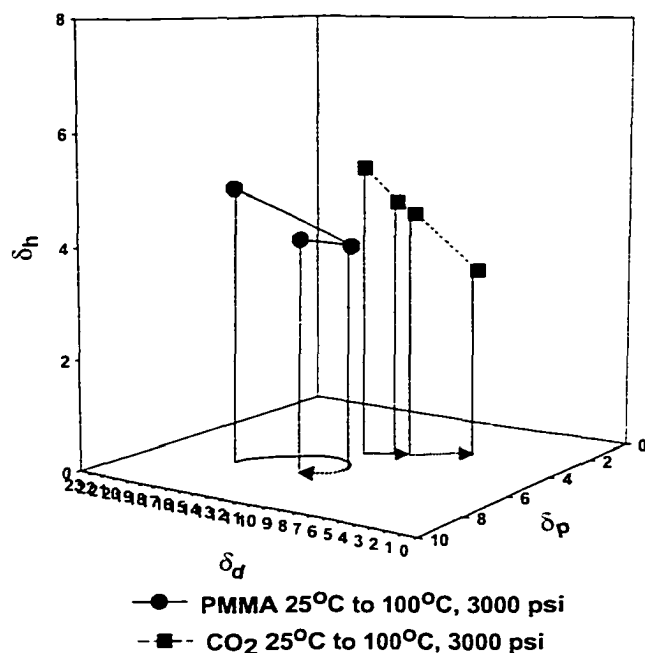


Figure 8-7. Predicted PMMA and CO₂ mixture HSP values as the temperature varies from 25 to 100°C and at 3000 psi.

From Figure 8-7, the HSP values of PMMA can be seen to approach those of the solvent as the temperature is increased, up to a temperature of approximately 70°C. Above 70°C, the PMMA HSP values begin to increase with increasing temperature. At the two treatment conditions of $T = 50^\circ\text{C}$ and 60°C and $P = 3000$ psi, the radius of interaction is minimized, i.e., $Ra < R_o^{liq} < R_o^{SCF}$, and the predicted conditions are optimal for experimental testing.

It should also be noted that the distance between the HSP values of pure CO₂ and of the PMMA, at the given experimental conditions, is $Ra = 1.9$ and $4.5 \text{ MPa}^{1/2}$, respectively. The estimated depression in T_g , and the match of HSP values, as quantified by Ra , indicates that pure CO₂ should also be a “good” solvent for PMMA.

8.2.2 Polymer Removal from Photoconductor Drums

Aluminum photoconductor drums were provided by Lexmark Corporation with three coating schemes, as seen in Figure 1-2; (1) PC only, (2) poly(vinyl butyral) only, and (3) poly(vinyl butyral) and PC,. The drums, originally 12 inches long, were cut into 1 inch lengths so that one of each of the three types of coated drums could be run simultaneously in the 105 ml pressure vessel. The vessel, with the drums placed inside, was heated to the desired processing temperature with an external heat tape. The vessel temperature was monitored with an external thermocouple, and adjusted to maintain the desired temperature during the experiment. This external thermocouple temperature was assumed to equal the drum temperature throughout the experiment. CO₂ or CO₂/cosolvent mixture was injected at the desired experimental pressure, but for all experiments the temperature of the solvent was initially equal to room temperature (approximately 25°C). At the end of each experiment the CO₂ or CO₂/cosolvent mixture temperature was assumed to equal the temperature noted by the external thermocouple.

All experiments using the bench top system were conducted for 20 minutes at static (non-flowing) conditions, followed by two pressure pulses; 3000 to approximately 1000 psi, or 1500 to 1000 psi; followed by a rapid depressurization to atmospheric pressure. The experimental conditions are given in Table 8-3. Also given in Table 8-3 are the HSP values for pure CO₂ or CO₂/cosolvent mixture (initial and final conditions), PC, and PVB at the experimental conditions. Unlike the wafer experiments discussed earlier, where the solvent and polymer temperatures are assumed to be equal throughout the experiment, the CO₂ and/or CO₂/cosolvent mixture temperature, and consequently the HSP values of the solvent, vary from values at room temperature (approximately

25°C) to the final experimental temperature (see Table 8-3). Therefore, there is an initial radius of interaction, Ra_i , and a final radius of interaction, Ra_f , reflecting the range of conditions between the solvent and polymer HSP's, where each Ra is the distance from the HSP's of the polymer at T and P to the HSP's of pure CO₂ or CO₂/cosolvent mixture at its initial and final T and P.

Presentations of the model results include plots of the HSP values of the solvent (pure CO₂ or CO₂/cosolvent mixture) at the initial and final experimental T and P, as well as the polymer HSP values at the experimental T and P. These HSP values, representing a point in three-dimensional solubility parameter space, can be represented in a two-dimensional diagram using fractional solubility parameters,

$$f_D = \frac{\delta_D}{\delta_D + \delta_P + \delta_H} \quad (8-2)$$

$$f_P = \frac{\delta_P}{\delta_D + \delta_P + \delta_H} \quad (8-3)$$

$$f_H = \frac{\delta_H}{\delta_D + \delta_P + \delta_H} \quad (8-4)$$

Plots of fractional solubility parameters, such as Figure 8-9, are known as a Teas plot.⁵⁵³ The fractional solubility parameters, as given in a Teas plot, along with the initial and final total solubility parameters, completely define the extent of HSP matching between the solvent and polymer as the solvent temperature varies from room temperature to the final experimental temperature. In terms of fractional parameters on the Teas plots, consideration must be given to the proximity of the points as well as the total solubility parameter value. As an aid in making this comparison, the initial and

final Ra values are given, as well as the R_o^{liq} for the polymer, which, again, is the radius of (dissolution) interaction of the respective polymer in liquid solvents. Optimum conditions are predicted for $T_{CO_2} > T_g^{CO_2}$ and $Ra < R_o^{SCF}$ (where R_o^{SCF} is assumed to be $> R_o^{liq}$). Photographs of the treated drums are also included for each experiment.

Table 8-3. Experiment conditions of temperature, pressure and cosolvent concentrations for the photoconductor drum experiments.

T (°C)	P (psi)	cosolvent	vol. %	Mix HSP (MPa ^{1/2}) (initial)			Mix HSP (MPa ^{1/2}) (final)			PC HSP (MPa ^{1/2}) Ra _i = initial radius Ra _f = initial radius					PVB HSP (MPa ^{1/2}) Ra _i = initial radius Ra _f = initial radius				
				δ _d	δ _p	δ _h	δ _d	δ _p	δ _h	δ _d	δ _p	δ _h	Ra _i	Ra _f	δ _d	δ _p	δ _h	Ra _i	Ra _f
45	1500	none		10.7	4.5	5.0	6.7	3.7	4.0	16	5.6	6.4	10.8	18.9	16.6	7.0	11.4	13.7	21.4
45	3000	none		12.2	4.7	5.3	10.6	4.5	4.8	16.3	5.7	6.8	8.4	11.6	16.7	7.0	11.5	11.2	14.1
75	1500	none		10.7	4.5	5.0	2.4	2.5	2.6	15.6	5.6	6.1	9.9	26.8	16.2	6.9	11.3	13.7	29.3
75	3000	none		12.2	4.7	5.3	7.8	3.9	4.1	16.0	5.6	6.7	7.8	16.7	16.3	6.9	11.4	11.2	18.7
100	1500	none		10.7	4.5	5.0	1.8	2.2	2.2	14.6	5.4	5.7	7.9	26.0	15.9	6.8	11.3	13.7	30.0
100	3000	none		12.2	4.7	5.3	5.7	3.5	3.5	15.2	5.5	6.6	6.2	19.4	16.0	6.9	11.3	11.2	22.3
75	3000	hexane	10.0	12.4	4.2	4.8	8.4	3.5	3.7	16.0	5.6	6.7	7.7	15.6	16.3	6.9	11.4	10.6	17.9
40	1500	ethanol	3.8	10.9	4.7	5.5	8.5	4.2	5.0	16.0	5.6	6.5	10.3	15.2	16.7	7.0	11.5	13.3	17.9
40	3000	ethanol	3.8	12.3	4.9	5.8	11.2	4.7	5.4	16.4	5.7	6.8	8.2	10.6	16.8	7.0	11.5	10.8	13.0
85	1500	ethanol	3.8	10.8	4.7	5.5	2.7	2.6	3.0	15.3	5.5	6.0	9.0	25.6	16.0	6.9	11.3	12.1	28.3
75	3000	ethanol	3.8	12.3	4.8	5.8	8.0	4.0	4.5	16.0	5.6	6.8	7.5	16.3	16.3	6.9	11.4	10.0	18.2
100	1500	ethanol	2.8	10.9	4.7	5.5	2.1	2.4	2.6	14.6	5.4	5.8	7.7	25.3	15.9	6.8	11.3	12.1	29.2
100	3000	ethanol	2.8	12.3	4.9	5.8	5.9	3.6	3.9	15.2	5.5	6.6	6.0	18.9	16.0	6.9	11.3	9.7	19.6
40	1500	acetone	3.8	10.9	4.7	5.1	8.5	4.2	4.5	16.0	5.6	6.5	10.4	15.3	16.7	7.0	11.5	13.5	18.1
40	3000	acetone	3.8	12.3	4.9	5.4	11.2	4.7	5.0	16.4	5.7	6.8	8.3	10.7	16.8	7.0	11.5	11.1	13.2
85	1500	acetone	3.8	10.9	4.7	5.1	8.0	4.1	4.2	15.3	5.5	6.0	9.1	25.7	16.0	6.9	11.3	12.3	28.5
75	3000	acetone	3.8	12.3	4.9	5.4	2.6	2.7	2.5	16.0	5.6	6.7	7.6	16.2	16.3	6.9	11.4	10.3	18.3
40	3000	cyclohexanone	1.5	12.3	4.7	5.3	11.1	4.5	4.9	16.4	5.7	6.8	8.4	10.8	16.8	7.0	11.5	11.2	13.4
65	1500	cyclohexanone	2.6	10.8	4.5	5.0	3.3	2.8	2.8	15.7	5.6	6.2	9.9	25.2	16.3	6.9	11.4	12.9	27.7.
65	3000	cyclohexanone	2.6	12.3	4.7	5.3	8.9	4.1	4.4	16.1	5.6	6.7	7.8	14.7	16.4	6.9	11.4	10.5	16.8
75	3000	cyclohexanone	2.6	12.3	4.7	5.3	8.5	4.1	4.2	16.0	5.6	6.7	7.5	15.2	16.3	6.9	11.4	10.3	17.4
100	1500	cyclohexanone	2.6	10.8	4.5	5.0	2.2	2.3	2.3	14.6	5.4	5.7	7.6	25.3	15.9	6.8	11.3	12.1	29.3
100	3000	cyclohexanone	2.6	12.3	4.7	5.3	4.5	5.9	3.6	15.2	5.5	6.6	6.0	18.8	16.0	6.9	11.3	9.8	21.8
40	3000	THF	3.0	12.3	4.7	5.4	11.2	4.5	5.0	16.4	5.7	6.8	8.3	10.7	16.8	7.0	11.5	11.1	13.2
75	1500	THF	2.8	10.8	4.5	5.1	3.0	2.6	2.8	15.6	5.6	6.1	9.6	25.7	16.2	6.9	11.4	12.7	28.2
100	1500	THF	2.0	10.8	4.5	5.1	2.1	2.3	2.3	14.6	5.4	5.7	7.7	25.5	15.9	6.8	11.3	12.2	29.5
100	3000	THF	2.0	12.3	4.7	5.4	5.9	3.5	3.6	15.2	5.5	6.6	6.1	19.0	16.0	6.9	11.3	9.8	21.9

Prior to discussing the results of the coatings removal experiments on the photoconductor drums a few comments regarding the poly(vinyl butyral) coating are necessary. While the surface of the silicon wafers were nearly atomically smooth, the surface of the photoconductor drums are anodized to provide a desired surface roughness and protective oxide coating. This surface roughness, combined with the thinness of the PVB coating ($\sim 1 \mu\text{m}$), produces a mechanical bond between the PVB and the drum surface, in addition to any chemical bond. The model framework developed here, however, does not account for substrate/polymer interactions nor mechanical bonding. The extreme thinness of the PVB coating results in a very limited ability of the PVB to swell, making this specific combination of substrate and polymer a particularly difficult application for the current model, which considers only intermolecular forces of attraction between the polymer and solvent). Visual results of the treatments on the PVB film are included in the following figures, however no direct comparisons with the HSP model are made.

Figure 8-8 shows examples of the three types of polymer-coated drums prior to treatment by supercritical fluid solvents.

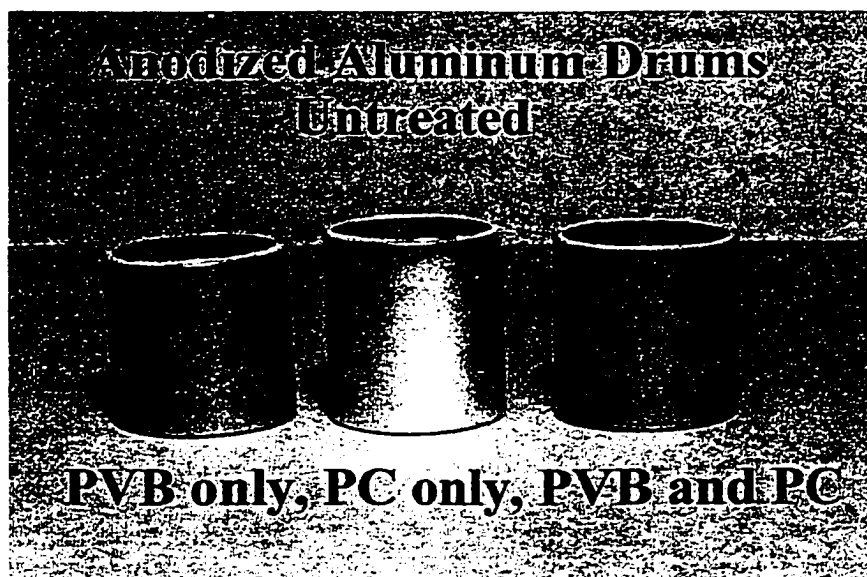


Figure 8-8. Untreated aluminum photoconductor drums with polymer coatings; (left) $\sim 1\ \mu\text{m}$ -thick poly(vinyl butyral) coating only, (center) $\sim 25\ \mu\text{m}$ -thick polycarbonate coating only, (right) $\sim 25\ \mu\text{m}$ -thick polycarbonate coating over $\sim 1\ \mu\text{m}$ -thick poly(vinyl butyral) coating.

8.2.2.1 Pure CO_2

Photoconductor drums coated with PC only, PVB only, and PC/PVB were treated with pure CO_2 at $T = 45^\circ\text{C}$, 75°C , and 100°C , and $P = 1500\ \text{psi}$ and $3000\ \text{psi}$. The resulting HSP values for CO_2 (initial and final) and PC at these conditions, are plotted in Figures 8-9, 8-11, and 8-13. Also indicated on these Teas plots is the initial Ra_i values and the final Ra_f values, where Ra is the distance from the HSP value of PC at T and P (open symbols), to the HSP values of CO_2 at its initial and final T and P (filled symbols), calculated using eqn. (5-20) in Section 5.2.1. The R_o^{liq} values indicated for PC^{554} represent the interaction radius for the polymer, based on its dissolution behavior in a range of liquid solvents. A corresponding interaction radius for PC in a SCF system is

not known, R_o^{SCF} , but its value is expected to be greater than, due to the increased diffusion capabilities of a SCF solvent versus a liquid solvent.

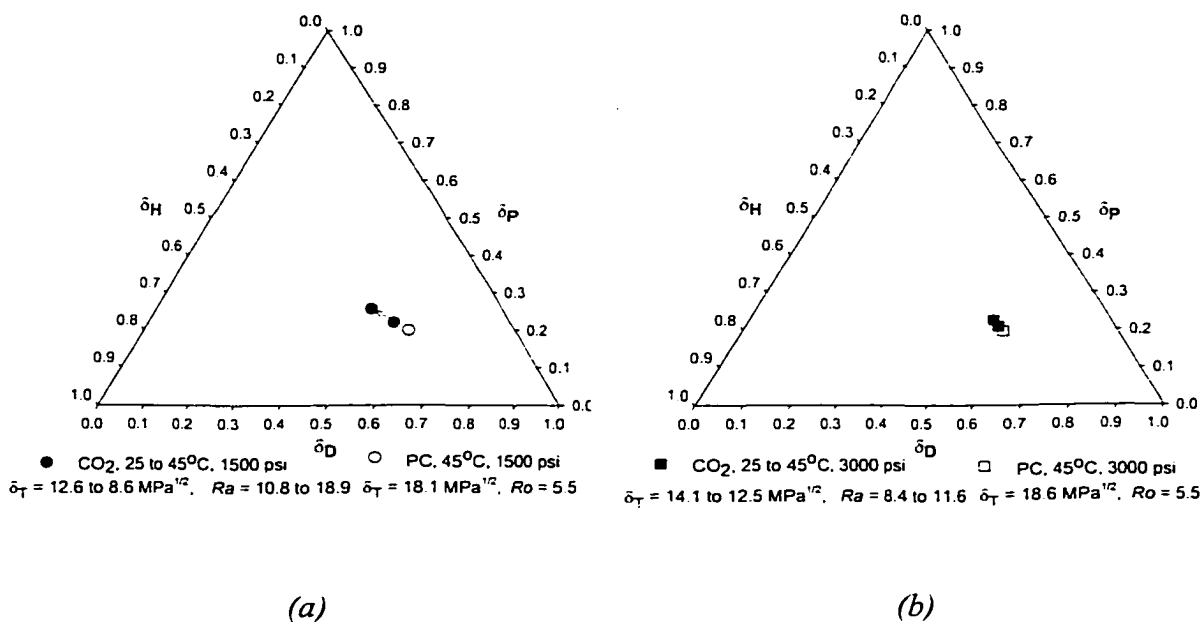


Figure 8-9. (a) HSP values of CO_2 and PC, at $T = 25$ to 45°C and $P = 1500$ psi. (b) HSP values of CO_2 and PC, at $T = 25$ to 45°C and $P = 3000$ psi.

Visual results of the pure CO_2 treatments, at the temperature and pressures indicated in Figure 8-9(a) and 8-9(b), are shown Figure 8-10(a) and 8-10(b).

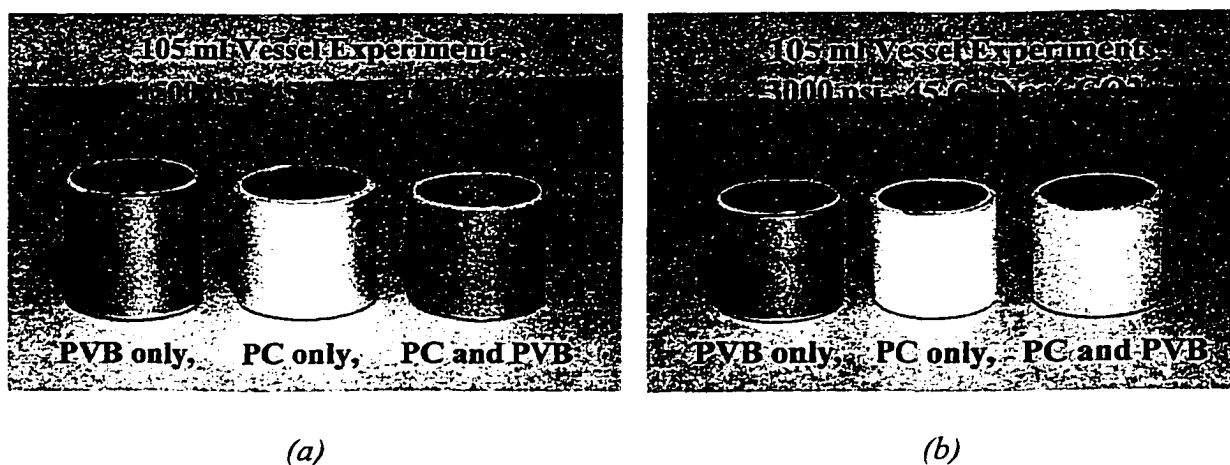
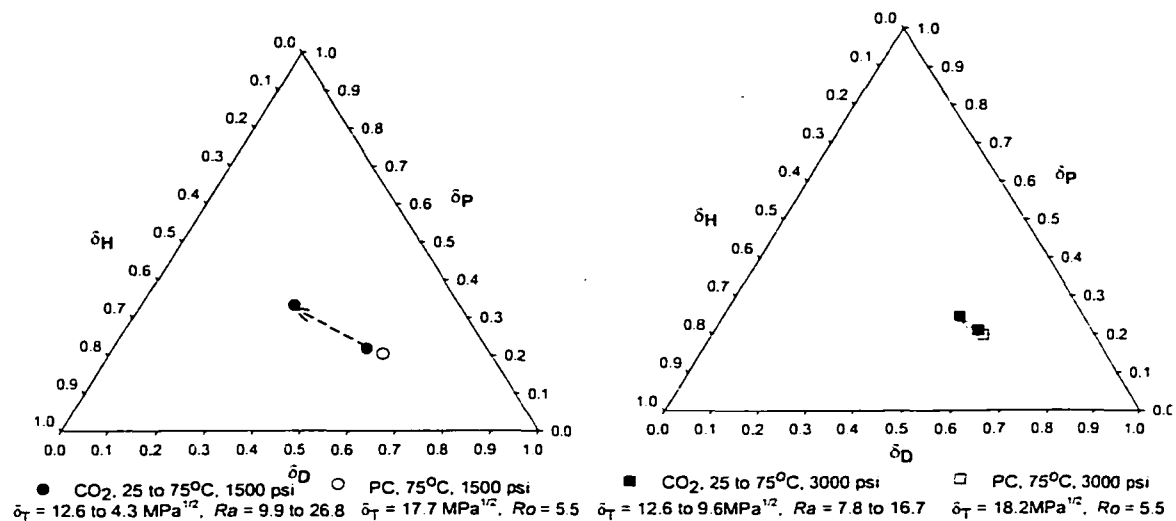


Figure 8-10. Appearance of polymer coated photoconductor drums treated with pure CO_2 at (a) $T = 25$ to 45°C , $P = 1500$ psi, (b) $T = 25$ to 45°C , $P = 3000$ psi.

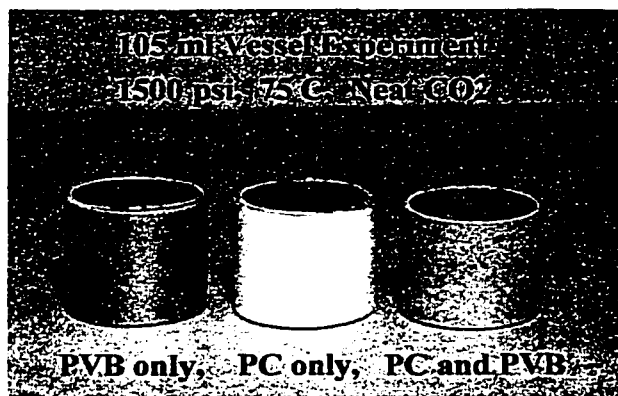


(a)

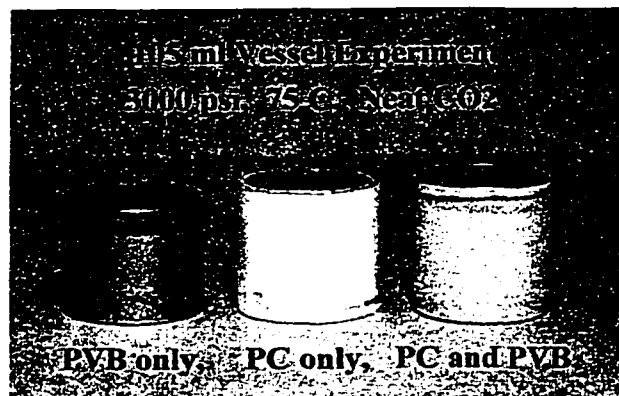
(b)

Figure 8-11. (a) HSP values of CO₂ and PC at $T = 25$ to 75°C and $P = 1500 \text{ psi}$. (b) HSP values of CO₂ and PC at $T = 25$ to 75°C and $P = 3000 \text{ psi}$.

Visual results of the pure CO₂ treatment, at the temperature and pressures indicated in Figure 8-11(a) and 8-11(b), are shown Figure 8-12(a) and 8-12(b).



(a)



(b)

Figure 8-12. Appearance of polymer coated photoconductor drums treated with pure CO₂ at (a) $T = 25$ to 75°C and $P = 1500 \text{ psi}$, (b) $T = 25$ to 75°C and $P = 3000 \text{ psi}$.

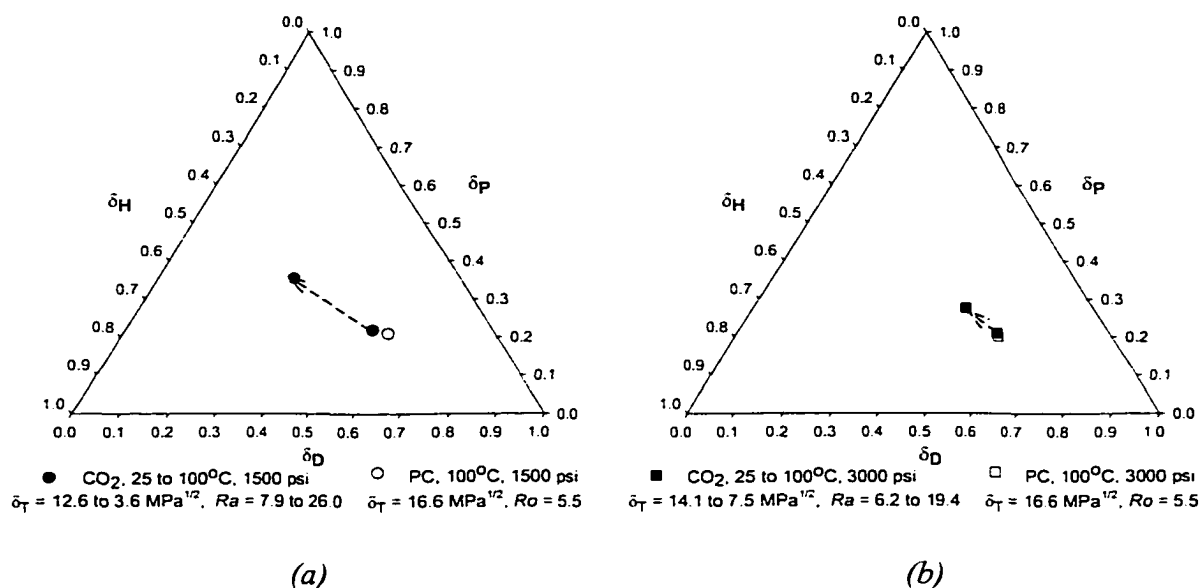


Figure 8-13. HSP values of CO₂ and PC at T = 25 to 100 °C and P = 1500 psi. (b) HSP values of CO₂ and PC at T = 25 to 100 °C and P = 3000 psi.

Visual results of the pure CO₂ treatment, at the temperature and pressures indicated in Figure 8-13(a) and 8-13(b), are given in Figure 8-14(a) and 8-14(b).

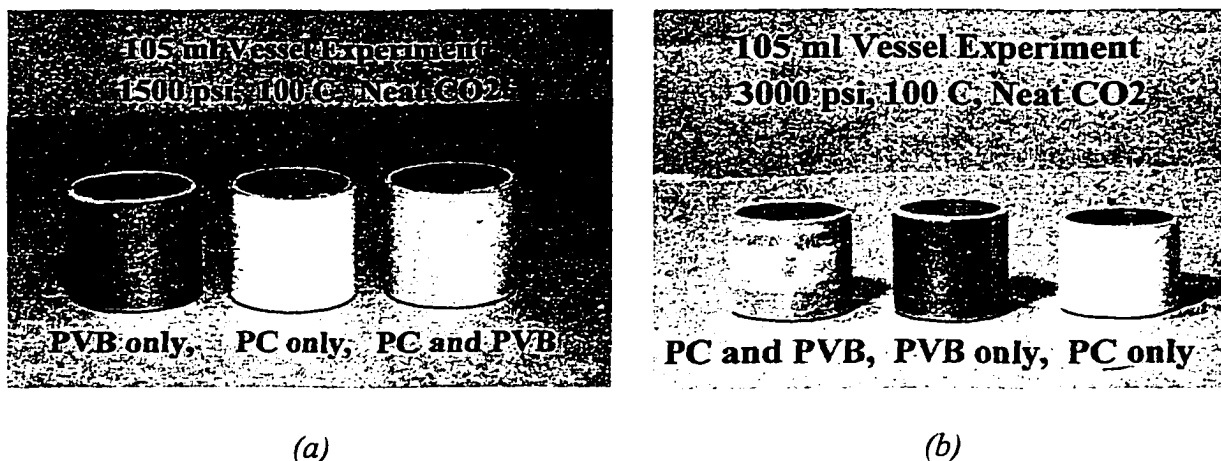


Figure 8-14. Appearance of polymer coated photoconductor drums treated with pure CO₂ at (a) T = 25 to 100 °C and P = 1500 psi. (b) T = 25 to 100 °C and P = 3000 psi.

8.2.2.1.1 Observations of Polymer Coating Removal Experiments using Pure CO₂

The results of the experiments described in Figures 8-10, 8-12, and 8-14 are ranked in Table 8-4, based on a visual assessment of the effect of the treatment on the PC coating. Since the ultimate objective of these experiments is the removal of the polymer coating through polymer swelling, a treatment is judged to have a favorable effect if the treatment results, in order of decreasing significance; complete coating removal (debonding), surface cracking, flaking, bubbling, or discoloration of the PC coating. The polymer glass transition temperature at the treatment conditions, T_g , is determined using eqn. (6-16). Column 4 in the table shows the difference between the treatment temperature, T_{CO_2} , and T_g of the polymer at the treatment temperature. In columns 5 and 6 give the initial and final Ra values, Ra_i and Ra_f , representing the distance (expressed as a radius) between the initial HSP values of CO₂, to the polycarbonate HSP values at $T = 25$ °C and P , Ra_i , and between the final HSP values of CO₂ to the polycarbonate HSP values, Ra_f , at T and P .

Table 8-4. Results of polymer removal experiments using pure CO₂.

T_{CO_2} (°C)	P_{CO_2} (psi)	Polymer T_g at (T_{CO_2} , P_{CO_2})	ΔT ($T_{CO_2} - T_g$)	Ra_i ($MPa^{1/2}$)	Ra_f ($MPa^{1/2}$)	R_o^{liq} ($MPa^{1/2}$)	Exp. result
100	3000	54.3	45.7	6.2	19.4	5.5	debonded
100	1500	85.6	14.4	7.9	26.0	5.5	bubbled
75	3000	88.0	-13.0	7.8	16.7	5.5	discolored
75	1500	103.0	-28.0	9.9	26.8	5.5	discolored
45	3000	88.0	-43.0	8.4	11.6	5.5	discolored
45	1500	103	-58.0	10.8	18.9	5.5	slight discoloring

Two important observations of the experimental summary presented in Table 8-4 are the increasingly favorable effects on the coating with increasing ΔT ($T_{\text{CO}_2} - T_g$) and the increasingly favorable effects on the coating as Ra_i decreases. As discussed in Chapter 6, absorption of CO_2 swells the polymer only when the polymer is in its rubber state, i.e., $T_{\text{CO}_2} > T_g$. As $(T_{\text{CO}_2} - T_g)$ increases, it is expected that the amount of CO_2 absorption during swelling will increase, as would the amount of mechanical disruption of the polymer during depressurization. Also, as discussed earlier, experiments conducted in the bench top set-up did not include preheating of the solvent. Therefore the HSP values of the solvent vary from the initial values shown in Table 8-3 to the final values, also shown in Table 8-3. The exact path of these values is dependent on the heating rate of the solvent, which could not be measured in this work. However, the initial and final values are available, allowing the calculation of both an initial and final Ra value. From a review of Table 8-3, increasingly favorable effects are seen as the initial Ra_i values decrease and ΔT increases. These results are entirely consistent with model predictions, where favorable effects are predicted as the polymer is plastized and Ra (whether initial or final) approaches Ro .

On the basis of a polycarbonate interaction radius of $5.5 \text{ MPa}^{1/2}$ (again, based on polycarbonate dissolution in organic liquid solvents) and $T = 45^\circ\text{C}$, the model predicts that a pressure of 9200 psi is required to achieve an Ra_f of $5.2 \text{ MPa}^{1/2}$, a value intermediate between the HSP values of pure CO_2 and the HSP values of polycarbonate.

8.2.2.2 CO₂/Hexane

Hexane, Figure 8-15, is a nonpolar solvent, and is not expected to exhibit any specific Lewis acid/base interactions with CO₂, PC, or PVB. This compound is not identified as a (pure) solvent for either PC or PVB, which are both reported to be insoluble in aliphatic hydrocarbons.^{555,556}



Figure 8-15. Hexane, HSP values⁵⁵⁷ $\delta_d = 14.9 \text{ MPa}^{1/2}$, $\delta_p = 0.0 \text{ MPa}^{1/2}$, and $\delta_h = 0.0 \text{ MPa}^{1/2}$.

The HSP values given in the caption of Figure 8-15 are ambient condition values and are taken from the literature. To adjust these parameters for temperature and pressure effects, we use the HSP equations derived in Section 5.3 and summarized in Table 5-8. These equations are given again as eqns. 8-5 to 8-11.

$$\delta^2 = \left[\delta_d + \left(\frac{\partial \delta_d}{\partial T} \right)_p \Delta T + \left(\frac{\partial \delta_d}{\partial P} \right)_T \Delta P \right]^2 + \left[\delta_p + \left(\frac{\partial \delta_p}{\partial T} \right)_p \Delta T + \left(\frac{\partial \delta_p}{\partial P} \right)_T \Delta P \right]^2 + \left[\delta_h + \left(\frac{\partial \delta_h}{\partial T} \right)_p \Delta T + \left(\frac{\partial \delta_h}{\partial P} \right)_T \Delta P \right]^2 \quad (8-5)$$

where

$$\left(\frac{\partial \delta_d}{\partial T} \right)_p = -1.25 \delta_d \alpha, \text{ and } \left(\frac{\partial \delta_d}{\partial P} \right)_T = 1.25 \delta_d \beta \quad (8-6) \text{ and } (8-7)$$

$$\left(\frac{\partial \delta_p}{\partial T} \right)_p = -\delta_p \left(\frac{\alpha}{2} \right), \text{ and } \left(\frac{\partial \delta_p}{\partial P} \right)_T = \delta_p \left(\frac{\beta}{2} \right) \quad (8-8) \text{ and } (8-9)$$

$$\left(\frac{\partial \delta_h}{\partial T}\right)_P = -\delta_h \left(1.32 \times 10^{-3} + \frac{\alpha}{2}\right), \text{ and } \left(\frac{\partial \delta_h}{\partial P}\right)_T = \delta_h \left(\frac{1.32 \times 10^{-3} \beta}{\alpha} + \frac{\beta}{2}\right) \quad (8-10) \text{ and } (8-11)$$

The data necessary for these adjustments are the thermal expansion coefficient, $\alpha(T)$, and isothermal compressibility, β , of the pure cosolvent compound. The thermal expansion coefficient is first used to adjust for temperature with eqn. (8-12),⁵⁵⁸

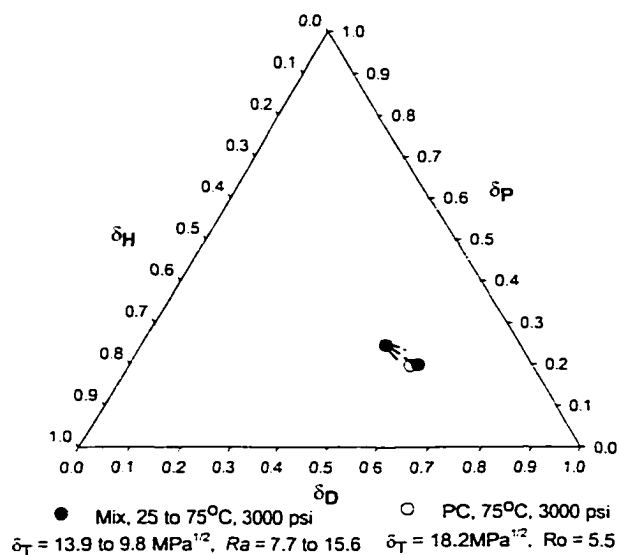
$$\alpha(T) = a \left(1 - \frac{T}{T_c}\right)^m \quad (8-12)$$

where $a = 0.000728$, $m = -0.7219$, and $T_c = 507.43 \text{ K}$.⁵⁵⁹ Next, the pressure adjustment is made using the compressibility. Isothermal compressibility values for all the cosolvent compounds have been made at high pressures,⁵⁶⁰ however, the variation of β with temperature, in the pressure range of interest, is not known, and a constant value is assumed in each case. A compressibility value of $0.000117 \text{ (bar}^{-1}\text{)}$ ⁵⁶¹ was used for hexane. The adjusted HSP values for hexane are shown in Table 8-5.

Table 8-5. HSP values for hexane, adjusted for temperature and pressure.

T (K)	$\alpha(T) \text{ (K}^{-1}\text{)}$	$\beta \text{ (bar}^{-1}\text{)}$	P (bar)	δ_d	δ_p	δ_h
298	0.001379	0.000117	1	14.9	0.0	0.0
348	0.001679	0.000117	200	13.8	0.0	0.0

An HSP value for the CO₂/hexane mixture is calculated using eqn. (6-22). The resulting HSP values for the CO₂/hexane mixture (initial and final), and for PC at $T = 75^\circ\text{C}$ and $P = 3000 \text{ psi}$ are plotted in Figures 8-16(a) and 8-16(b). Also indicated on the plots are the resulting Ra (initial and final) values, from eqn. (5-20), where Ra is the distance from the HSP value of PC at T and P (open symbols), to the initial and final HSP value of CO₂/hexane at T and P (filled symbols).



(a)

Figure 8-16. HSP values of CO_2 /hexane and PC at $T = 25$ to 75°C and $P = 3000 \text{ psi}$.

Visual results of the treatment using the CO_2 /hexane mixture, at the temperature and pressure indicated in Figure 8-16, are given in Figure 8-17.

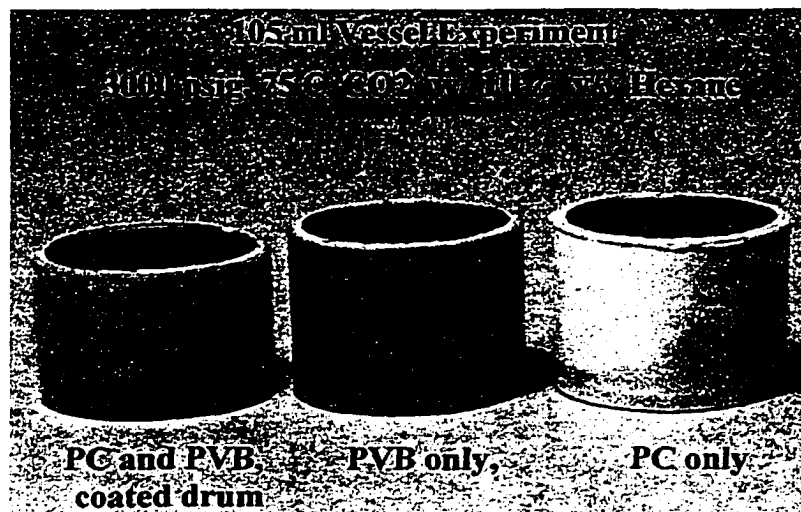


Figure 8-17. Appearance of polymer coated photoconductor drums treated with a CO_2 /hexane mixture at $T = 25$ to 75°C and $P = 3000 \text{ psi}$, hexane concentration = 10 vol.%.

8.2.2.2.1 Observations of Polymer Coating Removal Experiments using CO₂/Hexane Mixtures.

Only one treatment was conducted using a CO₂/hexane mixture, Table 8-6. The result of this treatment did not significantly differ from that using pure CO₂. This is an expected outcome, as no specific interactions between hexane and PC are anticipated. The only added benefit of hexane addition is a slight increase in the dispersion component of the mixture HSP's.

Table 8-6. Treatment conditions and results on polycarbonate coating using CO₂/hexane mixture.

T _{CO₂} (°C)	P _{CO₂} (psi)	Polymer T _g at (T _{CO₂} , P _{CO₂})	ΔT (T _{CO₂} - T _g)	R _{a<i>i</i>} (MPa ^{1/2})	R _{a<i>f</i>} (MPa ^{1/2})	R _{o^{liq}} (MPa ^{1/2})	Exp. result
75	3000	88.0	-13.0	7.7	15.6	5.5	discolored

8.2.2.3 CO₂/Ethanol

Ethanol, Figure 8-18, is a Lewis acid (see Table 6-1) and therefore specific interactions with Lewis bases are possible. PVB⁵⁶² is reported to have partial solubility in ethanol, and while not identified specifically, alcohols are reported to be nonsolvents for PC.⁵⁶³

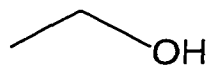


Figure 8-18. Ethanol, HSP's ⁵⁶⁴δ_d = 15.8 MPa^{1/2}, δ_p = 8.8 MPa^{1/2} and δ_h = 19.4 MPa^{1/2}.

The thermal expansion coefficient, α(T), of ethanol is determined from eqn. (8-13) with *a* = 0.000611, *m* = -0.7633, and T_c = 516.25 K⁵⁶⁵. The isothermal compressibility

value used for ethanol is $0.000063 \text{ (bar}^{-1}\text{)}$.⁵⁶⁶ Adjusted HSP values for ethanol are shown in Table 8-7.

Table 8-7. *HSP values for ethanol adjusted for temperature and pressure.*

$T \text{ (K)}$	$\alpha(T) \text{ (K}^{-1}\text{)}$	$\beta \text{ (bar}^{-1}\text{)}$	$P \text{ (bar)}$	δ_d	δ_p	δ_h
298	0.001178	0.000063	1	15.8	8.8	19.4
313	0.001244	0.000063	100	15.6	8.8	19.0
313	0.001244	0.000063	200	15.7	8.8	19.2
348	0.001437	0.000063	200	14.6	8.5	17.8
358	0.001506	0.000063	100	14.1	8.4	17.2
358	0.001506	0.000063	200	14.3	8.5	17.3
373	0.001625	0.000063	100	13.5	8.3	16.5
373	0.001625	0.000063	200	13.6	8.3	16.6

An HSP value for the CO₂/ethanol mixture is calculated using eqn. (6-22). The resulting HSP values for the CO₂/ethanol mixture (initial and final), and for PC at $T = 40^\circ\text{C}$ and $P = 1500 \text{ psi}$ and 3000 psi are plotted in Figures 8-19(a) and 8-19(b). Also indicated on the plots are the resulting Ra values, from eqn. (5-20), where Ra is the distance from the HSP value of PC at T and P (open symbols), to the initial and final HSP value of CO₂/ethanol at T and P (filled symbols).

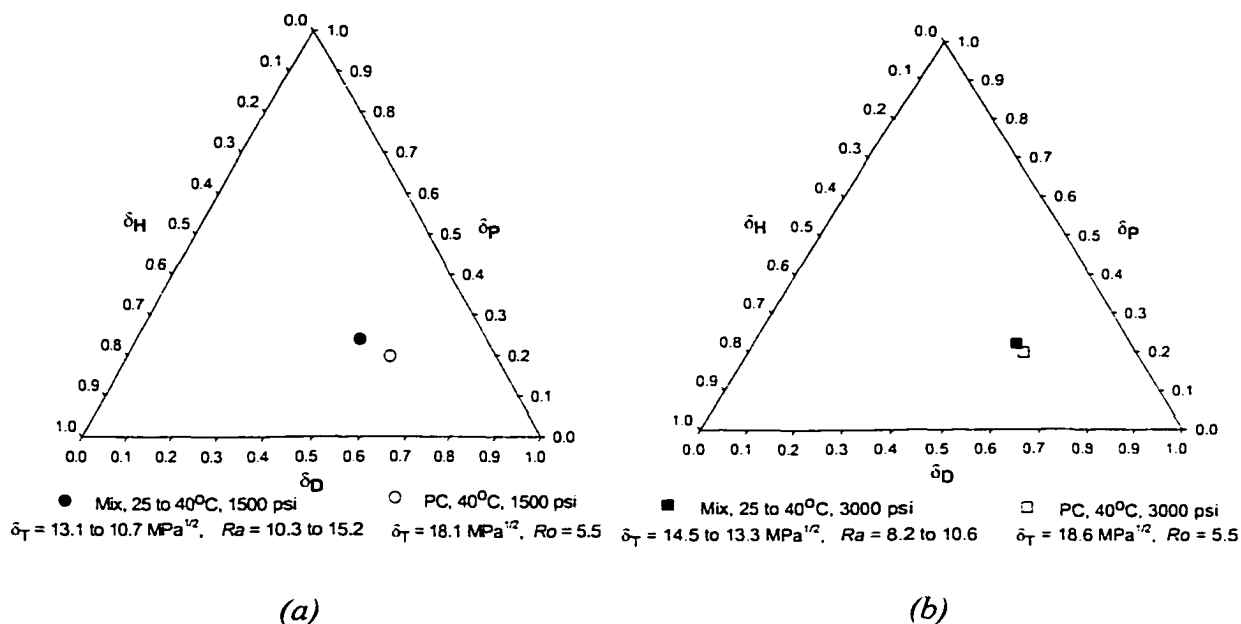


Figure 8-19. (a) HSP values of CO₂/ethanol and PC, at 25 to 40 °C and 1500 psi, (b) HSP values of CO₂/ethanol and PC, at 25 to 40 °C and 3000 psi.

Visual results of the treatment using the CO₂/ethanol mixture, at the temperature and pressures indicated in Figure 8-19(a) and 8-19(b), are given in Figure 8-20(a) and 8-20(b).

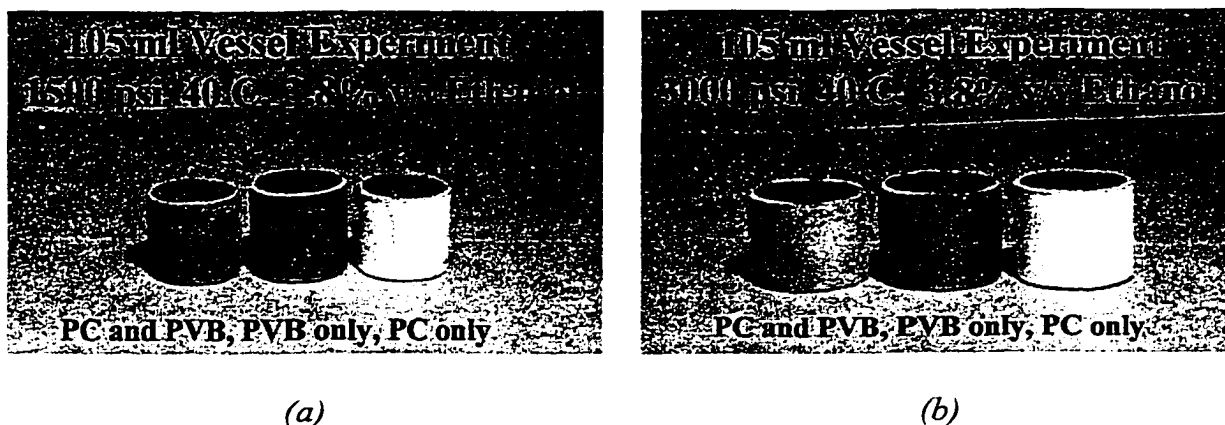


Figure 8-20. Appearance of polymer coated photoconductor drums treated with a CO₂/ethanol mixture at (a) $T = 25$ to 40°C , $P = 1500$ psi, and ethanol concentration = 3.8 vol.%, (b) $T = 25$ to 40°C , $P = 3000$ psi, and ethanol concentration = 3.8 vol.%.

The resulting HSP values for the CO₂/ethanol mixture (initial and final), and for PC at T = 85°C and P = 1500 psi; and at T = 75°C and P = 3000 psi are plotted in Figures 8-21(a) and 8-21(b). Also indicated on the plots are the resulting *Ra* values, from eqn. (5-20), where *Ra* is the distance from the PC HSP value at T and P (open symbols), to the initial and final HSP value of CO₂/ethanol at T and P (filled symbols).

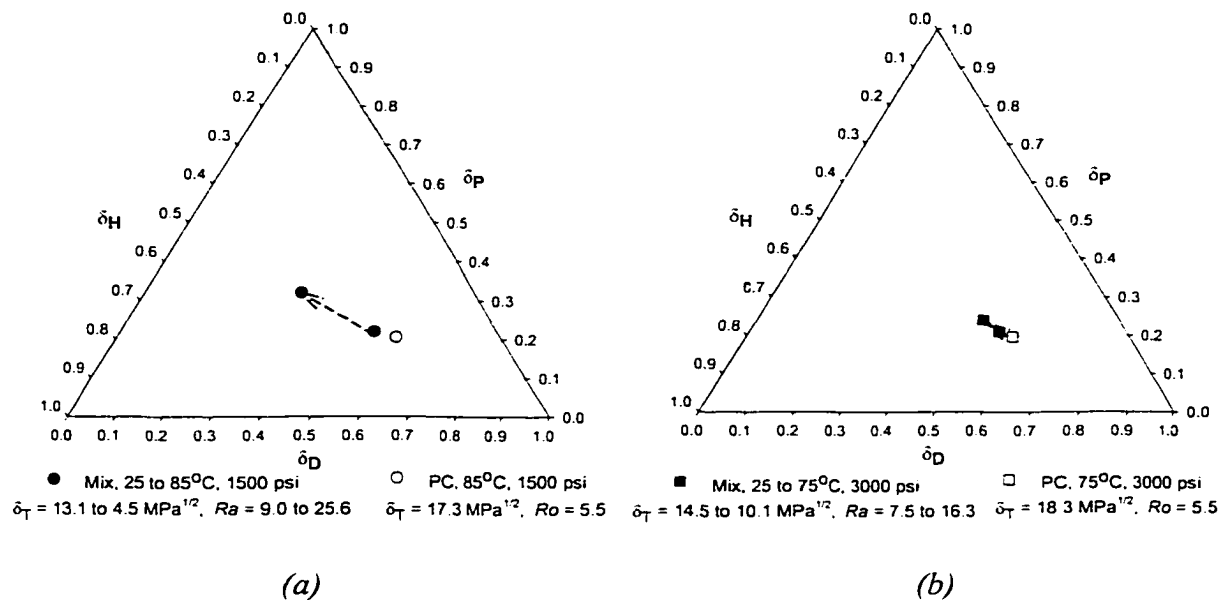
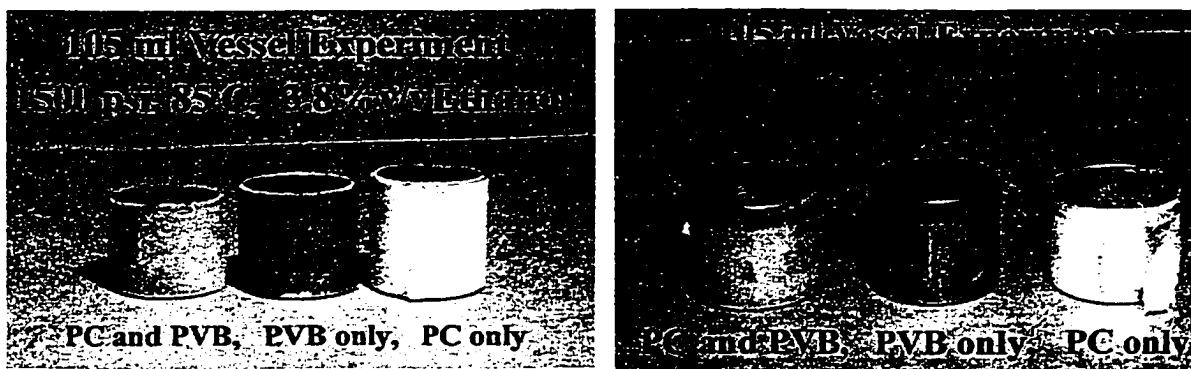


Figure 8-21. (a) HSP values of CO₂/ethanol and PC, at T = 25 °C to 85°C and P = 1500 psi. (b) HSP values of CO₂/ethanol and PC at T = 25°C to 75 °C and P = 3000 psi.

Visual results of the treatments using the CO₂/ethanol mixture, at the temperature and pressures indicated in Figure 8-21(a) and 8-21(b), are given in Figure 8-22(a), and 8-22(b).



(a) (b)
Figure 8-22. Appearance of polymer coated photoconductor drums treated with a CO₂/ethanol mixture at (a) $T = 25$ to 85°C , $P = 1500$ psi, and ethanol concentration = 3.8 vol.%, (b) $T = 25$ to 75°C , $P = 3000$ psi, and ethanol concentration = 3.8 vol.%,.

An HSP value for the CO₂/ethanol mixture is calculated using eqn. (6-22). The resulting HSP values for the CO₂/ethanol mixture (initial and final) and for PC at $T = 100^{\circ}\text{C}$ and $P = 1500$ psi and 3000 psi are plotted in Figures 8-23(a) and 8-23(b). Also indicated on the plots are the resulting Ra values, from eqn. (5-20), where Ra is the distance from the HSP value of PC at T and P (open symbols), to the initial and final HSP value of CO₂/ethanol at T and P (filled symbols).

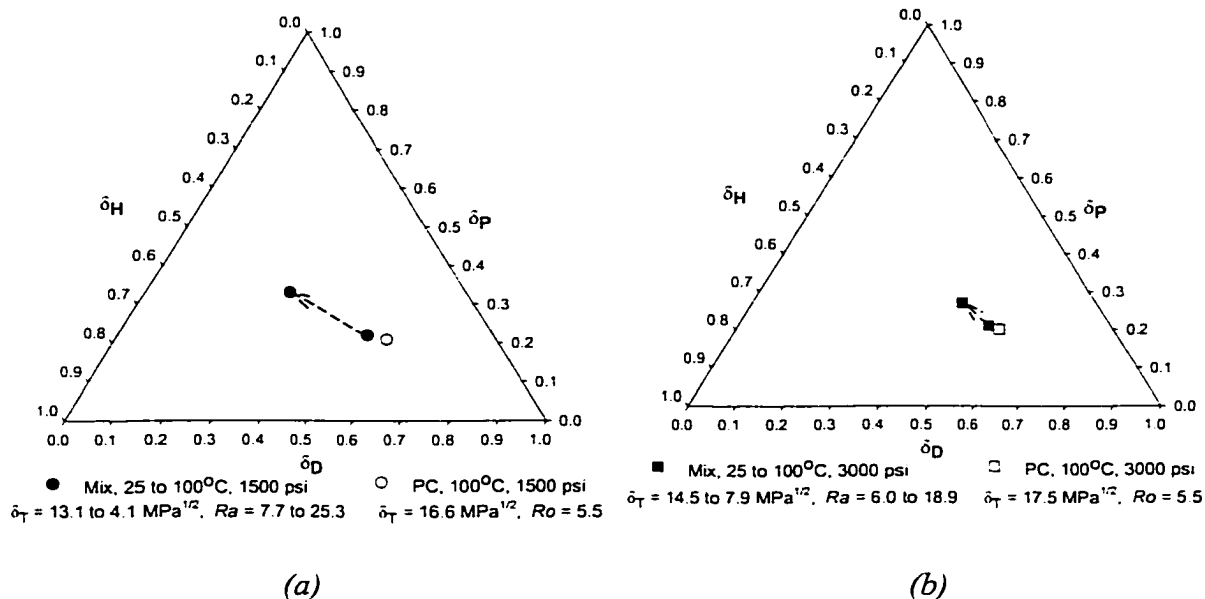


Figure 8-23. (a) HSP values of CO₂/ethanol and PC at $T = 25 \text{ to } 100^\circ\text{C}$ and $P = 1500 \text{ psi}$. (b) HSP values of CO₂/ethanol and PC at $T = 25 \text{ to } 100^\circ\text{C}$ and $P = 3000 \text{ psi}$.

Visual results of the treatments using the CO₂/ethanol mixture, at the temperature and pressures indicated in Figure 8-23(a) and 8-23(b), are given in Figure 8-24(a) and 8-24(b).

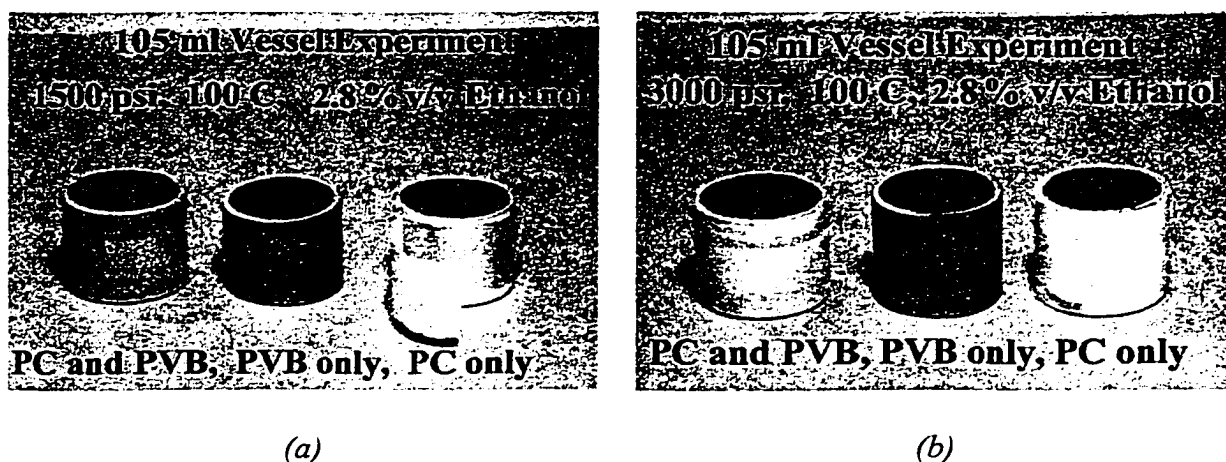


Figure 8-24. Appearance of polymer coated photoconductor drums treated with a CO₂/ethanol mixture at (a) $T = 25 \text{ to } 100^\circ\text{C}$, $P = 1500 \text{ psi}$, and ethanol concentration = 2.8 vol.%, (b) $T = 25 \text{ to } 100^\circ\text{C}$, $P = 3000 \text{ psi}$, and ethanol concentration = 2.8 vol.%.

8.2.2.3.1 Observations of Polymer Coating Removal Experiments using CO₂/Ethanol Mixtures

The results of the experiments described in Figures 8-20, 8-22, and 8-24, are ranked in Table 8-8 according a visual assessment of the effect on the PC coating, from most favorable to least favorable.

Table 8-8. Experimental results of polymer coating removal using CO₂/ethanol mixtures.

T _{CO₂} (°C)	P _{CO₂} (psi)	Polymer T _g at (T _{CO₂} , P _{CO₂})	ΔT (T _{CO₂} - T _g)	R _a _i (MPa ^{1/2})	R _a _f (MPa ^{1/2})	R _o ^{liq} (MPa ^{1/2})	Exp. result
100	3000	54.3	45.7	6.0	18.9	5.5	debonded
100	1500	85.6	14.4	7.7	25.0	5.5	debonded
85	1500	91.1	-6.1	9.0	25.3	5.5	debonded
75	3000	88.0	-13.0	7.5	16.3	5.5	debonded
40	1500	88.0	-63.0	10.3	15.2	5.5	flaking
40	3000	103.0	-48.0	8.2	10.4	5.5	cracked

The results for the CO₂/ethanol mixtures are similar to those seen for the pure CO₂ experiments in that favorable effects become more pronounced as (T_{CO₂} - T_g) increases and the difference between R_a and R_o^{liq} is minimized. However, the addition of a cosolvent capable of Lewis acid/base interactions with the polymer, appears to significantly enhance the effects on the PC coating. Specifically, with the ethanol cosolvent, debonding of the PC coating occurred at all temperature and pressure conditions, except those at T = 40°C. This behavior suggests an increased sorption due to specific interactions between the cosolvent (ethanol) and PC that promote the removal at conditions of temperature and pressure not possible with pure CO₂.

Targeting this type of behavior is of significant importance to Industrial applications. Specifically, the ability to achieve a desired result, polymer coating removal, at lower pressures and temperatures directly results in lower capital equipment

costs (thinner pressure vessel wall thickness) and increased throughput (larger vessel size).

8.2.2.4 CO₂/Acetone

Acetone, Figure 8-25, is expected to act as a Lewis base in CO₂, and could participate in specific interactions with Lewis acids, such as PVB. However, acetone should not exhibit specific (favorable) interactions with PC, which should also act as a Lewis base. Pure acetone is reported to be a nonsolvent for both PC⁵⁶⁷ and PVB.⁵⁶⁸

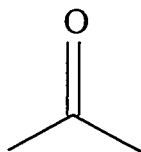


Figure 8-25. Acetone, HSP values⁵⁶⁹ $\delta_d = 15.5 \text{ MPa}^{1/2}$, $\delta_p = 10.4 \text{ MPa}^{1/2}$, and $\delta_h = 7.0 \text{ MPa}^{1/2}$.

The thermal expansion coefficient for acetone, $\alpha(T)$, is determined using eqn. (8-13) with $a = 0.000798$, $m = -0.701$, and $T_c = 508.2 \text{ (K)}$ ⁵⁷⁰. The isothermal compressibility value used for acetone is $0.000061 \text{ (bar}^{-1}\text{)}$.⁵⁷¹ HSP values for acetone, adjusted for T and P effects, are shown in Table 8-9.

Table 8-9. HSP values for acetone adjusted for temperature and pressure.

$T \text{ (K)}$	$\alpha(T) \text{ (K}^{-1}\text{)}$	$\beta \text{ (bar}^{-1}\text{)}$	$P \text{ (bar)}$	δ_d	δ_p	δ_h
298	0.001482	0.000061	1	15.5	10.4	7.0
313	0.001561	0.000061	100	15.2	10.3	6.8
313	0.001561	0.000061	200	15.3	10.3	6.9
348	0.001793	0.000061	200	14.0	10.0	6.3
358	0.001876	0.000061	100	13.4	9.9	6.1

An HSP value for the CO₂/acetone mixture is calculated using eqn. (6-22). The resulting HSP values for the CO₂/acetone mixture (initial and final) and for PC at T = 40°C and P = 1500 psi and P = 3000 psi are plotted in Figures 8-26(a) and 8-26(b). Also indicated on the plots are the resulting *Ra* values, from eqn. (5-20), where *Ra* is the distance from the HSP value of PC at T and P (open symbols), to the initial and final HSP value of CO₂/acetone at T and P (filled symbols).

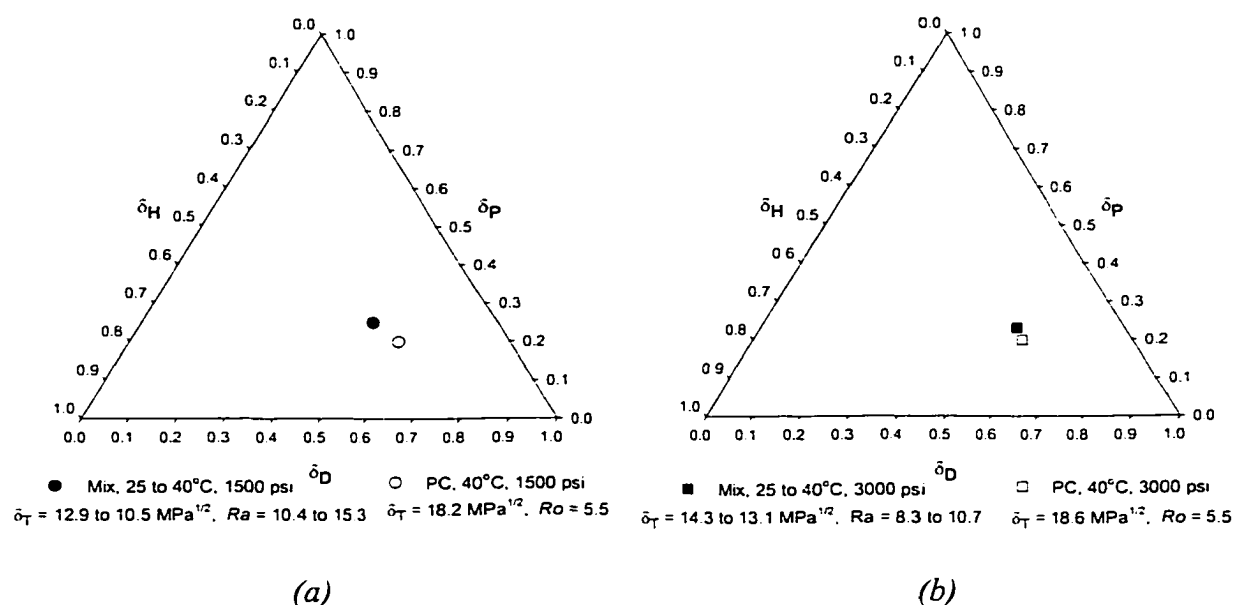


Figure 8-26. (a) HSP values of CO₂/acetone and PC at T = 25 to 40°C and P = 1500 psi. (b) HSP values of CO₂/acetone and PC at T = 25 to 40°C and P = 3000 psi.

Visual results of the CO₂/acetone treatment, at the temperature and pressures indicated in Figure 8-26(a) and 8-26(b), are given in Figure 8-27(a) and 8-27(b).

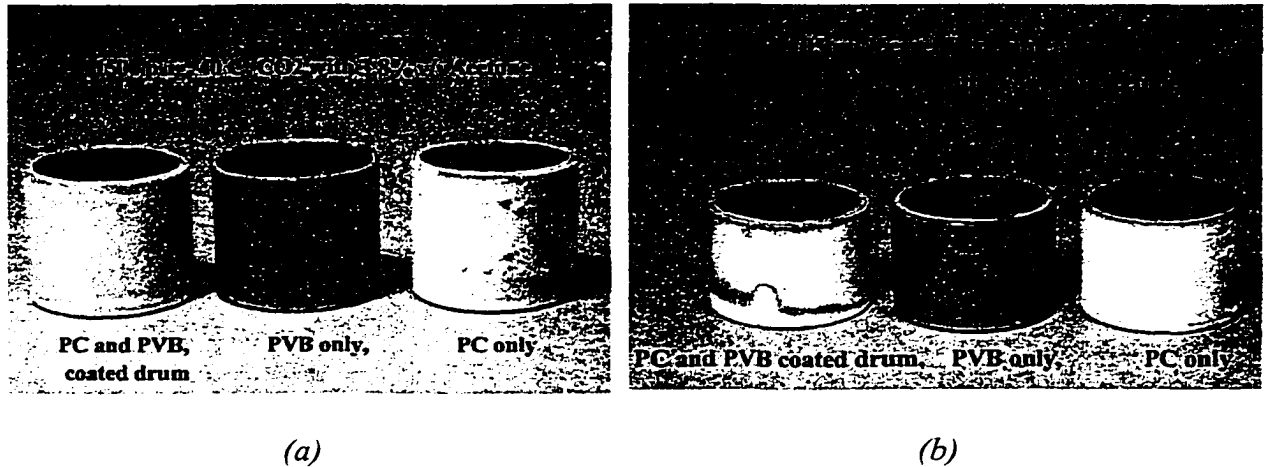


Figure 8-27. Appearance of polymer coated photoconductor drums treated with a CO_2 /acetone mixture at (a) $T = 25$ to 40°C , $P = 1500$ psi, and acetone concentration = 3.8 vol.%, (b) $T = 25$ to 40°C , $P = 3000$ psi, and acetone concentration = 3.8 vol.%.

The resulting HSP values for the CO_2 /acetone mixture (initial and final) and for PC at $T = 85^\circ\text{C}$ and $P = 1500$ psi; and $T = 75^\circ\text{C}$ and $P = 3000$ psi are plotted in Figures 8-28(a) and 8-28(b). Also indicated on the plots are the resulting Ra values, from eqn. (5-20), where Ra is the distance from the HSP value at T and P of PC (open symbols), to the initial and final HSP value of CO_2 /acetone at T and P (filled symbols).

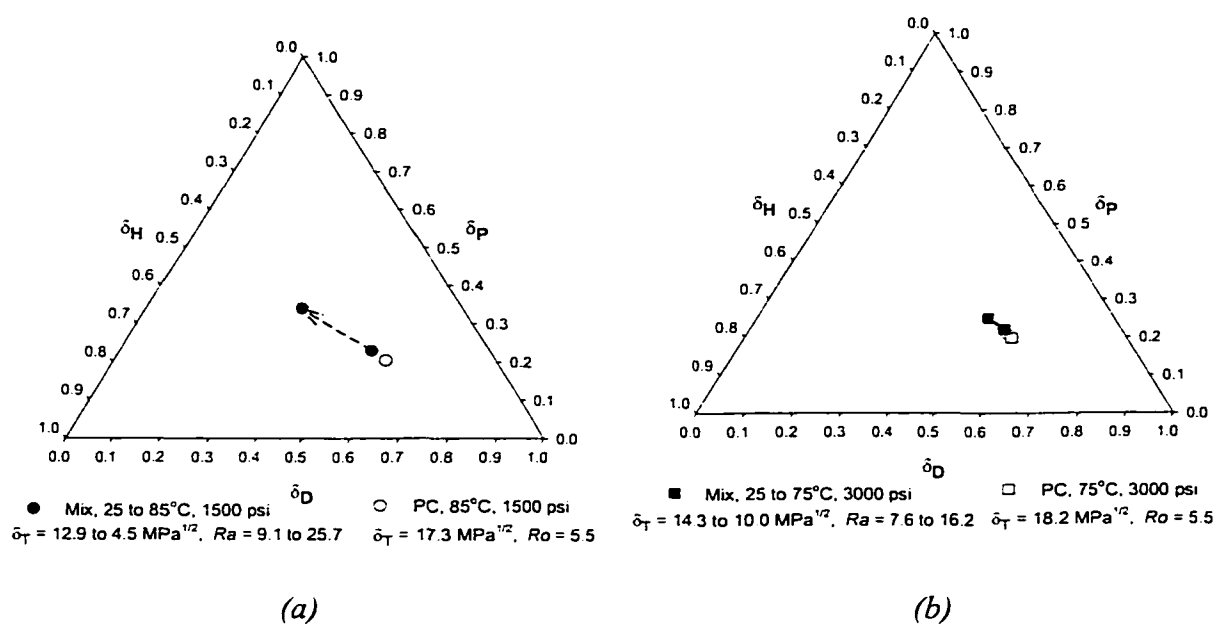


Figure 8-28. (a) HSP values of CO_2 /acetone and PC at $T = 25$ to 85°C and $P = 1500$ psi, (b) HSP values of CO_2 /acetone and PC at $T = 25$ to 75°C and $P = 3000$ psi.

Visual results of the treatments using the CO_2 /acetone mixtures, at the temperature and pressures indicated in Figure 8-28(a) and 8-28(b), are given in Figure 8-29(a) and 8-29(b).

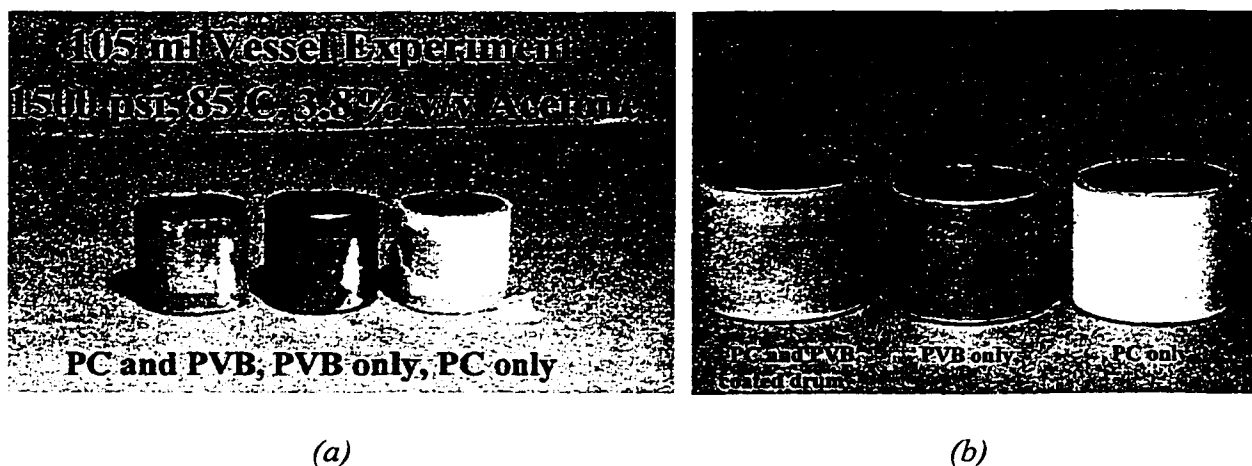


Figure 8-29. Appearance of polymer coated photoconductor drums treated with a CO_2 /acetone mixture at (a) $T = 25$ to 85°C , $P = 1500$ psi, and acetone concentration = 3.8 vol.%, (b) $T = 25$ to 75°C , $P = 3000$ psi, and acetone concentration = 3.8 vol.%.

8.2.2.4.1 Observations of Polymer Coating Removal Experiments using a CO₂/Acetone Mixture

On the basis of visual observations, Table 8-10 gives a ranking of the results of the experiments using CO₂/acetone mixtures, according to most favorable to least favorable effect on the PC coating.

Table 8-10. Results on Polycarbonate coating to CO₂/acetone experiments.

T _{CO₂} (°C)	P _{CO₂} (psi)	Polymer T _g at (T _{CO₂} , P _{CO₂})	ΔT (T _{CO₂} - T _g)	R _{a<i>i</i>} (MPa ^{1/2})	R _{a<i>f</i>} (MPa ^{1/2})	R _{o^{liq}} (MPa ^{1/2})	Exp. result
85	1500	91.1	-6.1	9.1	25.7	5.5	flaking
40	3000	88.0	-48.0	8.3	10.7	5.5	cracked
40	1500	103.0	-63.0	10.4	15.3	5.5	bubbled
75	3000	88.0	-13.0	7.6	16.2	5.5	discolored

As with experiments discussed previously, the depression of the polymer T_g to below the treatment temperature, T_{CO₂}, leading to enhanced polymer sorption and swelling, promotes the most favorable results. However, unlike the CO₂/ethanol mixture, where the potential for specific cosolvent/polymer interactions exist, experimental results with the acetone (a Lewis base) cosolvent, at the same treatment temperature and pressure, produce far less favorable results.

8.2.2.5 CO₂/Cyclohexanone

Cyclohexanone, Figure 8-30, is expected to act as a Lewis base in CO₂, and could participate in specific interactions with Lewis acids, such as PVB. Pure cyclohexanone is reported to be a solvent for both PVB⁵⁷² and PC⁵⁷³.

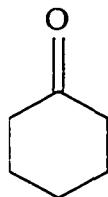


Figure 8-30. Cyclohexanone, HSP values⁵⁷⁴: $\delta_d = 17.8 \text{ MPa}^{1/2}$, $\delta_p = 6.3 \text{ MPa}^{1/2}$, and $\delta_h = 5.1 \text{ MPa}^{1/2}$.

Parameters used for determining the coefficient of thermal expansion of cyclohexanone are $a = 0.000563$, $m = -0.7283$, and $T_c = 629.15 \text{ K}$. The isothermal compressibility value used for cyclohexanone⁵⁷⁵ is $0.000066 \text{ (bar}^{-1}\text{)}$. Adjusted HSP values for cyclohexanone are shown in Table 8-11.

Table 8-11. HSP values for cyclohexanone adjusted for temperature and pressure.

$T \text{ (K)}$	$\alpha(T) \text{ (K}^{-1}\text{)}$	$\beta \text{ (bar}^{-1}\text{)}$	$P \text{ (bar)}$	δ_d	δ_p	δ_h
298	0.000898	0.000066	1	17.8	6.3	5.1
313	0.000929	0.000066	200	17.8	6.3	5.1
328	0.000962	0.000066	200	17.5	6.3	5.0
338	0.000986	0.000066	100	17.1	6.2	4.8
338	0.000986	0.000066	200	17.2	6.2	4.9
343	0.000998	0.000066	100	17.0	6.2	4.7
348	0.001011	0.000066	200	17.0	6.2	4.8
363	0.001053	0.000066	100	16.4	6.1	4.6
373	0.001082	0.000066	100	16.1	6.1	4.5

With the HSP values for both CO_2 and cosolvent adjusted for temperature and pressure, an HSP value for the CO_2 /cyclohexanone mixture is calculated using eqn. (6-22). The resulting HSP values for the CO_2 /cyclohexanone mixture (initial and final) and PC at $T = 40^\circ\text{C}$ and $P = 3000 \text{ psi}$; and $T = 75^\circ\text{C}$ and $P = 3000 \text{ psi}$ are plotted in Figures 8-31(a) and 8-31(b). Also indicated on the plots are the resulting Ra values, from eqn. (5-20), where Ra is the distance from the HSP value of PC or PVB at T and P (open symbols), to the initial and final HSP value of CO_2 /cyclohexanone at T and P (filled symbols).

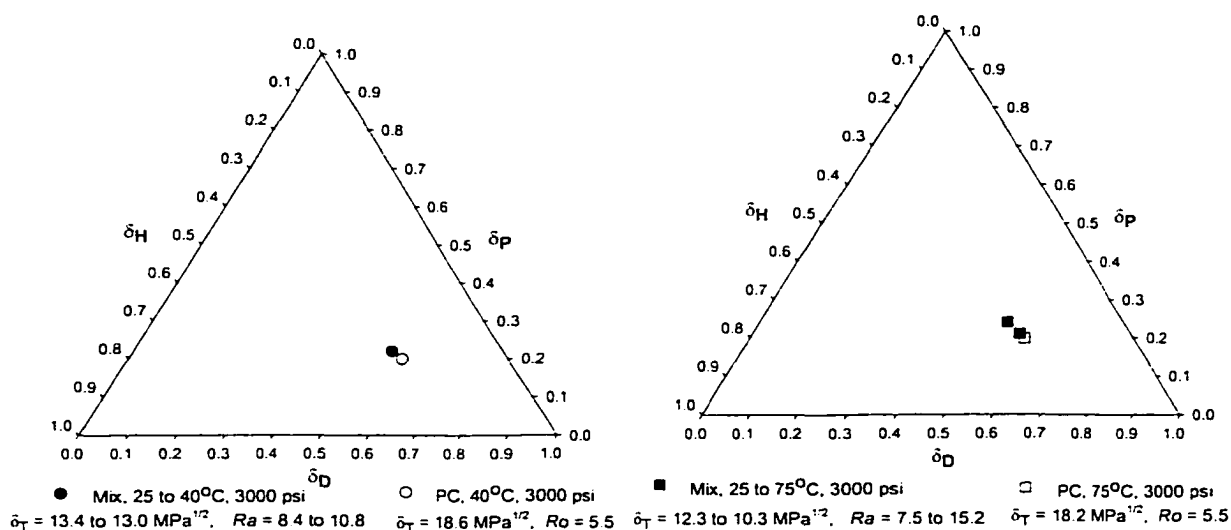


Figure 8-31. (a) HSP values of CO_2 /cyclohexanone mixture and PC at $T = 25$ to 40°C and $P = 3000$ psi. (B) HSP values of CO_2 /cyclohexanone mixture and PC at $T = 25$ to 40°C and $P = 3000$ psi.

Visual results of the CO_2 /cyclohexanone treatments, at the temperature and pressures indicated in Figure 8-31(a) and 8-31(b), are given in Figure 8-32(a) and 8-32(b).

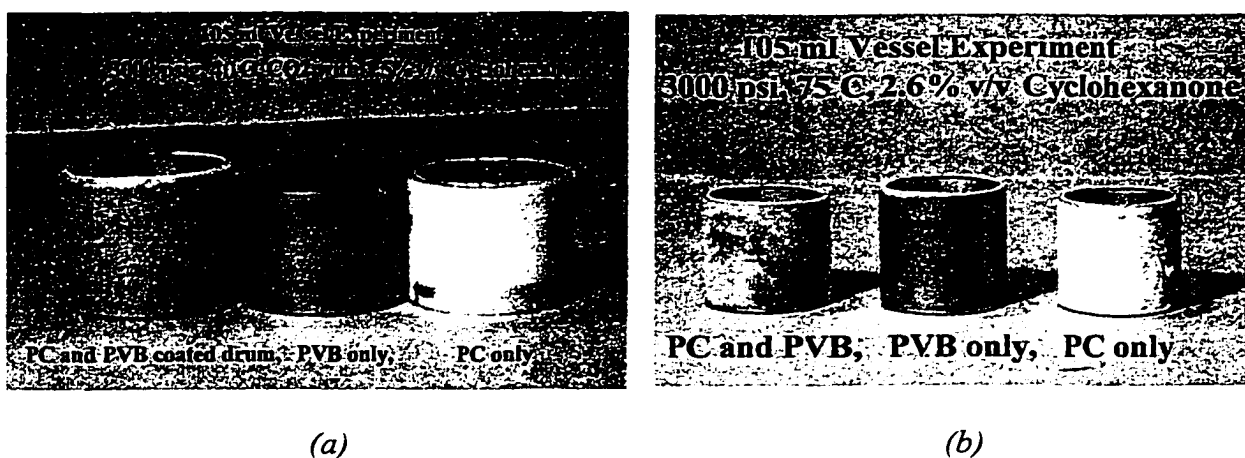


Figure 8-32. Appearance of polymer coated photoconductor drums treated with a CO_2 /cyclohexanone mixture at (a) $T = 25$ to 40°C , $P = 3000$ psi, and cyclohexanone concentration = 1.5 vol.%, (b) $T = 25$ to 75°C , $P = 3000$ psi, and cyclohexanone concentration = 2.6 vol.%.

The resulting HSP values for the CO₂/cyclohexanone mixture (initial and final) and for PC at T = 65°C and P = 1500 psi and P = 3000 psi are plotted in Figures 8-33(a) and 8-33(b). Also indicated on the plots are the resulting *Ra* values, from eqn. (5-20), where *Ra* is the distance from the HSP value of PC at T and P (open symbols), to the initial and final HSP value of CO₂/cyclohexanone at T and P (filled symbols).

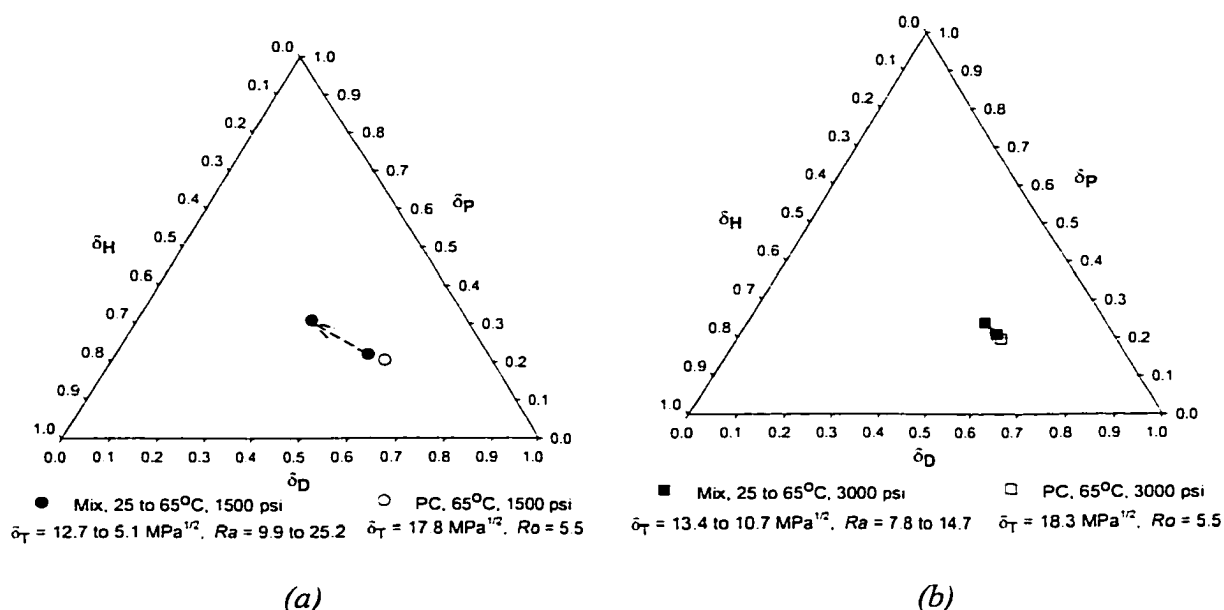
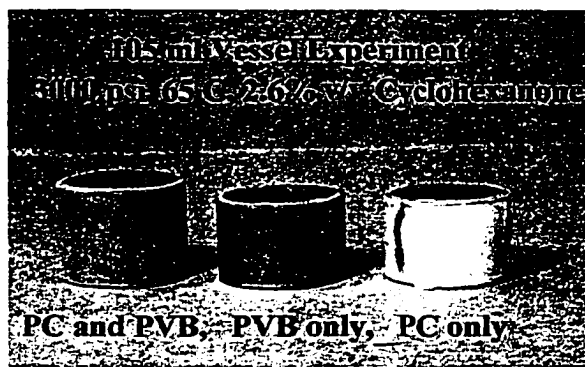
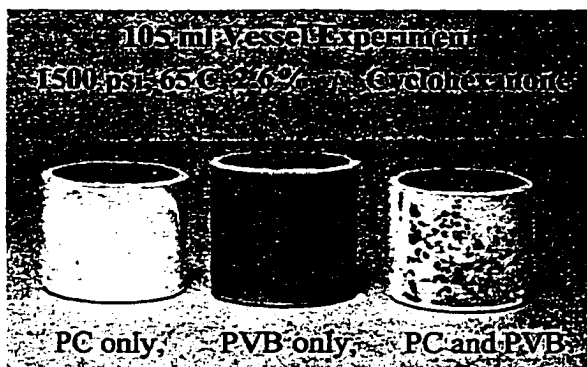


Figure 8-33. (a) HSP values of CO₂/cyclohexanone mixture and PC at T = 25 to 65°C and P = 1500 psi. (B) HSP values of CO₂/cyclohexanone mixture and PC at T = 25 to 65°C and P = 3000 psi.

Visual results of the CO₂/cyclohexanone treatments, at the temperature and pressures indicated in Figure 8-33(a) and 8-33(b), are given in Figure 8-34(a) and 8-34(b).



(a) (b)
Figure 8-34. Results of CO_2 /cyclohexanone treatment of polymer coated photoconductor drums. (a) $T = 25$ to 65°C , $P = 1500$ psi, and cyclohexanone concentration = 2.6 vol.%. (b) $T = 25$ to 65°C , $P = 3000$ psi, and cyclohexanone concentration = 2.6 vol.%.

The resulting HSP values for the CO_2 /cyclohexanone mixture (initial and final) and for PC at $T = 100^\circ\text{C}$ and $P = 1500$ psi and $P = 3000$ psi are plotted in Figures 8-35(a) and 8-35(b). Also indicated on the plots are the resulting Ra values, from eqn. (5-20), where Ra is the distance from the HSP value of PC at T and P (open symbols), to the initial and final HSP value of CO_2 /cyclohexanone at T and P (filled symbols).

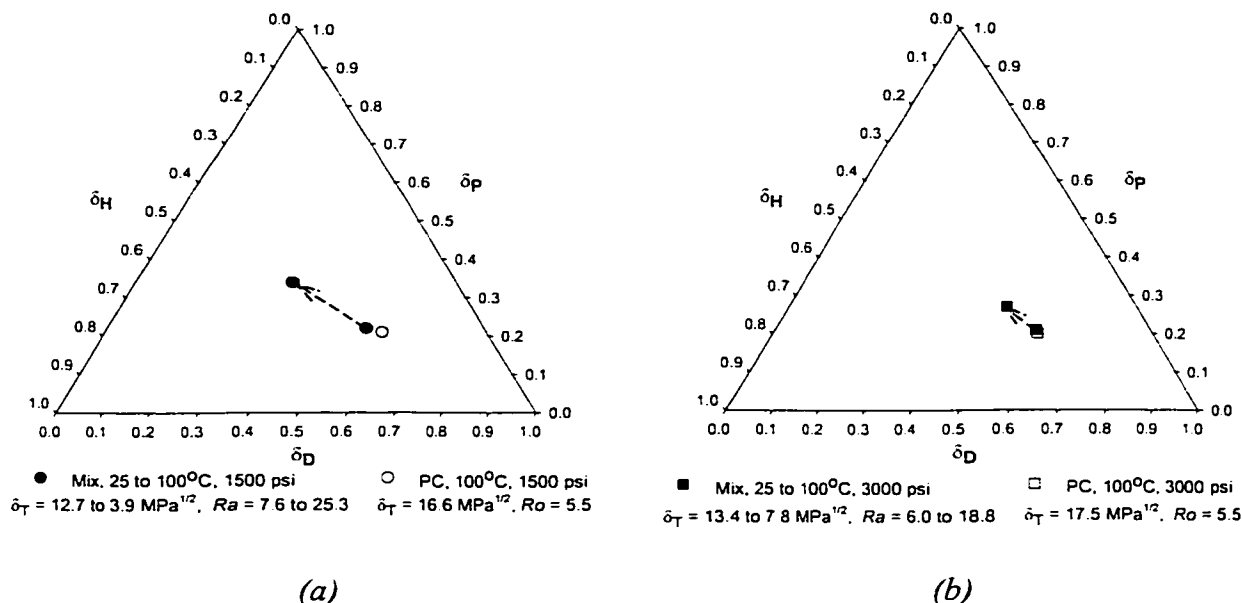


Figure 8-35. (a) HSP values of CO_2 /cyclohexanone mixture and PC at $T = 25$ to 100°C and $P = 1500$ psi. (b) HSP values of CO_2 /cyclohexanone mixture and PC at $T = 25$ to 100°C and $P = 3000$ psi.

Visual results of the CO_2 /cyclohexanone treatments, at the temperature and pressures indicated in Figure 8-35(a) and 8-35(b), are given in Figure 8-36(a) and 8-36(b).

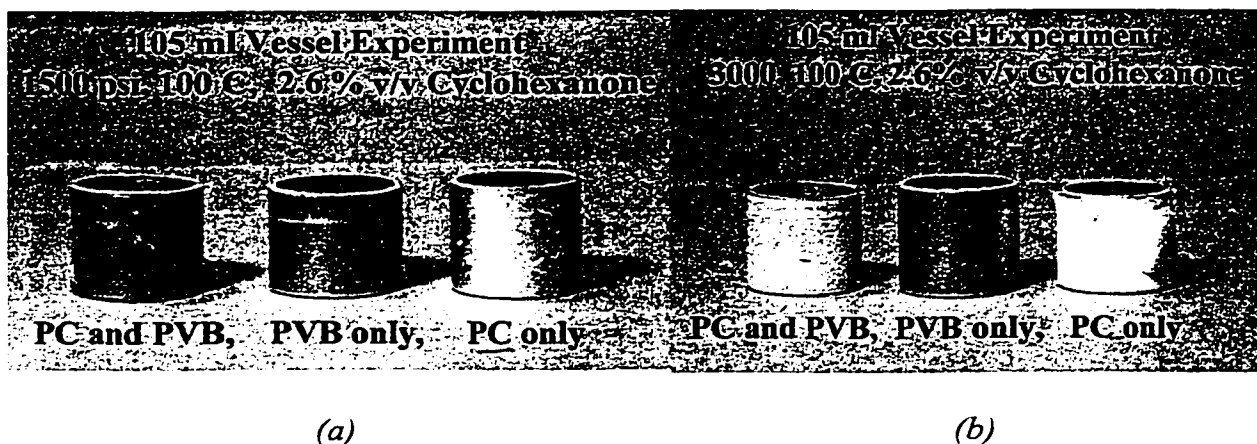


Figure 8-36. Results of CO_2 /cyclohexanone treatment of polymer coated photoconductor drums. (a) $T = 25$ to 100°C , $P = 1500$ psi, and cyclohexanone concentration = 2.6 vol.%. (b) $T = 25$ to 100°C , $P = 3000$ psi, and cyclohexanone concentration = 2.6 vol.%.

8.2.2.5.1 Observations of Polymer Coating Removal Experiments using CO₂/Cyclohexanone Mixtures

On the basis of the visual observations, the results of the experiments shown in Figures 8-32, 8-34 and 8-36, are ranked in Table 8-12 according to most favorable to least favorable effects on the PC coating.

Table 8-12. Results on polycarbonate coating to CO₂/cyclohexanone experiments.

T _{CO₂} (°C)	P _{CO₂} (psi)	Polymer T _g at (T _{CO₂} , P _{CO₂})	ΔT (T _{CO₂} - T _g)	R _{a<i>i</i>} , (MPa ^{1/2})	R _{a<i>f</i>} , (MPa ^{1/2})	R _{o^{liq}} , (MPa ^{1/2})	Exp. results
100	3000	54.3	45.7	6.0	18.9	5.5	debonded
65	3000	88.0	-23.0	7.8	14.7	5.5	debonded
75	3000	88.0	-13.0	7.5	15.2	5.5	flaking
100	1500	85.6	14.4	7.6	25.3	5.5	cracked
65	1500	103.0	-38.0	9.9	25.2	5.5	cracked
40	3000	88.0	-48.0	8.4	10.8	5.5	discolored

The results obtained with the CO₂/cyclohexanone mixtures follow a similar trend to those discussed previously for pure CO₂ and CO₂/ethanol, with a strong correlation between favorable effects on the polymer coating and ΔT = (T_{CO₂} - T_g). The result which contradicts this trend is the one conducted at T = 100°C and P = 1500 psi. Small surface cracks in the PC coating were evident, however, at the completion of this particular experiment the drum components were noted to have been in contact with liquid cyclohexanone. This was not a result noted with other experiments and solvent/cosolvent mixtures. The solubility of cyclohexanone in CO₂ was not evaluated at all experimental temperature and pressures, however, as a Lewis base with a carbonyl functional group, some level of solubility is expected. However, this solubility is reduced at higher temperatures and lower pressures, and the molecular weight of cyclohexanone

is larger than the other Lewis base cosolvents evaluated in this study, which is a rough indicator of lower solubility.

Also, unlike the CO₂/ethanol mixture, where the potential for specific cosolvent/polymer interactions exist, experimental results with the (Lewis base) cyclohexanone cosolvent, for a range of temperature and pressures, produce less favorable results.

8.2.2.6 CO₂/Tetrahydrofuran

Tetrahydrofuran (THF), Figure 8-37, is expected to act as a Lewis base in CO₂ and therefore specific interactions with Lewis acids, such as PVB, are possible. Pure, liquid THF is reported to be a solvent for both PVB⁵⁷⁶ and PC⁵⁷⁷.

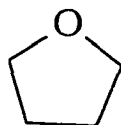


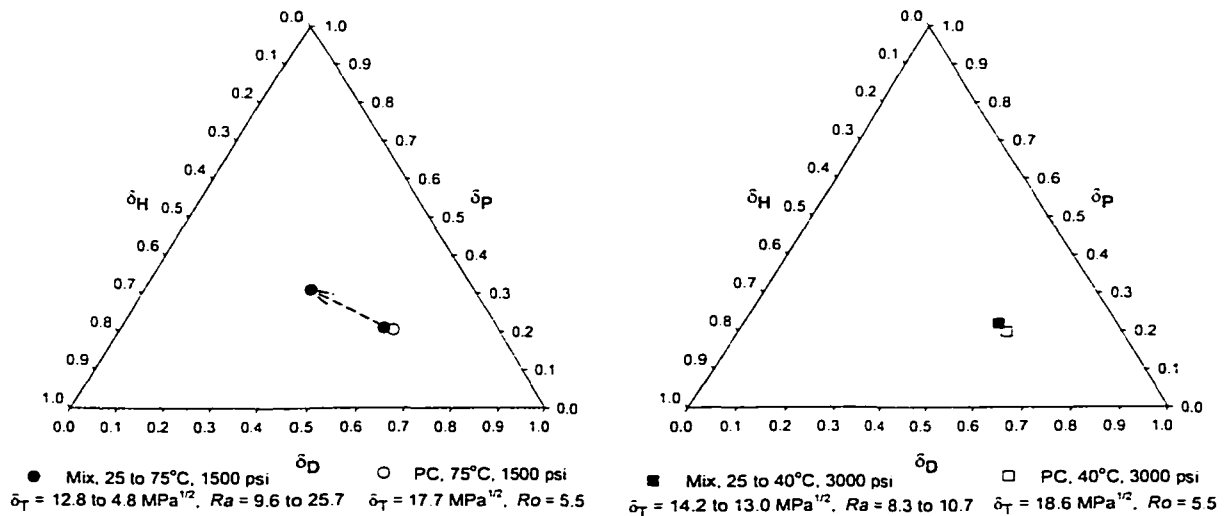
Figure 8-37. Tetrahydrofuran (THF), HSP values⁵⁷⁸ $\delta_d = 16.8 \text{ MPa}^{1/2}$, $\delta_p = 5.7 \text{ MPa}^{1/2}$, and $\delta_h = 8.0 \text{ MPa}^{1/2}$.

The HSP's given in the caption of Figure 8-37 are ambient condition values and are taken from the literature. These parameters are adjusted for temperature and pressure effects as described in Section 7.2.2. The thermal expansion coefficient, $\alpha(T)$, is determined from eqn. (8-13) with $a = 0.000685$, $m = -0.7088$, and $T_c = 540.15 \text{ K}$ ⁵⁷⁹. An isothermal compressibility value for THF could not be located, and the value for cyclohexanone was assumed, based on the similarity of their chemical structures. Adjusted HSP values for THF are given in Table 8-13.

Table 8-13. THF HSP values adjusted for temperature and pressure.

T (K)	$\alpha(T)$ (K^{-1})	β (bar^{-1})	P (bar)	δ_d	δ_p	δ_h
298	0.001209	0.000066	1	16.8	5.7	8.0
313	0.001265	0.000066	200	16.7	5.7	7.9
333	0.001351	0.000066	200	16.1	5.6	7.6
343	0.001399	0.000066	100	15.6	5.5	7.4
373	0.001572	0.000066	100	14.5	5.4	6.8
373	0.001572	0.000066	200	14.6	5.4	6.9

An HSP value for the CO₂/THF mixture is calculated using eqn. (6-22). The resulting HSP values for the CO₂/THF mixture (initial and final) and for PC at $T = 75^\circ\text{C}$ and $P = 1500$ psi; and $T = 40^\circ\text{C}$ and $P = 3000$ psi are plotted in Figures 8-38(a) and 8-38(b). Also indicated on the plots are the resulting Ra values, from eqn. (5-20), where Ra is the distance from the HSP value of PC at T and P (open symbols), to the initial and final HSP value of CO₂/THF at T and P (filled symbols).



(a)

(b)

Figure 8-38. (a) HSP values of CO₂/THF and PC at $T = 25$ to 75°C and $P = 1500$ psi. (b) HSP values of CO₂/THF and PC at $T = 25$ to 40°C and $P = 3000$ psi.

Visual results of the CO₂/THF treatment, at the temperature and pressures indicated in Figure 8-38(a) and 8-38(b), are given in Figure 8-39(a) and 8-39(b).

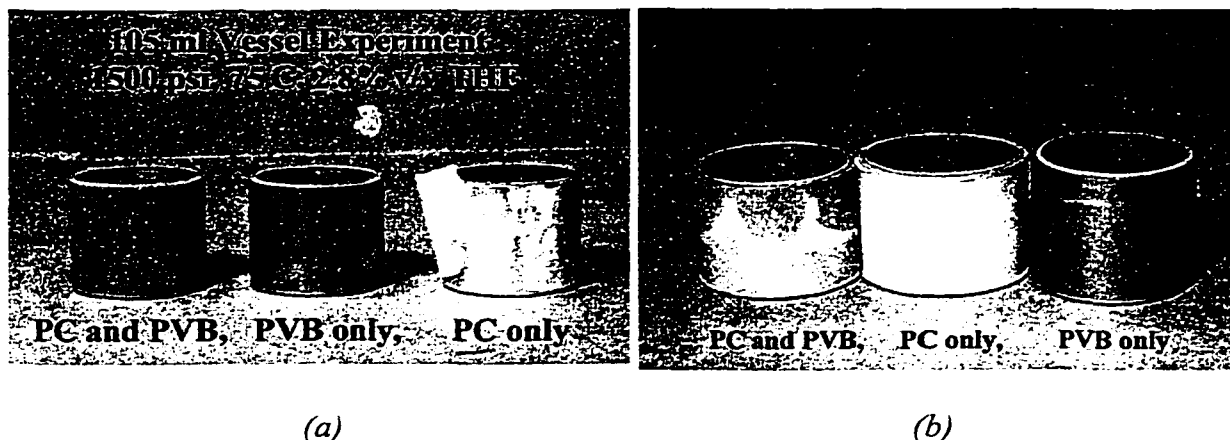


Figure 8-39. Appearance of polymer coated photoconductor drums treated with a CO₂/THF mixture at (a) $T = 25$ to 75°C , $P = 1500$ psi, and THF concentration = 2.8 vol.%, (b) $T = 25$ to 40°C , $P = 3000$ psi, and THF concentration = 3.0 vol.%.

The resulting HSP values for the CO₂/THF mixture (initial and final) and for PC at $T = 100^{\circ}\text{C}$ and $P = 1500$ psi and $P = 3000$ psi are plotted in Figures 8-40(a) and 8-40(b). Also indicated on the plots are the resulting Ra values, from eqn. (5-20), where Ra is the distance from the HSP value of PC at T and P (open symbols), to the initial and final HSP value of CO₂/THF at T and P (filled symbols).

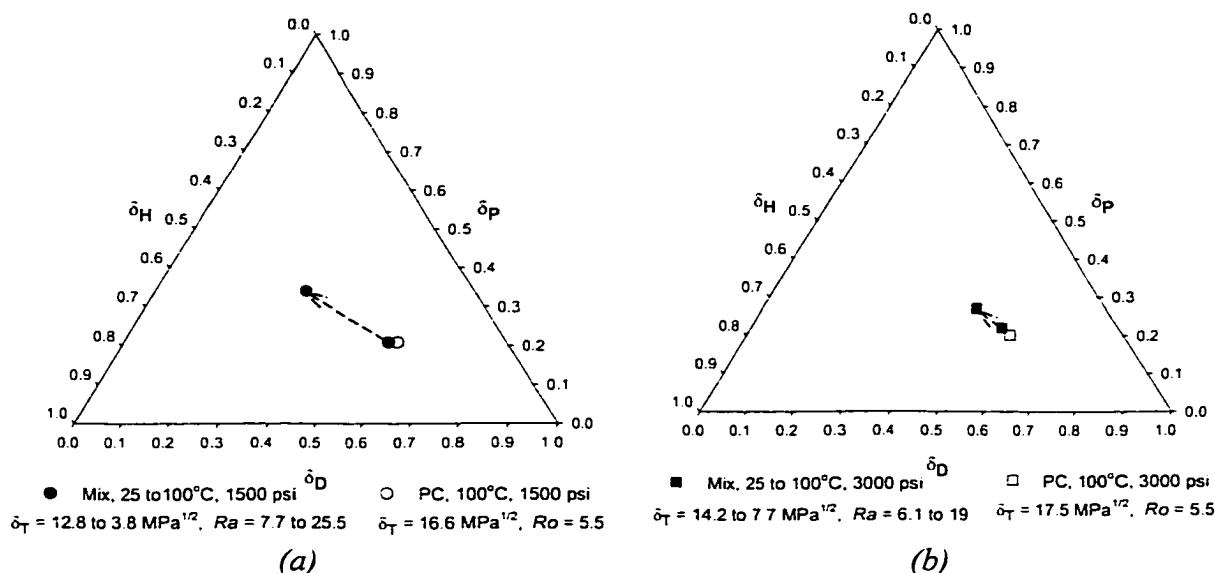


Figure 8-40. (a) HSP values of CO_2/THF and PC $T = 25$ to 100°C and $P = 1500 \text{ psi}$
(b) HSP values of CO_2/THF and PC $T = 25$ to 100°C and $P = 3000 \text{ psi}$.

Visual results of the CO_2/THF treatments, at the temperature and pressures indicated in Figure 8-40(a) and 8-40(b), are given in Figure 8-41(a), and 8-41(b).

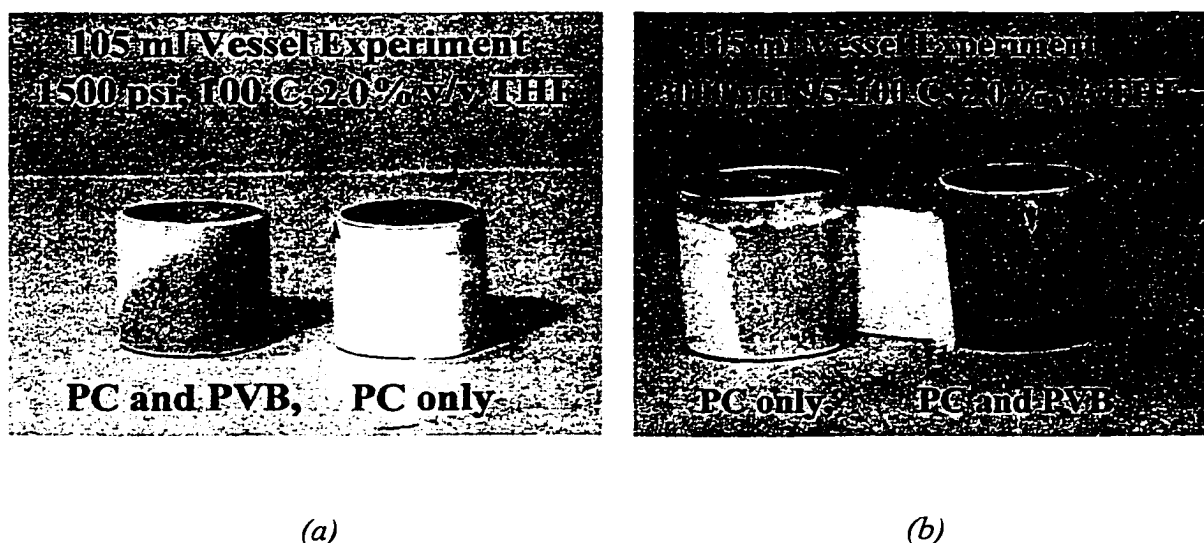


Figure 8-41. Appearance of polymer coated photoconductor drums treated with a CO_2/THF mixture at (a) $T = 25$ to 100°C , $P = 1500 \text{ psi}$, and THF concentration = 2.0 vol.%, (b) $T = 25$ to 100°C , $P = 3000 \text{ psi}$, and THF concentration = 2.0 vol.%.

8.2.2.6.1 Observations of Polymer Coating Removal Experiments using CO₂/THF Mixtures

On the basis of the visual observations, the results of the experiments shown in Figures 8-39, and 8-41, are ranked in Table 8-14, according to most favorable to least favorable effects on the PC coating.

Table 8-14. Results of polymer removal experiments using CO₂/THF mixtures.

T _{CO₂} (°C)	P _{CO₂} (psi)	Polymer T _g at (T _{CO₂} , P _{CO₂})	ΔT (T _{CO₂} - T _g)	R _{a<i>i</i>} (MPa ^{1/2})	R _{a<i>f</i>} (MPa ^{1/2})	R _{o^{liq}} (MPa ^{1/2})	Exp. result
100	3000	54.3	45.7	6.1	19.0	5.5	debonded
100	1500	85.6	14.4	7.7	25.5	5.5	debonded
75	1500	103.0	-28.0	9.6	25.7	5.5	debonded
40	1500	88.0	-48.0	8.3	10.7	5.5	discolored

The results of the CO₂/THF mixtures are very similar to the results using the CO₂/cyclohexanone mixtures in that the effects on the PC correlate strongly with ΔT

8.2.2.7 Comparison of Polymer Coating Removal Experiments – Photoconductor Drums

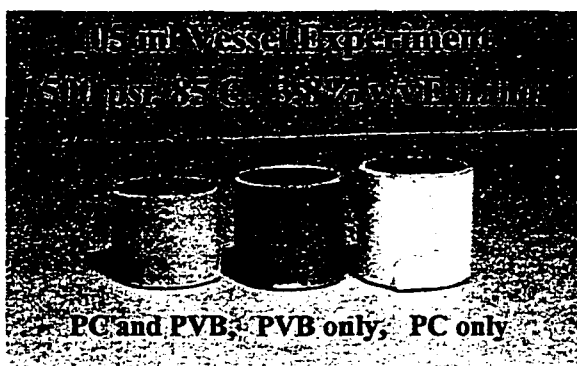
Table 8-15. Overall results on Polycarbonate coating removal experiments, ranked according to the effect on the PC coating.

Cosolvent	T _{CO₂} (°C)	P _{CO₂} (psi)	Polymer T _g at (T _{CO₂} , P _{CO₂})	ΔT (T _{CO₂} - T _g)	R _{ai} (MPa ^{1/2})	R _{af} (MPa ^{1/2})	R _o ^{liq} (MPa ^{1/2})	Exp. result
ethanol	100	3000	54.3	45.7	6.0	18.9	5.5	debonded
ethanol	100	1500	85.6	14.4	7.7	25.3	5.5	debonded
ethanol	85	1500	91.1	-6.1	9.0	25.3	5.5	debonded
ethanol	75	3000	88.0	-13.0	7.5	16.3	5.5	debonded
cyclohexanone	100	3000	54.3	45.7	6.0	18.9	5.5	debonded
THF	100	3000	54.3	45.7	6.1	19.0	5.5	debonded
THF	100	1500	85.6	14.4	7.7	25.5	5.5	debonded
CO ₂	100	3000	54.3	45.7	6.2	19.4	5.5	debonded
cyclohexanone	65	3000	88.0	-23.0	7.8	14.7	5.5	debonded
THF	75	1500	103.0	-28.0	9.6	25.7	5.5	debonded
cyclohexanone	75	3000	88.0	-13.0	7.5	15.2	5.5	flaking
ethanol	40	1500	103.0	-63.0	10.8	15.2	5.5	flaking
acetone	85	1500	91.1	-6.1	9.1	25.7	5.5	flaking
cyclohexanone	100	1500	85.6	14.4	7.6	25.3	5.5	cracked
ethanol	40	3000	88.0	-48.0	10.6	10.6	5.5	cracked
acetone	40	3000	88.0	-48.0	8.3	10.7	5.5	cracked
cyclohexanone	65	1500	103.0	-38.0	9.9	25.2	5.5	cracked
CO ₂	100	1500	85.6	14.4	7.9	26.0	5.5	bubbled

acetone	40	1500	103.0	-63.0	10.4	15.3	5.5	Bubbled
acetone	75	3000	88.0	-13.0	7.6	16.2	5.5	discolored
CO ₂	75	3000	88.0	-23.0	7.8	16.7	5.5	discolored
THF	40	3000	85.6	-48.0	8.3	10.7	5.5	discolored
CO ₂	45	3000	88.0	-43.0	8.4	11.6	5.5	discolored
cyclohexanone	40	3000	88.0	-48.0	8.4	10.8	5.5	discolored
CO ₂	75	1500	103.0	-28.0	9.9	26.8	5.5	discolored
hexane	75	3000	91.1	-16.1	7.7	15.6	5.5	discolored
CO ₂	45	1500	103.0	-58.0	10.8	18.9	5.5	discolored

Table 8-15 is a ranking of all of the photoconductor drum polymer coating removal experiments. The results, ranked according to the most desirable (top) to least desirable (bottom) effect on the PC coating, are based on visual observations. The ranking in Table 8-15 clearly indicate that, of the cosolvents examined, ethanol produces the best results for the PC coatings removal application. This supports the concept discussed in Section 3.4 where it was noted that specific interactions, such as Lewis acid/base interactions, generally have a greater influence than the combined van der Waals interactions. Direct comparisons of experimental results at the same temperature and pressure, using a Lewis acid or Lewis base cosolvent, are shown in Figures 8-42 and 8-43.

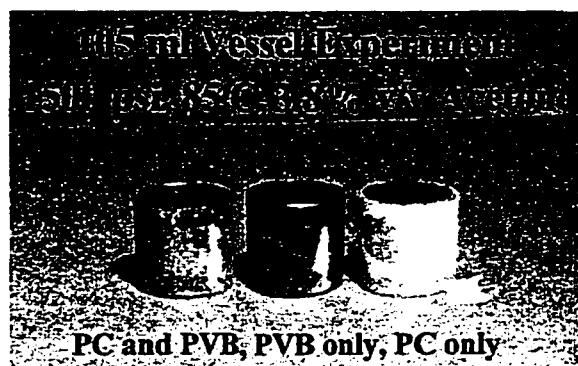
In Figure 8-42, a greater effect on the PC coating (partial debonding) is observed when a Lewis acid cosolvent is used versus the effect when a Lewis base is used (bubbling). In Figure 8-43, a similar comparison is made at a higher experimental temperature (85°C)



$$\Delta T = T_{CO_2} - T_g^{CO_2} = -6^\circ C$$

$$Ra = 9.5 \text{ to } 25.3 \text{ MPa}^{1/2}$$

(a)



$$\Delta T = T_{CO_2} - T_g^{CO_2} = -6^\circ C$$

$$Ra = 9.5 \text{ to } 25.7 \text{ MPa}^{1/2}$$

(b)

Figure 8-42. (a) Results of CO_2 /Lewis acid treatment of polymer coated photoconductor drums, $T = 25$ to $85^\circ C$, $P = 1500$ psi, and ethanol concentration = 3.8 vol.%. (b) Results of CO_2 /Lewis base treatment of polymer coated photoconductor drums, $T = 25$ to $85^\circ C$, $P = 1500$ psi, and acetone concentration = 3.8 vol.%.

Again, the result with the Lewis acid cosolvent, debonding of the PC coating, is significantly better than the result observed with the Lewis base cosolvent, flaking of the PC coating. The initial and final Ra values, representing the distance (expressed as a radius) between the initial solvent mixture HSP values to the PC HSP value (Ra_i), and between the final mixture HSP values to the PC HSP value (Ra_f), at T and P , ranged from an initial value of 9.5 to a final value of approximately $25 \text{ MPa}^{1/2}$ versus values in Figure 8-42 of 11 to $15.2 \text{ MPa}^{1/2}$. An optimum radius of interaction, R_o^{SCF} , that can be used to design test conditions for the PC/SCF is unknown, although, as discussed earlier, it is expected to be greater than the optimum radius of interaction for the dissolution of PC in liquid solvents, $R_o^{liq} = 5.5$. Based on the results in Figure 8-42(a) and 8-43(a) an optimum value of Ra for the CO_2 /ethanol/PC system appears to lie between 11 to $9.5 \text{ MPa}^{1/2}$.

Another set of comparisons, of experimental results at the same temperature and pressure, using a Lewis acid or Lewis base cosolvent that is a known solvent for the PC, are shown in Figures 8-44 and 8-45.

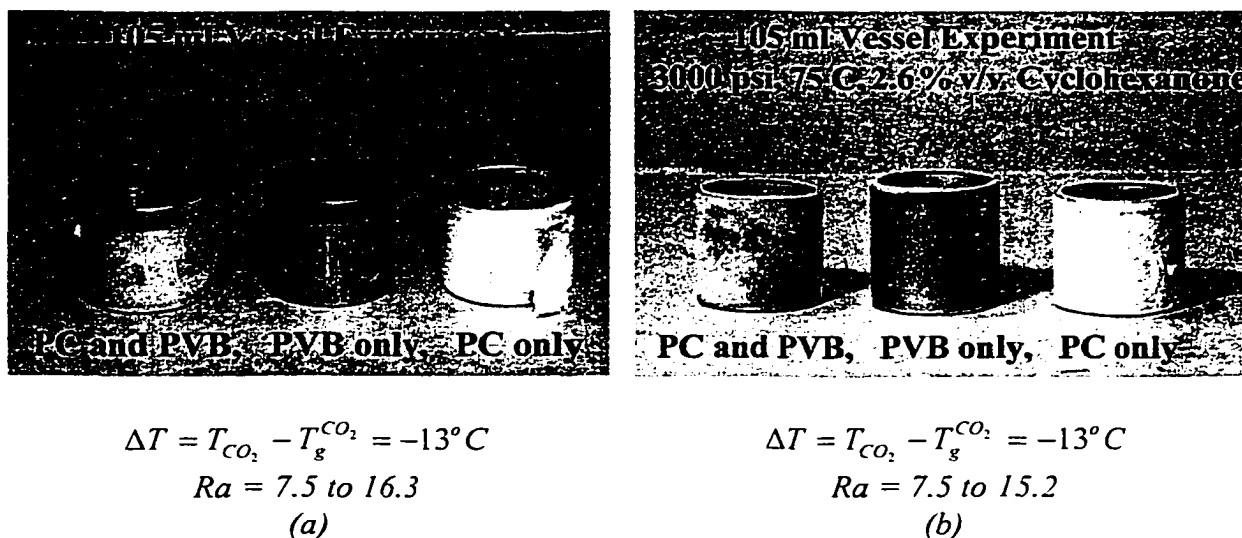
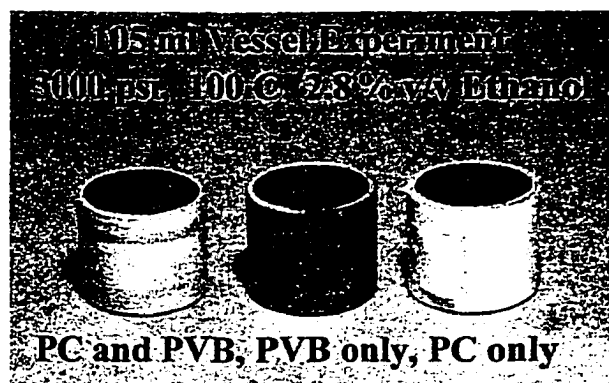


Figure 8-43. (a) Results of CO₂/Lewis acid treatment of polymer coated photoconductor drums, $T = 25$ to $75^\circ C$, $P = 3000$ psi, and ethanol concentration = 3.8 vol.%. (b) Results of CO₂/Lewis base treatment of polymer coated photoconductor drums, $T = 25$ to $75^\circ C$, $P = 3000$ psi, and cyclohexanone concentration = 2.6 vol.%.

As seen in the previous two figures, the result with the Lewis acid cosolvent, debonding of the PC coating, is significantly better than the result observed with the Lewis base cosolvent, flaking of the PC coating. This also indicates a difference between supercritical and liquid solvent environments, as well as the change in the polymer behavior in the two environments. For although identifying typical liquid solvents that are noted to be good solvents for a particular polymer can still provide information in determining the HSP values of a polymer at atmospheric conditions, these same liquid solvents do not necessarily represent good cosolvent selections for the supercritical fluid application discussed here. In Figure 8-45, a similar comparison is made at a higher temperature ($100^\circ C$).

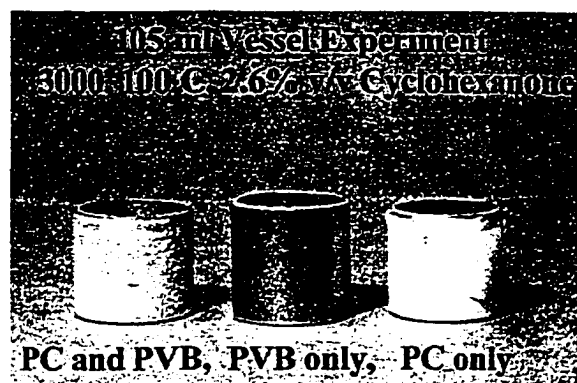
As the temperature is increased from 75°C to 100°C, favorable effects on the PC



$$\Delta T = T_{CO_2} - T_g^{CO_2} = 46^\circ C$$

$$Ra = 6.2 \text{ to } 18.9$$

(a)



$$\Delta T = T_{CO_2} - T_g^{CO_2} = 46^\circ C$$

$$Ra = 6.2 \text{ to } 18.9$$

(b)

Figure 8-44. (a) Results of CO_2 /Lewis acid treatment of polymer coated photoconductor drums, $T = 25$ to $100^\circ C$, $P = 3000$ psi, and ethanol concentration = 2.8 vol.%. (b) Results of CO_2 /Lewis base treatment of polymer coated photoconductor drums, $T = 25$ to $100^\circ C$, $P = 3000$ psi, and cyclohexanone concentration = 2.6 vol.%.

coating are observed with either a Lewis acid or Lewis base cosolvent. At these conditions, the radius of interaction required for PC/SCF systems with Lewis base cosolvents also begins to emerge, and appears to be between 7.5 and $9.5 \text{ MPa}^{1/2}$, as determined from the comparison of Figure 8-44(b) and Figure 8-45(b).

In schematic form, the model predictions of HSP values for PC and CO_2 are plotted in Figure 8-46.

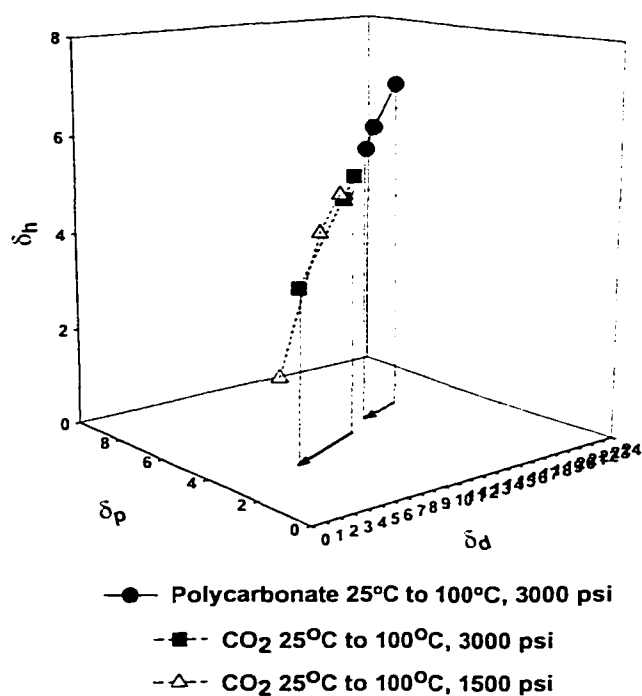


Figure 8-45. Predicted HSP values for PC and CO₂ as the temperature varies from $T = 25$ to 100°C at $P = 1500$ psi and 3000 psi.

From Figure 8-46 it can be seen that the HSP values of PC decrease with increasing temperature and pressure, and are nearest to the HSP values of CO₂ when the CO₂ and/or CO₂/cosolvent enters the pressure vessel at 25°C and 3000 psi. As the CO₂, and or CO₂/cosolvent temperature increases from these initial conditions, to the final vessel temperature, the solvent HSP values decrease, away from the PC values.

In addition to the proximity of the match in HSP's between the PC and solvent, plasitization of the polymer at the experimental temperature and pressure is a factor in predicting favorable results. From Table 8-4, and in the preceding images, it is observed that the greater the ΔT ($T_{\text{CO}_2} - T_g^{\text{CO}_2}$), in combination with a smaller Ra , the more favorable the effect on the PC coating. This emphasizes the importance of polymer

swelling, which can be significant when the polymer is in a rubber rather than glassy state. In addition, the relationship between Ra and ΔT should be appreciated. Whereby, the ability to swell the polymer, which occurs primarily above the polymer T_g , also affects the polymer HSP values in a manner that promotes a favorable interaction radius. This is readily seen in Figure 8-46 where the HSP values of PC, adjusted for temperature, pressure and swelling due to CO_2 absorption (ΔV^{CO_2}), approach those of CO_2 .

In terms of the model framework, complete characterization of the binary pairs (solvent/solvent, polymer/polymer, and solvent/polymer) in terms of HSP values allows for optimization of experimental conditions of temperature and pressure to ensure $Ra < R_o^{liq}$, or $Ra < R_o^{SCF}$ (if known), where $R_o^{liq} < R_o^{SCF}$. This situation, however, assumes experimental capabilities that are not limited by temperature or pressure. Where temperature or pressure limitations are encountered, the experimental results observed in this work indicate the enhanced favorable results are achievable by targeting specific interactions (Lewis acid/base) between a cosolvent and the polymer. This has direct effect not only on the design and construction on new equipment, but also allows facilities with existing equipment to operate supercritical fluid/polymer coating removal applications without new costly capital expenditures.

A direct effect of these interactions is the use of ethanol as a cosolvent in the PC/ CO_2 coatings removal application where removal of the PC coating was achieved in a Ra range of 9.5 to 11 $MPa^{1/2}$, versus a Ra range of 7.5 to 9.5 $MPa^{1/2}$ for the PC/ CO_2 /cyclohexanone system, and a value of less than 6.2 $MPa^{1/2}$ for pure CO_2 or 5.5 $MPa^{1/2}$ for a liquid solvent.

9 Summary and Discussion

9.1 Summary of the Current Work

The use of supercritical fluids for the extraction of organic compounds has been a commercial process for many years. More recently, supercritical fluids are receiving wide attention in manufacturing processes as cleaning solvents and reaction media. This research work has investigated the use of supercritical solvents in yet another area of potential manufacturing application: the removal of polymer coatings by (supercritical) solvent swelling.

The Supercritical Fluids Facility at LANL has engaged in experimental work on a wide range of polymer coatings, applied to a range of substrates. Historically, the experimental approach has been largely trial and error, since no method was available to predict, the effect of a given solvent composition, at arbitrary processing conditions, on an arbitrary polymer/substrate combination. This meant that the amount of necessary experimentation is usually quite large. The situation was doubly problematic since even the data obtained from successful experiments could not be used to benefit subsequent applications, involving other polymers and/or solvent systems. Consequently, the focus of this work has been the development of a model framework, which explains the past experimental results, and which can incorporate these results so that predictions could be made on untested polymer/substrate combinations.

This raises the question as to what the ultimate goal of such a predictive model framework should be. It is intended that the model developed in this work be able to reduce the amount of experimental trials required to achieve a particular supercritical solvent/polymer interaction. Because of the nature of the equipment required to conduct high-pressure experiments/processes, eliminating even a few experimental runs represents a significant cost savings, not only in terms of manpower, but also more importantly in terms of equipment, as high-pressure systems are relatively expensive to maintain and operate.

The model framework, developed and presented in the previous chapters of this dissertation, is built upon (1) the assumption that the molecular interactions present in a three-component system (solvent/cosolvent/polymer) can be accurately described by a suitable combination of the molecular interactions present in a matrix of two-component systems, (2) a means of describing the molecular interactions present in the various two-component systems that is valid over a wide range of temperatures and pressures, and (3) the method used to describe the molecular interactions in the pure components is largely independent on the identity of the pure component. The method chosen to describe the molecular interactions for the pure components is the three-component solubility parameter concept proposed originally by Crowley⁵⁸⁰ and Hansen (HSP).⁵⁸¹ This particular approach was chosen over several alternate possibilities (Section 4-2) because it has been shown to provide a relatively good description of the solubility behavior of a wide range of liquid and gaseous solvents and polymer systems. As a result, a fairly large industrial following has been built up, including the publishing of numerous compilations

of measured and/or calculated solubility parameters, as well as well-developed calculation methods, in the absence of tabulated values.

The development of the model required the development of a methodology for expressing HSP values for solvents and cosolvents in the gaseous, liquid, and supercritical fluid phases, as well as polymers. The approach adopted in this work was to first determine a set of ambient-condition HSP's for the solvent, and then to devise a method of extending this single point in solubility parameter space to any arbitrary temperature and pressure. This entailed the verification of previously available temperature derivative functions, and, for the derivation of novel pressure derivative functions. Such a methodology was developed and demonstrated for pure solvents and cosolvents, using CO₂ as an example. CO₂ has been extensively studied and its use as a supercritical fluid is well established in high-pressure chromatography and fluid extraction applications. The resulting ability to express molecular interactions, in terms of HSP's, for a pure fluid solvent in a way which unites the liquid, gas, and supercritical phases, represents an advancement in understanding the role of solvents in both existing applications, as well as the new, proposed, application (polymer coatings removal). It is important to note that the equations developed are not specific to any particular compound and are applicable to any solvent, cosolvent, or polymer HSP's.

Following the development of temperature- and pressure-dependent HSP's for the pure components, methodologies were developed to combine these pure component HSP's to describe the six, unique pairs of components present in a ternary system (Section 2.3). Also required at this step was the development of a method to describe the

influences of not only temperature and pressure, but also swelling into the resulting polymer HSP's.

Finally, the various two-component HSP descriptions were used to model the behavior of two coatings removal applications involving different solvent/cosolvent/polymer systems. Several organic compounds were evaluated as model cosolvents, including at least one example each of a non-polar fluid, a Lewis acid, and a Lewis base. These examples, allow the evaluation of the relative magnitude of intermolecular effects that can be expected when dealing with a generalized supercritical fluid/polymer system. With the solvent and cosolvent(s) thus fully described by HSP's, mixture values are developed.

The polymers evaluated in this work were selected from two example applications. These polymers are pure and relatively well characterized. In addition, existing experimental data was available for evaluating polymer/solvent interactions, specifically polymer swelling in a supercritical fluid. This is necessary in order to incorporate the change in polymer volume (due to swelling) into the polymer HSP values. Further, as was the case for the polymers evaluated here, the behavior of polymers in a supercritical fluid environment can vary. As will be discussed in the following section, a particular polymers behavior may be predicted with an appropriate polymer/fluid EOS, however, for the development of a descriptive methodology, the use of experimental data alleviates the potential of overlapping models generating a desired outcome.

Use of HSP values for new applications generally involve matching parameters between two (or more) components in terms of some previously defined radius of interaction. The radius of interaction used for the polymers in this research are based on

the dissolution behavior of these polymers in organic liquid solvents, R_o^{liq} . The direct applicability of this radius for polymer/supercritical fluid interactions is not known, but based on the results of this work, a larger interaction radius (R_o^{SCF}) appears to be available for the prediction of favorable interactions. As with the database generated overtime and as a result of numerous polymer/liquid evaluations for the determination of R_o^{liq} , the creation of a similar database for polymer/supercritical fluid systems, R_o^{SCF} , will be necessary to increase the usability of the model framework developed here.

Chapter 8 serves as a compilation and review between the observed, experimental results, and the effects that would be predicted by the current model. In the first general application, photoresist on silicon wafers, the experimental result was known and the model predicted favorable results for both the experimental conditions – in agreement with experiments. The second general application, polymer film on aluminum drums, an application where the answer was not known, but the polymer was well characterized, the model predictions were consistent with experimental results at different temperatures and pressures.

Results of the research indicate significant promise in the use of supercritical fluids for replacement of organic liquid solvents for polymer coating removal applications. In terms of the goal of reducing the amount of required experimentation, predictive capabilities are attainable for supercritical fluid/polymer systems, where the steps undertaken in this work are carried out and no equipment limitations in terms of temperature or pressure are encountered. Specifically, full characterization of the solvent and polymer in terms of HSP values, and matching these components such that $Ra < R_o^{liq}$, allows the development of a very narrowly defined experimental matrix. This is a

significant improvement over the current trial and error approach, and greatly reduces the required experimentation.

If equipment limitations are a factor, or if reduction of the required temperature and/or pressure is desirable for a particular application, this research demonstrates that the use of cosolvents, specifically cosolvents chosen to target specific interactions (Lewis acid/base) with the polymer, broadens the temperature and pressure range where favorable effects are achievable. A complete understanding of these effects, and a quantitative incorporation of these interactions into the model framework will required further research and is a consideration in Section 9.2

It is highly unlikely that a predictive model will ever be developed that would eliminate all experimentation, simply because of the range of solvents, cosolvents, and polymers that would be encountered in real applications. However, it is entirely possible that the proposed model framework could be expanded and refined to encompass more and more experimental situations, and provide increasing levels of predictive accuracy. To achieve this goal of a comprehensive model, the areas of expertise that would need to be enlisted will be described.

1. Supercritical (and high-pressure) fluids, including the design and operation of high-pressure experimental equipment; solubility parameters, including the development of equipment to make measurements on both fluids and polymers; polymer chemistry, including the measurement of composition (if the polymer is not pure) T_g (and its variation with both T and P), molecular weight, morphology (degree of crystallinity), cross-link density, as well as measurements of thermal expansion coefficient and compressibility, and their temperature and pressure variation (if extensive PVT data

are not available or are not measured). Expertise in polymer equations of state might well be required to either transform the measured PVT into a form amenable to automation, or to make use of data available for a similar polymer.

2. Organic chemistry, to understand the behavior of conventional liquid solvents, as well as the behavior of solvent mixtures, and perhaps the synthesis of new solvents, tailored to specific situations.
3. Thermodynamics, including the measurement of PVT data over a useful range of T and P, and the determination or development of methods to predict physical parameters such as thermal expansion coefficient and compressibility, as well as their temperature and pressure variation, especially for those compounds intended as the minority component of a supercritical solvent.

It will also be necessary to generate vapor-liquid equilibrium measurements for binary (or higher-order) solvent-cosolvent systems in which published data are not available.

Phase equilibria models, including VLE models, will have to be brought to bear which can accommodate the behavior of complex, possibly multicomponent, liquid-liquid and liquid-polymer systems. This would most certainly include models for describing phase equilibria behavior of polymers exposed to supercritical fluids, such as swelling, solvent sorption, and glass transition depression.

All of these areas have been touched on in the basic model developed in this work. It remains only to incorporate these improvements. This will be discussed as future work.

9.2 *Suggestions for Future Work*

The development of HSP values for CO₂ was initiated with total solubility parameter values determined using fundamental thermodynamics and a CO₂ EOS. The use of a more accurate CO₂ EOS, such as that given by the IUPAC⁵⁸², may be available and an area of future research may explore this issue in greater detail. However, the methodology developed in this work is not limited to, nor is it specific to, CO₂. Therefore, depending on the particular application, solvent selection can include a range of fluids for which the same framework considered here can be used. Appendix D contains an alternative EOS reference for CO₂, as well as EOS references for other fluids which might see use as a supercritical fluid solvent: argon, nitrogen, water, ammonia, and toluene.

The use of thermodynamics for the development of solubility parameter values for a given fluid, however, requires consideration in the applicability of equating internal pressure to cohesive energy density. As noted in Chapter 4, these two quantities are fundamentally different, especially for highly polar fluids or molecules which exhibit specific interactions. Therefore, future work should include research into a means of either evaluating directly through a correlation with other properties the ratio of internal pressure to cohesive energy density (n). A proposed concept is a relationship correlating n with a fluid's dielectric constant.

For the determination of the CO₂ HSP values an extensive evaluation of CO₂ gas solubility was conducted (Appendix B, Table B-3) and from this one set of HSP values was derived. Two comments are worth noting in this determination. First is the method used for optimizing the data set. More sophisticated optimization techniques are, of

course, available, however the focus of this work was to illustrate the idea of the determination of a set of HSP's using solubility data. If additional experimentation data were made available on the solubility of CO₂ in a wider range of solvents for which the CO₂ solubility were high, such improved optimization techniques would be worth pursuing. A more difficult, although perhaps more interesting issue is the implicit assumption of equating the HSP value to that of the solvent in which it is found to have the greatest solubility, and whether there is such a thing as a perfect solvent for CO₂. In a "perfect" solvent, the solvent/solvent forces and solute/solute forces must be of similar type and magnitude if solvent/solute interactions are just as likely to occur as the self-associations, in essence an ideal mixture. And yet HSP's do not necessarily represent all the subtleties of intermolecular interactions, they are instead a generalized tool whose use has been promoted by their balance between accuracy and simplicity. Solvents, therefore, which exactly match the HSP's of CO₂, may not even then represent all of the intermolecular interactions of that compound! These theories could be pursued with research directed towards building or manufacturing "perfect" or "ideal" solvents, and subsequently polymers as well, to develop compounds which result in HSP values (or some other quantification of intermolecular interactions) for CO₂.

Another key in the applicability of this research is characterization of polymers to be processed by a solvent. This is because while the prediction of favorable or unfavorable interactions with CO₂ can be initiated from an analysis of the polymer chemical structure, including type and location of functional groups, the polymer's behavior following the sorption of CO₂ is difficult to predict. As exhibited in two of the polymers studied in this work, PMMA and PC, very different behavior can occur as a

result of changes in temperature and pressure during CO₂ sorption. From the literature, it was observed that PMMA initially solubilizes a large amount of CO₂, resulting in considerable swellings and significant depressions in T_g . However this behavior changes with increasing temperature, where PMMA sorption of CO₂ decreases, a behavior characteristic of systems possessing a lower critical solution temperature. Alternatively, PC sorption of CO₂ increases with increasing temperature, a behavior of systems possessing an upper critical solution temperature. Further understanding in these opposite behaviors is necessary, and the contribution of collaborative efforts with a polymer scientist would be extremely valuable in continuing this work.

The need for a model to describe polymer sorption behavior was circumvented by the use of experimental sorption data available in the literature. An improvement in this approach however, would be the use of models which can be used to describe equilibrium behavior of polymer phases exposed to gases, such as swelling, solvent sorption, and glass-transition temperature depression for glassy and rubbery polymers. Models for polymer phase equilibrium calculations fall into two general areas; lattice theories and cubic EOS's.

Lattice theories have been developed from the quasicrystalline nature of polymers. For although polymers are considered liquid like when in a rubbery state, each molecule also tends to stay in a small region, a more or less fixed position in space, about which it vibrates back and forth. The quasicrystalline picture of the liquid state supposes molecules to sit in a regular array in space, called a lattice, and therefore theories of polymers and polymer mixtures are called lattice theories.⁵⁸³ One of the best known attempts to formulate a model for these systems was the Flory-Huggins lattice model.⁵⁸⁴

Other lattice theories evolved out of this work, including the Sanchez-Lacombe EOS^{585,586} and the Panayioutou-Vera EOS.^{587,588} Alternatively, polymer/fluid systems are also modeled with cubic EOS's. Two references for this type of approach include: (1) a modification of the SRK EOS,⁵⁸⁹ and (2) a modification of the PR EOS.⁵⁹⁰

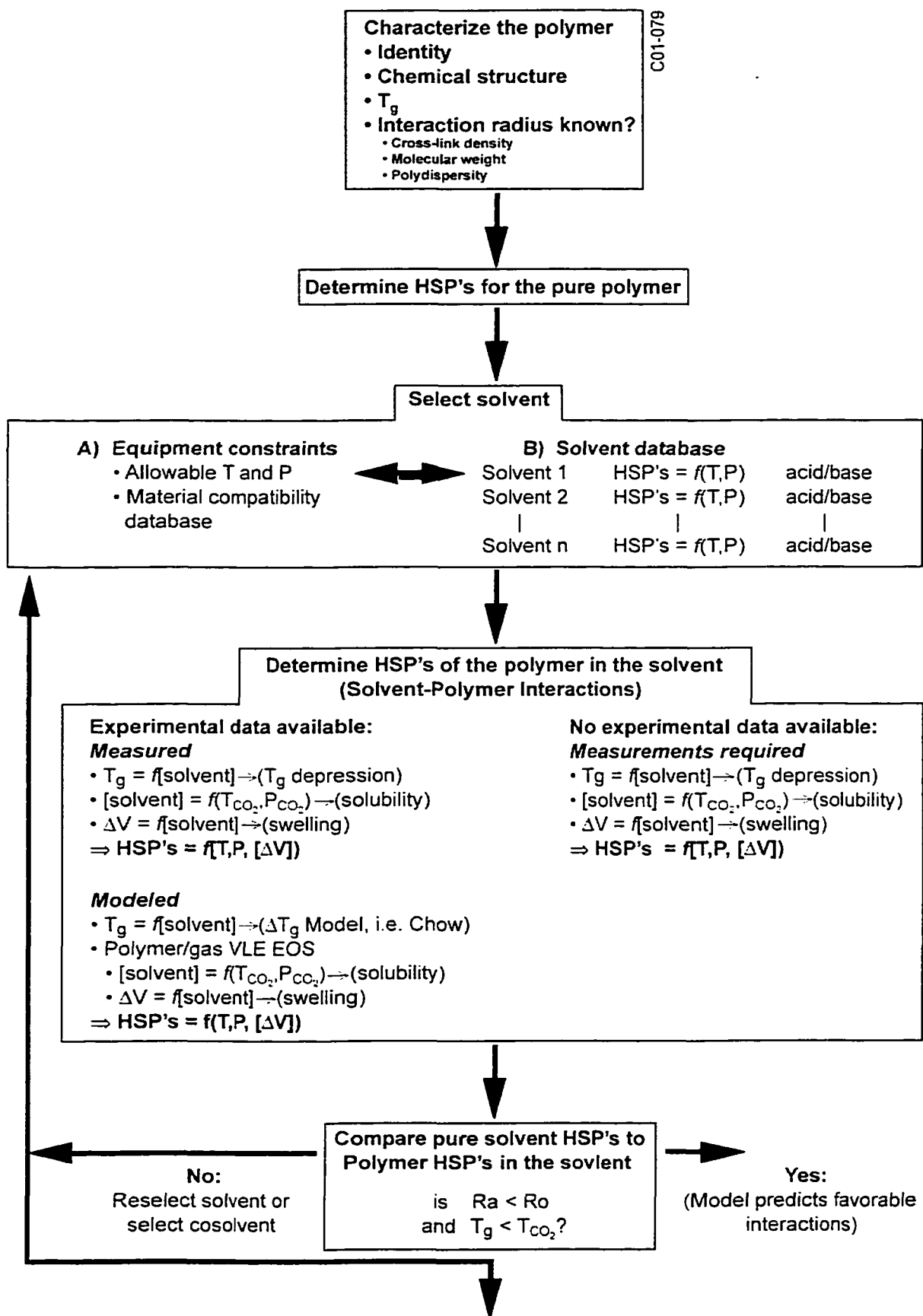
A suggestion in future work would incorporate these theoretical methods, to develop a larger polymer/SCF database. This will quickly expand the polymer/solvent systems which can be evaluated and greatly enhance the models usability. The successful incorporation of modeled data can potentially include EOS for all the systems evaluated. Such systems would include: (1) Pure Fluids (either liquid or gas) EOS, such as the Huang EOS used in this work or those referenced in appendix D; (2) Vapor/Liquid Equilibria for supercritical fluid/cosolvent mixtures such as the Redlich-Kwong EOS, the Soave-Redlich-Kwong EOS, or the Peng-Robinson EOS, with appropriate mixing rules; (3) Pure polymer EOS as outlined in Section 5.5.1; and (4) Polymer/Fluid Equilibria, discussed above.

Systems that are not suited to theoretical modeling must also be addressed. This will require equipment and experimentation techniques capable of generating the data needed to optimize the conditions for the desired effect. Specific measurements required include; polymer glass transition behavior in the SCF or SCF mixture environment, polymer sorption of the SCF or SCF mixture as a function of temperature and pressure, and polymer swelling as a result of solvent sorption as a function of temperature and pressure. Additionally, purpose built equipment, capable of precisely measuring the temperature of the polymer film, as well as the solvent throughout the experiment is essential. This in combination with a visual indication, or some other experimental

evidence of precisely when the polymer coating is removed or effected in a desirable manner, is necessary to accurately develop experimental and ultimately industrial testing. This is also necessary for building a supercritical fluid radius of interaction database.

Where it is necessary to use cosolvents to promote polymer coatings removal, experimental results in Chapter 8 indicate that cosolvents capable of interactions such as hydrogen bonding or Lewis acid/base complexing with the polymer should be considered. However, the ability to predict this type of enhanced interaction was not quantified in this research. Therefore, a suggestion for future research is an incorporation of the cosolvent effect (above the slight increase in the mixture HSP values), into the model framework. Such incorporation might take the shape of a quantified cosolvent “factor”, developed from an expanded cosolvent experimental matrix or investigations into the partitioning of the cosolvent towards the polymer phase. A method currently being used to measure the partitioning of cosolvents is an in-situ Fourier transform IR and UV-vis spectroscopy.⁵⁹¹ This type of data, for inclusion of a more developed model would be useful.

Figure 9-1 illustrates the use of the model framework, for any solvent/cosolvent/polymer system, and briefly touches upon potential areas of future work.



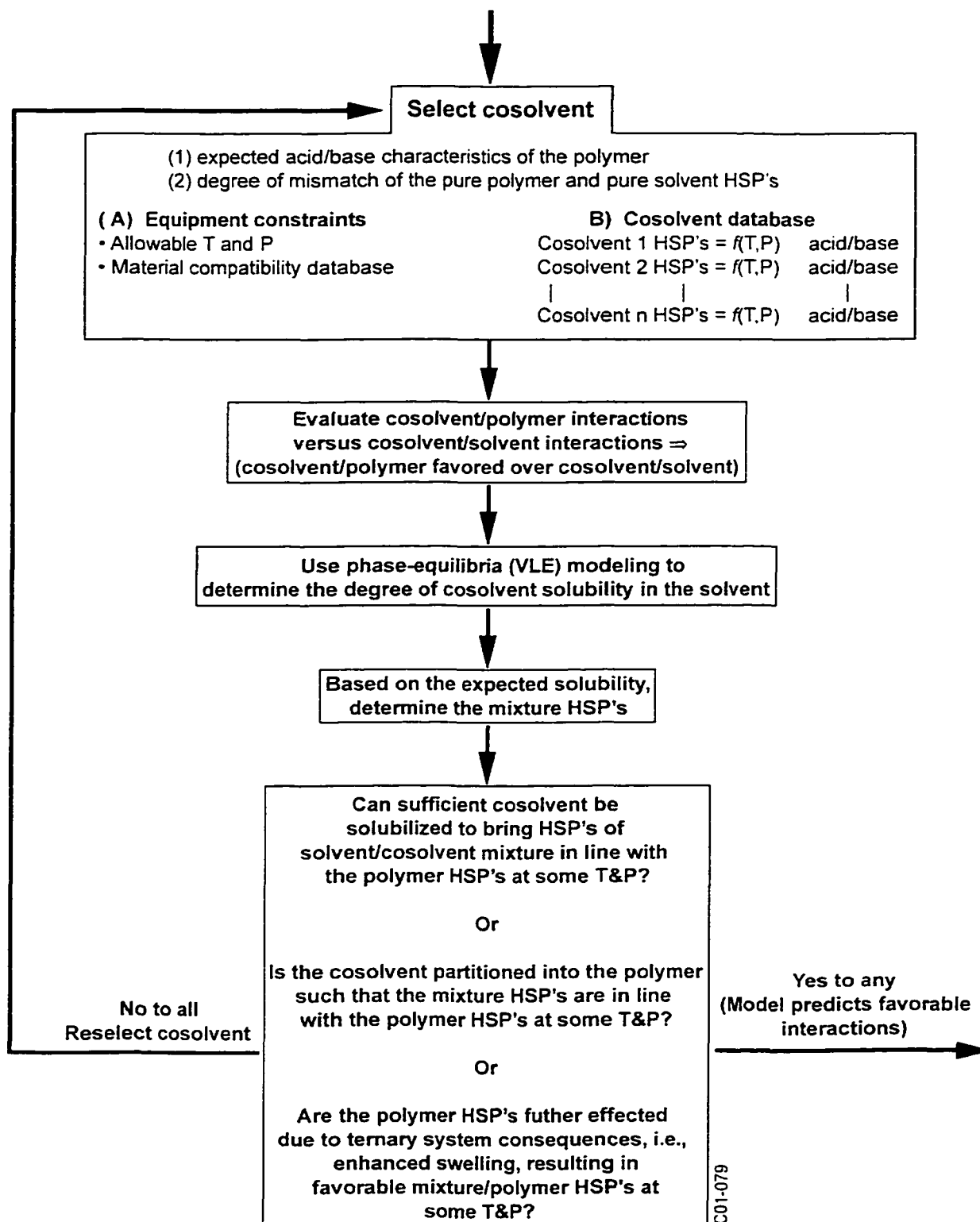


Figure 9-1 Model framework flow diagram.

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Appendix A: Empirical EOS for CO₂ and the Calculation of the Thermal Pressure Coefficient, Thermal Expansion Coefficient, and Isobaric Compressibility

The total solubility parameter for a pure fluid can be calculated using PVT data. From the thermodynamic equation of state, and the definition of the total solubility parameter,

$$\delta^2 \approx \left(\frac{\partial E}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_P - P \quad (\text{A-1})$$

Total (1-component) solubility parameters for CO₂ are calculated using the empirical equation of state (EOS) of Huang *et al.*¹ :

$$P = \rho R T \left[\begin{aligned} &1 + b_2 \rho' + b_3 \rho'^2 + b_4 \rho'^3 + b_5 \rho'^4 + b_6 \rho'^5 + b_7 \rho'^2 \exp(-c_{21} \rho'^2) + b_8 \rho'^4 \exp(-c_{21} \rho'^2) \\ &+ c_{22} \rho'^2 \exp[-c_{27} (\Delta T)^2] + c_{23} \frac{\Delta \rho}{\rho'} \exp[-c_{25} (\Delta \rho)^2 - c_{27} (\Delta T)^2] \\ &+ c_{24} \frac{\Delta \rho}{\rho'} \exp[-c_{26} (\Delta \rho)^2 - c_{27} (\Delta T)^2] \end{aligned} \right] \quad (\text{A-2})$$

where

$$T' = T/T_c; \quad \Delta T = 1 - T'; \quad \rho' = \rho/\rho_c; \quad \Delta \rho = 1 - 1/\rho' \quad (\text{A-3})$$

Table A-1. Huang Equation of State Constants, C_i .

i	C_i	i	C_i
1	0.376194	15	-2.79498
2	0.118836	16	5.62393
3	-3.04379	17	-2.93831
4	2.27453	18	0.988759
5	-1.23863	19	-3.04711
6	0.250442	20	2.32316
7	-0.115350	21	1.07379
8	0.675104	22	-0.599724×10^{-4}
9	0.198861	23	0.885339×10^{-4}
10	0.216124	24	0.316418×10^{-2}
11	-0.583148	25	10
12	0.119747×10^{-1}	26	50
13	0.537278×10^{-1}	27	80,000
14	0.265216×10^{-1}		

and,

$$\begin{aligned}
 b_2 &= \left(c_1 + \frac{c_2}{T} + \frac{c_3}{T^2} + \frac{c_4}{T^3} + \frac{c_5}{T^4} + \frac{c_6}{T^5} \right); & b_6 &= \left(\frac{c_{14}}{T} \right) \\
 b_3 &= \left(c_7 + \frac{c_8}{T} + \frac{c_9}{T^2} \right); & b_7 &= \left(\frac{c_{15}}{T^3} + \frac{c_{16}}{T^4} + \frac{c_{17}}{T^5} \right) \\
 b_4 &= \left(c_{10} + \frac{c_{11}}{T} \right); & b_8 &= \left(\frac{c_{18}}{T^3} + \frac{c_{19}}{T^4} + \frac{c_{20}}{T^5} \right) \\
 b_5 &= \left(c_{12} + \frac{c_{13}}{T} \right)
 \end{aligned} \tag{A-4}$$

The thermal pressure coefficient, or $\left(\frac{\partial P}{\partial T} \right)_r$, is calculated using

$$\left(\frac{\partial P}{\partial T} \right)_r = \frac{P}{T} + \rho RT \left[\begin{aligned} & x_2 \rho + x_3 \rho^2 + x_4 \rho^3 + x_5 \rho^4 + x_6 \rho^5 + x_7 \rho^2 \exp(-c_{21} \rho^2) + \\ & x_8 \rho^4 \exp(-c_{21} \rho^2) + (c_{22} \rho \exp(-c_{27} \Delta T^2)) (-x_9 c_{27} 2 \Delta T) + \\ & \left(c_{23} \frac{\Delta \rho}{\rho} \exp(-c_{25} \Delta \rho^2 - c_{27} \Delta T^2) \right) (-x_9 c_{27} 2 \Delta T) + \\ & \left(c_{24} \frac{\Delta \rho}{\rho} \exp(-c_{26} \Delta \rho^2 - c_{27} \Delta T^2) \right) (-x_9 c_{27} 2 \Delta T) \end{aligned} \right] \tag{A-5}$$

where,

$$\begin{aligned}
 x_2 &= -\frac{1}{T_c} \left(\frac{c_2}{T'^2} + \frac{2c_3}{T'^3} + \frac{3c_4}{T'^4} + \frac{4c_5}{T'^5} + \frac{5c_6}{T'^6} \right); & x_6 &= -\frac{1}{T_c} \left(\frac{c_{14}}{T'^2} \right) \\
 x_3 &= -\frac{1}{T_c} \left(\frac{c_8}{T'^2} + \frac{2c_9}{T'^3} \right); & x_7 &= -\frac{1}{T_c} \left(\frac{3c_{15}}{T'^4} + \frac{4c_{16}}{T'^5} + \frac{5c_{17}}{T'^6} \right) \\
 x_4 &= -\frac{1}{T_c} \left(\frac{c_{11}}{T'^2} \right); & x_8 &= -\frac{1}{T_c} \left(\frac{3c_{18}}{T'^4} + \frac{4c_{19}}{T'^5} + \frac{5c_{20}}{T'^6} \right) \\
 c_5 &= -\frac{1}{T_c} \left(\frac{c_{13}}{T'^2} \right); & x_9 &= -\frac{1}{T_c}
 \end{aligned} \tag{A-6}$$

The isothermal compressibility, or $\left(\frac{\partial V}{\partial P} \right)_T$, is calculated using

$$V = \frac{RT}{P} \left[\begin{aligned} &1 + b_2 \rho' + b_3 \rho'^2 + b_4 \rho'^3 + b_5 \rho'^4 + b_6 \rho'^5 + b_7 \rho'^2 \exp(-c_{21} \rho'^2) + b_8 \rho'^4 \exp(-c_{21} \rho'^2) \\ &+ c_{22} \rho'^2 \exp[-c_{27} (\Delta T)^2] + c_{23} \frac{\Delta \rho}{\rho'} \exp[-c_{25} (\Delta \rho)^2 - c_{27} (\Delta T)^2] \\ &+ c_{24} \frac{\Delta \rho}{\rho'} \exp[-c_{26} (\Delta \rho)^2 - c_{27} (\Delta T)^2] \end{aligned} \right]$$

$$\begin{aligned}
\left(\frac{\partial V}{\partial P}\right)_T = & -\frac{RT}{P^2} \left[1 + b_2 \rho' + b_3 \rho'^2 + b_4 \rho'^3 + b_5 \rho'^4 + b_6 \rho'^5 + b_7 \rho'^2 \exp(-c_{21} \rho'^2) + b_8 \rho'^4 \exp(-c_{21} \rho'^2) \right. \\
& + c_{22} \rho'^2 \exp[-c_{27} (\Delta T)^2] + c_{23} \frac{\Delta \rho}{\rho'} \exp[-c_{25} (\Delta \rho)^2 - c_{27} (\Delta T)^2] \\
& \left. + c_{24} \frac{\Delta \rho}{\rho'} \exp[-c_{26} (\Delta \rho)^2 - c_{27} (\Delta T)^2] \right] \\
\frac{RT}{P} & \left[-b_2 \frac{v_c}{v^2} - 2b_3 \frac{v_c^2}{v^3} - 3b_4 \frac{v_c^3}{v^4} - 4b_5 \frac{v_c^4}{v^5} - 5b_6 \frac{v_c^5}{v^6} - 2b_7 \frac{v_c^2}{v^3} \exp\left(-c_{21} \frac{v_c^2}{v^2}\right) + \right. \\
& 2b_7 c_{21} \frac{v_c^4}{v^5} \exp\left(-c_{21} \frac{v_c^2}{v^2}\right) - 4b_8 \frac{v_c^4}{v^5} \exp\left(-c_{21} \frac{v_c^2}{v^2}\right) + 2b_8 \frac{v_c^6}{v^7} \exp\left(-c_{21} \frac{v_c^2}{v^2}\right) - \\
& c_{22} \frac{v_c}{v^2} \exp(-c_{27} \Delta T^2) + c_{23} \left(\frac{1}{v_c} - \frac{2v}{v_c^2}\right) \exp\left(-c_{25} \left(1 - \frac{v}{v_c}\right)^2 - c_{27} \Delta T^2\right) + \\
& 2c_{23} c_{25} \left(\frac{v}{v_c} - \frac{v^2}{v_c^2}\right) \left(\frac{1}{v_c} - \frac{v}{v_c^2}\right) \exp\left(-c_{25} \left(1 - \frac{v}{v_c}\right)^2 - c_{27} \Delta T^2\right) + \\
& c_{24} \left(\frac{1}{v_c} - \frac{2v}{v_c^2}\right) \exp\left(-c_{26} \left(1 - \frac{v}{v_c}\right)^2 - c_{27} \Delta T^2\right) + \\
& \left. 2c_{24} c_{26} \left(\frac{v}{v_c} - \frac{v^2}{v_c^2}\right) \left(\frac{1}{v_c} - \frac{v}{v_c^2}\right) \exp\left(-c_{26} \left(1 - \frac{v}{v_c}\right)^2 - c_{27} \Delta T^2\right) \right]
\end{aligned}
\tag{A-7}$$

The isobaric thermal expansion coefficient, or $\left(\frac{\partial V}{\partial T}\right)_P$, is calculated using

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{\left(\frac{\partial P}{\partial T}\right)_V}{-\left(\frac{\partial P}{\partial V}\right)_T}
\tag{A-8}$$

where

$$\left(\frac{\partial P}{\partial v}\right)_T = -\frac{P}{v} - \frac{RT}{v} \left[\begin{aligned} & b_2 \frac{v_c}{v^2} + 2b_3 \frac{v_c^2}{v^3} + 3b_4 \frac{v_c^3}{v^4} + 4b_5 \frac{v_c^4}{v^5} + 5b_6 \frac{v_c^5}{v^6} + 2b_7 \frac{v_c^2}{v^3} \exp\left(-c_{21} \frac{v_c^2}{v^2}\right) - \\ & 2b_7 c_{21} \frac{v_c^4}{v^5} \exp\left(-c_{21} \frac{v_c^2}{v^2}\right) + 4b_8 \frac{v_c^4}{v^5} \exp\left(-c_{21} \frac{v_c^2}{v^2}\right) - 2b_8 \frac{v_c^6}{v^7} \exp\left(-c_{21} \frac{v_c^2}{v^2}\right) + \\ & c_{22} \frac{v_c}{v^2} \exp(-c_{27} \Delta T^2) - c_{23} \left(\frac{1}{v_c} - \frac{2v}{v_c^2}\right) \exp\left(-c_{25} \left(1 - \frac{v}{v_c}\right)^2 - c_{27} \Delta T^2\right) - \\ & 2c_{23} c_{25} \left(\frac{v}{v_c} - \frac{v^2}{v_c^2}\right) \left(\frac{1}{v_c} - \frac{v}{v_c^2}\right) \exp\left(-c_{25} \left(1 - \frac{v}{v_c}\right)^2 - c_{27} \Delta T^2\right) - \\ & c_{24} \left(\frac{1}{v_c} - \frac{2v}{v_c^2}\right) \exp\left(-c_{26} \left(1 - \frac{v}{v_c}\right)^2 - c_{27} \Delta T^2\right) - \\ & 2c_{24} c_{26} \left(\frac{v}{v_c} - \frac{v^2}{v_c^2}\right) \left(\frac{1}{v_c} - \frac{v}{v_c^2}\right) \exp\left(-c_{26} \left(1 - \frac{v}{v_c}\right)^2 - c_{27} \Delta T^2\right) \end{aligned} \right] \quad (\text{A-9})$$

and $\left(\frac{\partial P}{\partial T}\right)_v$ is given by eqns. (A-5) and (A-6).

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- 1 Huang, F., Li, M., Lee, L., and Starling, K., 1985. *An Accurate Equation of State for Carbon Dioxide*, Journal of Chemical Engineering of Japan, Vol. 18, No. 6.

Appendix B : Ideal Solubility of Gases in Liquids and Published CO₂ Solubility Data.

Published CO₂ gas solubility data in 103 liquid solvents was gathered from the available literature and is presented in Table B-3. Two of these solvents, triethylamine and 1,4-dioxane were subsequently deleted from the data set based on their known tendency to chemically react with CO₂, similar to the type of reaction shown in Section 2.2¹ All of the solubility data shown in Table B-3 was either experimentally determined at 25°C and a CO₂ partial pressure of 1 atmosphere, or, where the literature solubility data was reported at p_{CO_2} other than 1 atmosphere were converted to $p_{\text{CO}_2} = 1$ atm using Henry's law, eqn. (B-1).²

$$x_2 = \frac{p_2}{K_H} \quad (\text{B-1})$$

Where K_H is the Henry's law coefficient, p_2 is the partial pressure of the gas, and x_2 is the mole fraction of dissolved gas. Henry's Law, applicable for dilute solutions, states that the amount of gas which dissolves in a liquid is proportional to its partial pressure³

The literature data on CO₂ gas solubility is reported in several ways. Generally, solubilities were reported as the mole fraction of dissolved CO₂, x_2 , or as one of two dimensionless quantities; the Bunsen coefficient or the Ostwald coefficient. The Bunsen coefficient, Ω , is defined as the volume of gas, reduced to 0°C and 1 atmosphere, dissolved per unit volume of solvent at a system temperature T under a gas pressure of 1 atmosphere. The Ostwald coefficient, L , is defined as the ratio of the volume of gas

absorbed to the volume of the absorbing liquid, all measured at the same temperature.⁴ If the solubility is small and the gas phase is ideal, the Ostwald coefficient is independent of P and these two coefficients are simply related by.⁵

$$L = \frac{T}{273} \Omega \quad (\text{B-2})$$

The mole fraction of dissolved CO_2 can then be calculated using⁶

$$x_2 = \left[\left(\frac{RT}{Lp_2V_1^0} \right) + 1 \right]^{-1} \quad (\text{B-3})$$

where R is the gas constant, T is the absolute temperature, p_2 the partial pressure of the gas, and V_1^0 the molar volume of the pure solvent. This equation assumes ideal gas behavior.

Mole fraction CO_2 solubility, solvent property values, literature Hansen solubility parameter values, Ostwald coefficients, and the gas solubility reference are tabulated and follow this discussion.

Ideal Solubility of Gases in Liquids

Solutions which come close to approximating ideal solutions are those which are very dilute, or those where the molecular species are so nearly alike that a given molecule is subject to the same intermolecular forces (both attractive and repulsive) in the mixture as in its own pure phase. (In very dilute solutions, the intermolecular forces on a solute molecule may be quite different than in the pure solute phase, but the solute molecules are far enough apart that solute-solute interactions do not manifest themselves.) The

concept of an ideal solution is often an appropriate approximation for gases dissolved in liquids, since at modest pressures, most gases are only sparingly soluble in typical liquids⁷.

Thermodynamically, an ideal solution is defined as one in which the activity, a , equals the mole fraction, x_i , over the entire composition range and over a nonzero range of temperature and pressure.⁸

$$x_i = a_i = \frac{f_i}{f_i^o} \quad (\text{B-4})$$

The activity of a substance gives an indication of how “active” a substance is relative to its standard state since it provides a measure of the difference in chemical potential at the state of interest and that at the standard state.⁹ The term fugacity, f , was introduced by Lewis¹⁰ as a measure of thermodynamic escaping tendency and is equal to the effective gas pressure corrected for deviations from ideality. In eqn. (B-4) f_i is the fugacity of component i at partial pressure p_i , and f_i^o is the fugacity at the saturation pressure of i , P_i^s , at the solution temperature. Equation (B-4) is an empirical rule suggested by Lewis and Randall¹¹ that assumes imperfect gas mixtures behave as ideal mixtures.

When deviations from the ideal gas law are small, generally at low pressures, then the effect of pressure on the fugacity of component i is negligible and the fugacity terms in eqn. (B-4) approach the partial pressure and saturation pressure of i , respectively. In this situation, therefore, the ratio of the partial pressure and saturation pressure can now be used to express the mole fraction, x_i .

$$x_i = \frac{p_i}{P_i^s} \quad (\text{B-5})$$

Equation (B-5) is known as Raoult's law, and the mole fraction, as calculated from Raoult's law, is referred to as the ideal gas solubility. The ideal solubility calculated from eqn. (B-5) usually gives correct order of magnitude results provided that P_i^s is not large and the solution temperature is well below the critical temperature of the solvent and not excessively above the critical temperature of the gaseous solute.¹² Table B-1 evaluates the ideal solubility of CO₂ calculated using eqn. (B-5) for the temperature range 0°C to 30°C.

Table B-1. Ideal Carbon Dioxide Solubility Calculated using Raoult's law, $p_{\text{CO}_2} = 1 \text{ atm}$.

T (°C)	$P_{\text{CO}_2}^s$ (atm)	$x_{\text{CO}_2}^{\text{ideal}} = 1/P_{\text{CO}_2}^s$
0	34.40	0.0291
15	50.19	0.0199
20	56.60	0.0177
25	63.50	0.0157
30	71.12	0.0141

From Table B-1, Raoult's law predicts an ideal CO₂ solubility of $x_{\text{CO}_2}^{\text{ideal}} = 0.0157$ at T = 25°C, and this value has been used in several of the published CO₂ solubility studies.^{13,14,15}

It has been noted by Prausnitz, *et al.*,¹⁶ that the simplest way to reduce eqn. (B-4) to a more useful form is to rewrite it in the manner suggested by Raoult's law, eqn. (B-5). In doing so, however, they caution that several assumptions are made, and errors in the use of this estimation technique for the solubility of gases in liquids can be significant, especially when the saturation pressure of the gas is high. Therefore, in cases where the saturation pressure of the gas is above 1 atmosphere, it is necessary to consider the error in using p_i/P_i^s instead of f_i/f_i^o . Table B-2 gives the saturation pressures of CO₂ for

the temperature range 0°C to 30°C, as well as the fugacities and calculated ideal solubilities using both methodologies.

Table B-2. Ideal Carbon Dioxide Solubility Calculated using Raoult's law and Fugacities, $p_{CO_2} = 1$ atmosphere.

T (°C)	$P_{CO_2}^s$ (atm)	f_{CO_2} $p_{CO_2} = 1$ atm	$f_{CO_2}^o$ at $P_{CO_2}^s$	$x_{CO_2}^{ideal}$ $= 1/P_{CO_2}^s$	$x_{CO_2}^{ideal}$ $= f_{CO_2}/f_{CO_2}^o$	% Diff.
0	34.4	.9928	26.51	0.0291	0.0375	28
15	50.19	.9941	36.04	0.0199	0.0276	39
20	56.6	.9944	39.6	0.0177	0.0251	42
25	63.5	.9947	43.3	0.0157	0.0229	46
30	71.12	.9950	47.17	0.0141	0.0211	49

From Table B-2 it appears that the assumption of Raoult's law for the determination of ideal CO₂ solubility in liquids results in significant error. The ideal CO₂ solubility at 25°C and 1 atmosphere partial pressure as calculated from CO₂ fugacities¹⁷ is $x_{CO_2}^{ideal} = 0.0229$, compared with a Raoult's law prediction of $x_{CO_2}^{ideal} = 0.0157$. This value was also used by Gjalkbaek *et al.*^{18,19} in their work comparing experimental and calculated CO₂ gas solubilities.

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Appendix B: Table B-3: Literature Values of CO₂ gas solubility in Liquids.

CO ₂ solubility in various solvents											
Ideal Solubility		298.15		mole frac CO ₂	Actual/ Ideal 1						
						δ_D (Mpa) ^{1/2}	δ_P (Mpa) ^{1/2}	δ_H (Mpa) ^{1/2}	δ_T (Mpa) ^{1/2}		
Formula	Solvent	Temp (K)	Pvap	mole frac CO ₂		Ref ¹	Ref ¹	Ref ¹	Calc	Ostwald Coeff.	Ref
C2H4O2	Acetic Acid	298.15	0.9795	0.010894	0.4757	14.50	8.00	13.50	21.37	4.679	2
C2H4O2	Acetic Acid	298.15	0.9795	0.011219	0.4899	14.50	8.00	13.50	21.37	4.82	3
C4H6O3	Acetic Anhydride	298.15	0.9928	0.019774	0.8635	16.00	11.70	10.20	22.29	5.206	4
C3H6O	Acetone	298.15	0.6998	0.018763	0.8193	15.50	10.40	7.00	19.94	6.295	5
C3H6O	Acetone	298.15	0.6998	0.019028	0.8309	15.50	10.40	7.00	19.94	6.385	6
C3H6O	Acetone	298.15	0.6998	0.018960	0.8279	15.50	10.40	7.00	19.94	6.385	7
C3H6O	Acetone	298.15	0.6998	0.018959	0.8279	15.50	10.40	7.00	19.94		8
C3H6O	Acetone	298.15	0.6998	0.022591	0.9865	15.50	10.40	7.00	19.94	7.6	9
C3H6O	Acetone	298.15	0.6998	0.020922	0.9136	15.50	10.40	7.00	19.94	7.03	10
C7H14O2	Amyl Acetate	298.15	0.9954	0.028000	1.2227	15.80	3.30	6.10	17.26		11
C7H14O2	Amyl Acetate	298.15	0.9954	0.024522	1.0708	15.80	3.30	6.10	17.26	4.119	12
C7H14O2	Amyl Acetate	298.15	0.9954	0.026122	1.1407	15.80	3.30	6.10	17.26	4.395	13
C5H11Br	Amylbromide	298.15	0.9858	0.012353	0.5394	20.30	4.80	2.80	21.05	2.455	14
C5H11Cl	Amylchloride	298.15	0.9571	0.014244	0.6220	15.50	5.00	1.30	16.34	2.91	15
C6H7N	Aniline (Phenylamine)	298.15	0.9994	0.004926	0.2151	19.40	5.10	10.20	22.50	1.324	16
C6H7N	Aniline (Phenylamine)	298.15	0.9994	0.004856	0.2121	19.40	5.10	10.20	22.50	1.305	17
C6H7N	Aniline (Phenylamine)	298.15	0.9994	0.004874	0.2129	19.40	5.10	10.20	22.50	1.31	18
C6H7N	Aniline (Phenylamine)	298.15	0.9994	0.004874	0.2129	19.40	5.10	10.20	22.50	1.31	19
C7H6O	Benzaldehyde	298.15	0.9985	0.011401	0.4979	19.40	7.40	5.30	21.43	2.765	20
C7H6O	Benzaldehyde	298.15	0.9985	0.011711	0.5114	19.40	7.40	5.30	21.43	2.841	21
C6H6	Benzene	298.15	0.8633	0.009620	0.4201	18.40	0.00	2.00	18.51		22
C6H6	Benzene	298.15	0.8759	0.008801	0.3843	18.40	0.00	2.00	18.51	2.425	23
C7H7Cl	Benzylchloride	298.15		0.009120	0.3983	18.80	7.10	2.60	20.26	1.938	24
C6H5Br	Bromobenzene	298.15	0.9945	0.007887	0.3444	20.50	5.50	4.10	21.62	1.842	25

CO2 solubility in various solvents										
Ideal Solubility		298.15		mole frac CO2	Actual/ Ideal 1					
Formula	Solvent	Temp (K)	Pvap	mole frac CO2		δ_D (Mpa) ^{1/2}	δ_P (Mpa) ^{1/2}	δ_H (Mpa) ^{1/2}	δ_T (Mpa) ^{1/2}	Ostwald Coeff.
						Ref ²⁶	Ref ¹	Ref ¹	Calc	Ref
C4H10O	Butanol	298.15	0.9908	0.008868	0.3872	16.00	5.70	15.80	23.20	27
C4H10O	Butanol	298.15	0.9908	0.007343	0.3207	16.00	5.70	15.80	23.20	28
C4H10O	Butanol	298.15		0.007180	0.3135	16.00	5.70	15.80	23.20	29
C4H10O	2-Butanol	298.15		0.006599	0.2882	15.80	5.70	14.50	22.19	30
C4H10O	t-Butanol	298.15		0.007249	0.3166	15.20	5.10	14.70	21.75	31
C22H42O2	Butyl oleate	298.15		0.027900	1.2183	14.70	3.40	3.40	15.47	32
C4H8O2	Butyric Acid	298.15	0.9988	0.012973	0.5665	14.90	4.10	10.60	18.74	3.478 33
CS2	Carbon disulfide	298.15	0.5300	0.002153	0.0940	20.50	0.00	0.60	20.51	0.8699 34
CS2	Carbon disulfide	298.15	0.5300	0.003280	0.1432	20.50	0.00	0.60	20.51	35
CCl4	Carbon tetrachloride	298.15	0.8509	0.011000	0.4803	17.80	0.00	0.60	17.81	36
CCl4	Carbon tetrachloride	298.15	0.8326	0.010590	0.4624	17.80	0.00	0.60	17.81	2.69 37
CCl4	Carbon tetrachloride	298.15	0.8509	0.009041	0.3948	17.80	0.00	0.60	17.81	2.294 38
C6H5Cl	Chlorobenzene	298.15	0.9844	0.009377	0.4095	19.00	4.30	2.00	19.58	2.265 39
C6H5Cl	Chlorobenzene	298.15	0.9844	0.009808	0.4283	19.00	4.30	2.00	19.58	2.37 40
CHCl3	Chloroform	298.15	0.7422	0.011214	0.4897	17.80	3.10	5.70	18.95	3.43 41
CHCl3	Chloroform	298.15	0.7422	0.012769	0.5576	17.80	3.10	5.70	18.95	3.91 42
CHCl3	Chloroform	298.15	0.7422	0.011263	0.4918	17.80	3.10	5.70	18.95	3.445 43
C9H12	Methyl ethyl benzene	298.15	0.9991	0.010077	0.4401	16.10	7.00	0.00	17.56	1.782 44
C7H14	Cycloheptane	298.15	0.9718	0.007210	0.3148	17.20	0.00	0.00	17.20	45
C7H12O	Cycloheptanone	298.15	0.9951	0.015880	0.6934	17.20	10.60	4.80	20.77	46
C6H12	Cyclohexane	298.15	0.8713	0.007710	0.3367	16.80	0.00	0.20	16.80	47
C6H12	Cyclohexane	298.15	0.8713	0.007600	0.3319	16.80	0.00	0.20	16.80	48
C6H12	Cyclohexane	298.15	0.8713	0.007740	0.3380	16.80	0.00	0.20	16.80	49
C6H12O	Cyclohexanol	298.15	0.9990	0.004711	0.2057	17.40	4.10	13.50	22.40	1.11 50
C6H10O	Cyclohexanone	298.15		0.016000	0.6987	17.80	6.30	5.10	19.56	51

CO2 solubility in various solvents										
Ideal Solubility		298.15		mole frac CO2	Actual/ Ideal 1					
						δ_D (Mpa) ^{1/2}	δ_P (Mpa) ^{1/2}	δ_H (Mpa) ^{1/2}	δ_T (Mpa) ^{1/2}	
Formula	Solvent	Temp (K)	Pvap	mole frac CO2		Ref ⁵²	Ref ¹	Ref ¹	Calc	Ostwald Coeff.
C8H16	Cyclooctane	298.15	0.9930	0.006880	0.3004	17.50	0.00	0.00	17.50	
C8H16	Cyclooctane	298.15	0.9930	0.006860	0.2996	17.50	0.00	0.00	17.50	1.247
C5H10	Cyclopentane	298.15	0.9971	0.004914	0.2146	16.40	0.00	1.80	16.50	
C5H8O	Cyclopentanone	298.15	0.9955	0.016410	0.7166	17.90	11.90	5.20	22.11	
C10H22	Decane	298.15	0.9981	0.012036	0.5256	15.70	0.00	0.00	15.70	1.525
C10H22	Decane	298.15	0.9981	0.012500	0.5459	15.70	0.00	0.00	15.70	
C10H22O	Decanol	298.15	1.0000	0.009730	0.4249	17.50	2.60	10.00	20.32	2.085
C2H4Br2	1,2-Dibromoethane	298.15	0.9826	0.008120	0.3546	17.80	6.40	7.00	20.17	2.18
C2H4Br2	1,2-Dibromoethane	298.15	0.9826	0.008035	0.3509	17.80	6.40	7.00	20.17	2.157
C2H4Br2	1,2-Dibromoethane	298.15	0.9826	0.007972	0.3481	17.80	6.40	7.00	20.17	2.14
C2H4Br2	1,2-Dibromoethane	298.15	0.9826	0.008379	0.3659	17.80	6.40	7.00	20.17	2.25
C3H6Cl2O	1,3-dichloro-2-propanol	298.15		0.007460	0.3258	17.50	9.90	14.60	24.85	1.81
CH2Cl2	Dichloromethane	298.15		0.012500		18.20	6.30	6.10	20.20	
C8H14O	2,6-Dimethylcyclohexanone	298.15	0.9913	0.016800	0.7336	15.20	8.80	3.30	17.87	
C2H6OS	Dimethyl Sulfoxide	298.15	0.9992	0.009080	0.3965	18.40	16.40	10.20	26.68	
C2H6OS	Dimethyl Sulfoxide	298.15	0.9992	0.009074	0.3962	18.40	16.40	10.20	26.68	
C2H6OS	Dimethyl Sulfoxide	298.15	0.9992	0.009447	0.4125	18.40	16.40	10.20	26.68	3.27
C3H7NO	Dimethylformamide	298.15		0.016100	0.7031	17.40	13.70	11.30	24.86	
C4H8O2	1,4-Dioxane	298.15		0.022720	0.9921	19.00	1.80	7.40	20.47	
C12H26	Dodecane	298.15	0.9998	0.014279	0.6235	16.00	0.00	0.00	16.00	1.55
C12H26	Dodecane	298.15	0.9998	0.012900	0.5633	16.00	0.00	0.00	16.00	
C12H26	Dodecane	298.15	0.9998	0.011912	0.5202	16.00	0.00	0.00	16.00	1.29
C12H26O	Dodecanol	298.15	1.0000	0.018110	0.7908	15.50	6.50	10.80	19.98	2.01
C2H6O	Ethanol	298.15	0.9228	0.006422	0.2804	15.80	8.80	19.40	26.52	2.7
C2H6O	Ethanol	298.15	0.9228	0.006424	0.2805	15.80	8.80	19.40	26.52	

CO2 solubility in various solvents										
Ideal Solubility		298.15		mole frac CO2	Actual/ Ideal 1					
						δ_D (Mpa) ^{1/2}	δ_P (Mpa) ^{1/2}	δ_H (Mpa) ^{1/2}	δ_T (Mpa) ^{1/2}	
Formula	Solvent	Temp (K)	Pvap	mole frac CO2		Ref ⁷⁸	Ref ¹	Ref ¹	Calc	Ostwald Coeff.
C2H6O	Ethanol	298.15		0.007251	0.3166	15.80	8.80	19.40	26.52	79
C4H8O2	Ethyl acetate	298.15		0.023000	1.0044	15.80	5.30	7.20	18.15	80
C8H10	Ethylbenzene	298.15		0.010060	0.4393	17.80	0.60	1.40	17.87	81
C2H4Cl2	Ethylene Chloride	298.15	0.8966	0.011327	0.4946	19.00	7.40	4.10	20.80	3.525 82
C2H6O2	Ethylene Glycol	298.15		0.002200	0.0961	17.00	11.00	26.20	33.11	83
C10H12O2	Eugenol	298.15		0.010234	0.4469	15.10	8.80	9.80	20.04	1.539 84
C5H9NO2	N-Formyl morpholine	298.15		0.014750	0.6441	16.60	11.70	10.00	22.64	
C3H8O3	Glycerol (glycerin)	298.15	1.0000	0.000090	0.0039	17.40	12.10	29.30	36.16	0.0302 85
C7H16	Heptane	298.15	0.9405	0.013284	0.5801	15.30	0.00	0.00	15.30	2.24 86
C7H16	Heptane	298.15	0.9405	0.011900	0.5197	15.30	0.00	0.00	15.30	
C7H16	Heptane	298.15	0.9360	0.011936	0.5212	15.30	0.00	0.00	15.30	2.01 88
C7H16	Heptane	298.15	0.9405	0.012017	0.5248	15.30	0.00	0.00	15.30	
C7H16O	Heptanol	298.15	0.9997	0.012583	0.5495	15.10	8.00	13.00	21.47	2.2 90
C16H34	Hexadecane	298.15	1.0000	0.011608	0.5069	16.30	0.00	0.00	16.30	0.977 91
C16H34	Hexadecane	298.15	1.0000	0.014200	0.6201	16.30	0.00	0.00	16.30	
C6H14	Hexane	298.15	0.8005	0.013176	0.5754	14.90	0.00	0.00	14.90	2.48 93
C6H14	Hexane	298.15	0.8005	0.011900	0.5197	14.90	0.00	0.00	14.90	
C6H14O	Hexanol	298.15	0.9988	0.011735	0.5124	14.10	8.60	12.70	20.83	2.32 95
C5H5I	Iodobenzene	298.15	0.9986	0.005919	0.2585	19.50	6.00	6.10	21.29	1.301 96
C5H12O	Isoamyl Alcohol	298.15	0.9960	0.008085	0.3530	15.80	5.20	13.30	21.30	1.83 97
C4H10O	Isobutanol	298.15	0.9864	0.006963	0.3041	15.10	5.70	15.90	22.66	
C4H10O	Isobutanol	298.15	0.9864	0.006903	0.3014	15.10	5.70	15.90	22.66	1.849 99
C6H12O2	Isobutyl Acetate	298.15	0.9768	0.025004	1.0919	15.10	3.70	6.30	16.77	4.691 100
C4H9Cl	Isobutylchloride	298.15		0.014101	0.6158	14.70	5.30	0.90	15.65	3.105 101
C3H8O	Isopropanol	298.15		0.006540	0.2856	15.80	6.10	16.40	23.58	102

CO2 solubility in various solvents											
Ideal Solubility		298.15		mole frac CO2	Actual/ Ideal						
						δ_D (Mpa) $^{1/2}$	δ_P (Mpa) $^{1/2}$	δ_H (Mpa) $^{1/2}$	δ_T (Mpa) $^{1/2}$		
Formula	Solvent	Temp (K)	Pvap	mole frac CO2		Ref 103	Ref ¹	Ref ¹	Calc	Ostwald Coeff.	Ref
CH4O	Methanol	298.15	0.8354	0.006406	0.2797	15.10	12.30	22.30	29.61	3.87	104
CH4O	Methanol	298.15	0.8354	0.005640	0.2463	15.10	12.30	22.30	29.61	3.405	105
CH4O	Methanol	298.15	0.8354	0.005634	0.2460	15.10	12.30	22.30	29.61		106
CH4O	Methanol	298.15	0.8354	0.006351	0.2774	15.10	12.30	22.30	29.61	3.837	107
C3H6O2	Methyl Acetate	298.15	0.7199	0.020893	0.9123	15.50	7.20	7.60	18.70	6.494	108
C3H6O2	Methyl Acetate	298.15	0.7199	0.022526	0.9837	15.50	7.20	7.60	18.70	7.01	109
C7H14	Methyl cyclo hexane	298.15	0.9399	0.009266	0.4046	16.00	0.00	1.00	16.03	1.784	110
C7H12O	2-Methylcyclohexanone	298.15	0.9945	0.016600	0.7249	17.60	6.30	4.70	19.28		111
C4H8O	Methyl ethyl ketone	298.15	0.8752	0.024438	1.0672	16.00	9.00	5.10	19.05	6.77	112
C11H10	1-Methyl naphthalene	298.15		0.006740	0.2943	20.60	0.80	4.70	21.14		113
C19H36O2	Methyl oleate	298.15		0.026900	1.1747	14.50	3.90	3.70	15.46		114
C6H5NO2	Nitrobenzene	298.15	0.9997	0.010202	0.4455	20.00	8.60	4.10	22.15	2.456	115
C6H5NO2	Nitrobenzene	298.15	0.9997	0.009972	0.4355	20.00	8.60	4.10	22.15	2.4	116
C5H9NO	N-Methylpyrrolidone	298.15	0.9996	0.015900	0.6943	18.00	12.30	7.20	22.96		117
C9H20	Nonane	298.15	0.9942	0.012312	0.5376	15.70	0.00	0.00	15.70	1.7	118
C9H20O	Nonanol	298.15	1.0000	0.014805	0.6465	15.30	7.30	12.00	20.77	2.1	119
C8H18	Octane	298.15	0.9816	0.012535	0.5474	15.50	0.00	0.00	15.50	1.9	120
C8H18	Octane	298.15	0.9816	0.012100	0.5284	15.50	0.00	0.00	15.50		121
C8H18O	Octanol	298.15	0.9999	0.009301	0.4062	17.00	3.30	11.90	21.01	2.18	122
C18H34O2	Oleic acid	298.15		0.015700	0.6856	16.20	3.10	5.50	17.39		123
C15H32	Pentadecane	298.15	1.0000	0.011666	0.5094	16.80	0.00	0.00	16.80	1.04	124
C5H12	Pentane	298.15	0.3280	0.013851	0.6048	14.50	0.00	0.00	14.50	2.93	125
C5H12O	Pentanol (Amyl alcohol)	298.15	0.9968	0.008059	0.3519	15.90	4.50	13.90	21.59	1.831	126
C7F16	Perfluoroheptane	298.15	0.8997	0.020880	0.9118	12.00	0.00	0.00	12.00		127
C8H7N	Phenyl acetonitrile	298.15	1.0000	0.009572	0.4180	19.50	12.30	3.80	23.37	2.05	128

CO2 solubility in various solvents											
Ideal Solubility		298.15		mole frac CO2		Actual/ Ideal					
				0.022900		1					
								δ_D (Mpa) ^{1/2}	δ_P (Mpa) ^{1/2}	δ_H (Mpa) ^{1/2}	δ_T (Mpa) ^{1/2}
Formula	Solvent	Temp (K)	Pvap	mole frac CO2	Ref 129	Ref ¹	Ref ¹	Calc	Ostwald Coeff.	Ref	
C3H8O	Propanol	298.15	0.9730	0.007817	0.3414	16.00	6.80	17.40	24.60	2.8	130
C3H8O	Propanol	298.15		0.006800	0.2969	16.00	6.80	17.40	24.60	2.498	131
C3H8O	Propanol	298.15	0.9730	0.007594	0.3316	16.00	6.80	17.40	24.60	2.498	132
C3H6O2	Propionic Acid	298.15	0.9952	0.012344	0.5390	14.70	5.30	12.40	19.95	4.078	133
C3H5N	Propionitrile	298.15	0.9382	0.016769	0.7323	15.30	14.30	5.50	21.65	5.88	134
C5H10O2	Propylacetate	298.15	0.9566	0.024290	1.0607	15.30	4.30	7.60	17.62	5.26	135
C3H6Br2	Propylene bromide	298.15	0.9896	0.009768	0.4266	17.40	7.50	2.90	19.17	2.301	136
C4H6O3	Propylene carbonate	298.15		0.010736	0.4688	20.00	18.00	4.10	27.22		137
C4H6O3	Propylene carbonate	298.15	1.0000	0.011617	0.5073	20.00	18.00	4.10	27.22	3.38	138
C4H6O3	Propylene carbonate	298.15	1.0000	0.012100	0.5284	20.00	18.00	4.10	27.22	3.38	139
C5H5N	Pyridine	298.15	0.9729	0.011934	0.5211	19.00	8.80	5.90	21.75	3.656	140
C5H5N	Pyridine	298.15	0.9729	0.011689	0.5104	19.00	8.80	5.90	21.75	3.58	141
C5H5N	Pyridine	298.15	0.9729	0.011979	0.5231	19.00	8.80	5.90	21.75	3.67	142
C9H7N	Quinoline	298.15		0.009120	0.3983	19.40	7.00	7.60	21.98		143
C4H8O2S	Sulfolane	298.15	1.0000	0.007990	0.3489	18.40	16.60	7.40	25.86		144
C14H30	Tetradecane	298.15	1.0000	0.011714	0.5115	16.20	0.00	0.00	16.20	1.108	145
C14H30	Tetradecane	298.15	1.0000	0.013600	0.5939	16.20	0.00	0.00	16.20		146
C4H8O	Tetrahydrofuran	298.15		0.027000	1.1790	16.80	5.70	8.00	19.46		147
C10H12	Tetrahydronaphthalene	298.15		0.007523	0.3285	19.60	2.00	2.90	19.91		148
C7H9N	m-Toluidine	298.15	0.9996	0.006345	0.2771	19.30	3.80	10.10	22.11	1.436	149
C7H9N	o-Toluidine	298.15	0.9997	0.006048	0.2641	19.40	4.20	10.70	22.55	1.381	150
C7H8	Toluene (Methyl benzene)	298.15	0.9629	0.009940	0.4340	18.00	1.40	2.00	18.16	2.305	151
C7H8	Toluene (Methyl benzene)	298.15	0.9629	0.010102	0.4411	18.00	1.40	2.00	18.16	2.343	152
C7H8	Toluene (Methyl benzene)	298.15	0.9629	0.010419	0.4550	18.00	1.40	2.00	18.16		153
C7H8	Toluene (Methyl benzene)	298.15	0.9629	0.010388	0.4536	18.00	1.40	2.00	18.16	2.41	154

CO2 solubility in various solvents										
Ideal Solubility		298.15	mole frac CO2		Actual/ Ideal					
						δ_D (Mpa) ^{1/2}	δ_P (Mpa) ^{1/2}	δ_H (Mpa) ^{1/2}	δ_T (Mpa) ^{1/2}	
Formula	Solvent	Temp (K)	Pvap	mole frac CO2	Ref 155	Ref ¹	Ref ¹	Calc	Ostwald Coeff.	Ref
C12H27O4P	Tributyl phosphate	298.15	0.035500	1.5502	16.30	6.30	4.30	18.00		156
C2Cl3F3	1,1,2-Trichlorotrifluoroethane	298.15	0.5585	0.018230	0.7961	14.70	1.60	0.00	14.79	157
C13H28	Tridecane	298.15	0.9999	0.011753	0.5132	16.40	0.00	0.00	16.40	1.19 158
C6H15N	Triethylamine	298.15	0.9105	0.023207	1.0134	17.80	0.40	1.00	17.83	4.15 159
C8H18	2,2,4-Trimethylpentane	298.15	0.9356	0.013870	0.6057	14.10	0.00	0.00	14.10	160
C11H24	Undecane	298.15	0.9995	0.011483	0.5014	16.00	0.00	0.00	16.00	1.34 161
C11H24O	Undecanol	298.15	1.0000	0.017078	0.7457	15.40	6.70	11.20	20.19	2.05 162
H2O	Water	298.15	0.9690	0.000700	0.0306	15.50	16.00	42.30	47.81	163
H2O	Water	298.15	0.9690	0.000592	0.0258	15.50	16.00	42.30	47.81	0.8256 164
H2O	Water	298.15	0.9690	0.000597	0.0261	15.50	16.00	42.30	47.81	0.833 165
H2O	Water	298.15	0.9690	0.000612	0.0267	15.50	16.00	42.30	47.81	166
C8H10	o-Xylene	298.15	0.9913	0.009937	0.4339	17.80	1.00	3.10	18.10	2.026 167
C8H10	m-Xylene (dimethylbenzene)	298.15	0.9989	0.010424	0.4552	17.40	1.00	3.10	17.70	2.09 168
C8H10	m-Xylene (dimethylbenzene)	298.15	0.9989	0.010631	0.4642	17.40	1.00	3.10	17.70	2.127 169
C8H10	p-Xylene	298.15	0.9885	0.010865	0.4744	17.40	1.00	3.10	17.70	2.169 170

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Appendix B: Table B-4: CO₂ Solubility Sphere Optimization, RED Calculations

		CO2	δ_D (Mpa) ^{1/2}	δ_P (Mpa) ^{1/2}	δ_H (Mpa) ^{1/2}	Ro			
		Data Set (2)Opt best solvents	15.6	5.2	5.8	4.0			
		Data Set (1)Opt all solvents	16.4	5.5	5.8	4.7			
CO2 solubility in various solvents @ P _{CO2} = 1 atm, 25 C									
Formula	Solvent	mole frac CO2	δ_D (Mpa) ^{1/2}	δ_P (Mpa) ^{1/2}	δ_H (Mpa) ^{1/2}	Ra (2)	RED (2)	Ra (1)	RED (1)
C12H27O4P	Tributyl phosphate	0.035500	16.3	6.3	4.3	2.3	0.582	1.7	0.364
C7H14O2	Amyl Acetate	0.028000	15.8	3.3	6.1	2.0	0.491	2.5	0.537
C22H42O2	Butyl Oleate	0.027900	14.7	3.4	3.4	3.5	0.875	4.7	0.992
C4H8O	Tetrahydrofuran	0.027000	16.8	5.7	8.0	3.3	0.823	2.3	0.500
C19H36O2	Methyl oleate	0.026900	14.5	3.9	3.7	3.3	0.827	4.6	0.984
C6H12O2	Isobutyl Acetate	0.025004	15.1	3.7	6.3	1.9	0.468	3.2	0.681
C4H8O	Methyl ethyl ketone	0.024438	16.0	9.0	5.1	3.9	0.986	3.7	0.778
C5H10O2	Propylacetate	0.024290	15.3	4.3	7.6	2.1	0.525	3.1	0.656
C4H8O2	Ethyl acetate	0.023000	15.8	5.3	7.2	1.5	0.365	1.9	0.395
C3H6O2	Methyl Acetate	0.022526	15.5	7.2	7.6	2.7	0.675	3.1	0.651
C7F16	Perfluroheptane	0.020880	12.0	0.0	0.0	10.6	2.652	11.9	2.529
C3H6O	Acetone	0.019870	15.5	10.4	7.0	5.3	1.335	5.4	1.140
C4H6O3	Acetic Anhydride	0.019774	16.0	11.7	10.2	7.9	1.972	7.6	1.627
C2Cl3F3	1,1,2-Trichlorotrifluoroethane	0.018230	14.7	1.6	0.0	7.1	1.765	7.8	1.654
C12H26O	Dodecanol	0.018110	15.5	6.5	10.8	5.2	1.293	5.4	1.151
C11H24O	Undecanol (n-Undecyl alcohol)	0.017078	15.4	6.7	11.2	5.6	1.405	5.9	1.252
C8H14O	2,6-Dimethylcyclohexanone	0.016800	15.2	8.8	3.3	4.5	1.114	4.8	1.018
C3H5N	Propionitrile	0.016769	15.3	14.3	5.5	9.1	2.281	9.1	1.931
C7H12O	2-Methylcyclohexanone	0.016600	17.6	6.3	4.7	4.3	1.073	2.8	0.587
C5H8O	Cyclopentanone	0.016410	17.9	11.9	5.2	8.1	2.037	7.1	1.509
C3H7NO	Dimethylformamide	0.016100	17.4	13.7	11.3	10.7	2.686	10.1	2.143

		CO2	δ_D (Mpa) ^{1/2}	δ_P (Mpa) ^{1/2}	δ_H (Mpa) ^{1/2}	R _o			
		Data Set (2)Opt best solvents	15.6	5.2	5.8	4.0			
		Data Set (1)Opt all solvents	16.4	5.5	5.8	4.7			
CO2 solubility in various solvents @ P _{CO2} = 1 atm, 25 C									
Formula	Solvent	mole frac CO2	δ_D (Mpa) ^{1/2}	δ_P (Mpa) ^{1/2}	δ_H (Mpa) ^{1/2}	R _a (2)	RED (2)	R _a (1)	RED (1)
C6H10O	Cyclohexanone	0.016000	17.8	6.3	5.1	4.6	1.147	3.0	0.637
C5H9NO	N-Methylpyrrolidone	0.015900	18.0	12.3	7.2	8.7	2.171	7.6	1.627
C7H12O	Cycloheptanone	0.015880	17.2	10.6	4.8	6.4	1.589	5.4	1.157
C18H34O2	Oleic acid	0.015700	16.2	3.1	5.5	2.4	0.609	2.5	0.522
C9H20O	Nonanol	0.014805	15.3	7.3	12.0	6.6	1.643	6.8	1.451
C5H9NO2	N-Formyl morpholine	0.014750	16.6	11.7	10.0	8.0	1.998	7.5	1.596
C5H11Cl	Amylchloride (1-Chloropentane)	0.014244	15.5	5.0	1.3	4.5	1.127	4.9	1.037
C4H9Cl	Isobutylchloride	0.014101	14.7	5.3	0.9	5.2	1.305	6.0	1.270
C8H18	2,2,4-Trimethylpentane	0.013870	14.1	0.0	0.0	8.3	2.087	9.2	1.962
C5H12	Pentane	0.013851	14.5	0.0	0.0	8.1	2.024	8.9	1.883
C12H26	Dodecane	0.013030	16.0	0.0	0.0	7.8	1.958	8.0	1.709
C4H8O2	Butyric Acid	0.012973	14.9	4.1	10.6	5.1	1.280	5.8	1.241
C16H34	Hexadecane	0.012904	16.3	0.0	0.0	7.9	1.979	8.0	1.701
C14H30	Tetradecane	0.012657	16.2	0.0	0.0	7.9	1.970	8.0	1.703
C7H16O	Heptanol	0.012583	15.1	8.0	13.0	7.8	1.947	8.1	1.713
C6H14	Hexane	0.012538	14.9	0.0	0.0	7.9	1.979	8.5	1.817
CH2Cl2	Dichloromethane	0.012500	18.2	6.3	6.1	5.3	1.331	3.7	0.787
C5H11Br	Amylbromide (1-Bromopentane)	0.012353	20.3	4.8	2.8	9.9	2.469	8.4	1.784
C3H6O2	Propionic Acid	0.012344	14.7	5.3	12.4	6.8	1.710	7.4	1.580
C8H18	Octane	0.012318	15.5	0.0	0.0	7.8	1.948	8.2	1.743
C9H20	Nonane	0.012312	15.7	0.0	0.0	7.8	1.948	8.1	1.727
C7H16	Heptane	0.012284	15.3	0.0	0.0	7.8	1.953	8.3	1.764
C10H22	Decane	0.012268	15.7	0.0	0.0	7.8	1.948	8.1	1.727
C5H5N	Pyridine	0.011867	19.0	8.8	5.9	7.7	1.924	6.2	1.311
C13H28	Tridecane	0.011753	16.4	0.0	0.0	8.0	1.988	8.0	1.701

		CO2	δ_D (Mpa) ^{1/2}	δ_P (Mpa) ^{1/2}	δ_H (Mpa) ^{1/2}	Ro			
		Data Set (2)Opt best solvents	15.6	5.2	5.8	4.0			
		Data Set (1)Opt all solvents	16.4	5.5	5.8	4.7			
CO2 solubility in various solvents @ P _{CO2} = 1 atm, 25 C									
Formula	Solvent	mole frac CO2	δ_D (Mpa) ^{1/2}	δ_P (Mpa) ^{1/2}	δ_H (Mpa) ^{1/2}	Ra (2)	RED (2)	Ra (1)	RED (1)
CHCl3	Chloroform (Trichloromethane)	0.011749	17.8	3.1	5.7	4.9	1.219	3.7	0.785
C6H14O	Hexanol	0.011735	14.1	8.6	12.7	8.3	2.064	8.9	1.884
C15H32	Pentadecane	0.011666	16.8	0.0	0.0	8.2	2.038	8.0	1.709
C7H6O	Benzaldehyde	0.011556	19.4	7.4	5.3	7.9	1.982	6.3	1.343
C4H6O3	Propylene carbonate	0.011484	20.0	18.0	4.1	15.6	3.906	14.5	3.090
C11H24	Undecane	0.011483	16.0	0.0	0.0	7.8	1.958	8.0	1.709
C2H4Cl2	Ethylene Chloride (1,2-Dichloroethane)	0.011327	19.0	7.4	4.1	7.3	1.837	5.8	1.232
C2H4O2	Acetic Acid	0.011056	14.5	8.0	13.5	8.5	2.121	8.9	1.903
C8H10	p-Xylene	0.010865	17.4	1.0	3.1	6.2	1.539	5.6	1.195
C8H10	m-Xylene (dimethylbenzene)	0.010527	17.4	1.0	3.1	6.2	1.539	5.6	1.195
C10H12O2	Eugenol	0.010234	15.1	8.8	9.8	5.5	1.368	5.8	1.234
C7H8	Toluene (Methyl benzene)	0.010212	18.0	1.4	2.0	7.2	1.801	6.4	1.370
CCl4	Carbon tetrachloride	0.010210	17.8	0.0	0.6	8.6	2.142	8.1	1.717
C6H5NO2	Nitrobenzene	0.010087	20.0	8.6	4.1	9.6	2.396	8.0	1.707
C9H12	Cumene (Methyl ethyl benzene)	0.010077	16.1	7.0	0.0	6.2	1.539	6.0	1.281
C8H10	Ethylbenzene	0.010060	17.8	0.6	1.4	7.7	1.935	7.2	1.523
C8H10	o-Xylene	0.009937	17.8	1.0	3.1	6.7	1.664	5.9	1.266
C3H6Br2	Propylene bromide (1,2-dibromopropane)	0.009768	17.4	7.5	2.9	5.2	1.291	4.1	0.862
C10H22O	Decanol (Decyl alcohol)	0.009730	17.5	2.6	10.0	6.2	1.558	5.6	1.183
C6H5Cl	Chlorobenzene	0.009593	19.0	4.3	2.0	7.8	1.960	6.6	1.394
C8H7N	Phenyl acetonitrile	0.009572	19.5	12.3	3.8	10.7	2.684	9.4	2.004
C8H18O	Octanol	0.009301	17.0	3.3	11.9	7.0	1.744	6.6	1.403
C7H14	Methyl cyclo hexane	0.009266	16.0	0.0	1.0	7.1	1.780	7.3	1.562

		CO2	δ_D (Mpa) ^{1/2}	δ_P (Mpa) ^{1/2}	δ_H (Mpa) ^{1/2}	Ro			
		Data Set (2)Opt best solvents	15.6	5.2	5.8	4.0			
		Data Set (1)Opt all solvents	16.4	5.5	5.8	4.7			
CO2 solubility in various solvents @ P _{CO2} = 1 atm, 25 C									
Formula	Solvent	mole frac CO2	δ_D (Mpa) ^{1/2}	δ_P (Mpa) ^{1/2}	δ_H (Mpa) ^{1/2}	Ra (2)	RED (2)	Ra (1)	RED (1)
C6H6	Benzene	0.009210	18.4	0.0	2.0	8.5	2.134	7.8	1.658
C2H6OS	Dimethyl Sulfoxide	0.009200	18.4	16.4	10.2	13.3	3.318	12.4	2.642
C7H7Cl	Benzylchloride (Chlorophenylmethane)	0.009120	18.8	7.1	2.6	7.4	1.851	6.0	1.274
C9H7N	Quinoline	0.009120	19.4	7.0	7.6	8.0	2.004	6.4	1.370
C2H4Br2	1,2-Dibromoethane (Ethylene dibromide)	0.008127	17.8	6.4	7.0	4.7	1.179	3.2	0.676
C5H12O	Isoamyl Alcohol (3-Methyl-1-butanol)	0.008085	15.8	5.2	13.3	7.5	1.878	7.6	1.617
C5H12O	Pentanol (Amyl alcohol)	0.008059	15.9	4.5	13.9	8.2	2.038	8.2	1.749
C4H8O2S	Sulfolane	0.007990	18.4	16.6	7.4	12.8	3.200	11.9	2.533
C6H5Br	Bromobenzene	0.007887	20.5	5.5	4.1	10.0	2.488	8.4	1.782
C6H12	Cyclohexane	0.007683	16.8	0.0	0.2	8.0	2.002	7.9	1.679
C10H12	Tetrahydronaphthalene	0.007523	19.6	2.0	2.9	9.1	2.273	7.8	1.670
C3H6Cl2O	1,3-dichloro-2-propanol	0.007460	17.5	9.9	14.6	10.7	2.669	10.1	2.145
C4H10O	Butanol	0.007262	16.0	5.7	15.8	10.0	2.511	10.0	2.135
C4H10O	t-Butanol (2-methyl-2-propanol)	0.007249	15.2	5.1	14.7	8.9	2.234	9.2	1.963
C7H14	Cycloheptane	0.007210	17.2	0.0	0.0	8.4	2.105	8.2	1.734
C4H10O	Isobutanol	0.006933	15.1	5.7	15.9	10.2	2.540	10.4	2.219
C8H16	Cyclooctane	0.006870	17.5	0.0	0.0	8.7	2.167	8.3	1.764
C3H8O	Propanol	0.006800	16.0	6.8	17.4	11.7	2.934	11.7	2.489
C11H10	1-Methyl naphthalene	0.006740	20.6	0.8	4.7	11.0	2.745	9.7	2.061
C2H6O	Ethanol	0.006699	15.8	8.8	19.4	14.1	3.519	14.0	2.989
C4H10O	2-Butanol	0.006599	15.8	5.7	14.5	8.7	2.181	8.8	1.869
C3H8O	Isopropanol	0.006540	15.8	6.1	16.4	10.6	2.661	10.7	2.273
C7H9N	m-Toluidine	0.006345	19.3	3.8	10.1	8.7	2.168	7.4	1.578

CO2			δ_D (Mpa) ^{1/2}	δ_P (Mpa) ^{1/2}	δ_H (Mpa) ^{1/2}	Ro			
Data Set (2)Opt best solvents			15.6	5.2	5.8	4.0			
Data Set (1)Opt all solvents			16.4	5.5	5.8	4.7			
CO2 solubility in various solvents @ P _{CO2}									
= 1 atm, 25 C									
Formula	Solvent	mole frac CO2	δ_D (Mpa) ^{1/2}	δ_P (Mpa) ^{1/2}	δ_H (Mpa) ^{1/2}	Ra (2)	RED (2)	Ra (1)	RED (1)
C7H9N	o-Toluidine	0.006048	19.4	4.2	10.7	9.1	2.274	7.9	1.671
CH4O	Methanol	0.006008	15.1	12.3	22.3	18.0	4.498	18.0	3.837
C5H5I	Iodobenzene	0.005919	19.5	6.0	6.1	7.8	1.962	6.2	1.325
C5H10	Cyclopentane	0.004914	16.4	0.0	1.8	6.8	1.688	6.8	1.447
C6H7N	Aniline (Phenylamine)	0.004883	19.4	5.1	10.2	8.8	2.196	7.5	1.585
C6H12O	Cyclohexanol	0.004711	17.4	4.1	13.5	8.6	2.143	8.1	1.719
CS2	Carbon disulfide	0.002716	20.5	0.0	0.6	12.3	3.063	11.2	2.374
C2H6O2	Ethylene Glycol	0.002200	17.0	11.0	26.2	21.4	5.348	21.2	4.503
H2O	Water	0.000625	15.5	16.0	42.3	38.1	9.516	38.0	8.090
C3H8O3	Glycerol (glycerin)	0.000090	17.4	12.1	29.3	24.8	6.189	24.5	5.211

Appendix C : Calculated HSP values for Pure CO₂ from 10 to 905 bar and from 273 to 373 K.

T (K)	P (bar)	$\delta_d^{1/2}$ (MPa ^{1/2})	$\delta_p^{1/2}$ (MPa ^{1/2})	$\delta_h^{1/2}$ (MPa ^{1/2})	$\delta_T^{1/2}$ (MPa ^{1/2})	$\delta_{Hildebrand}$ (MPa ^{1/2})	T (K)	P (bar)	$\delta_d^{1/2}$ (MPa ^{1/2})	$\delta_p^{1/2}$ (MPa ^{1/2})	$\delta_h^{1/2}$ (MPa ^{1/2})	$\delta_T^{1/2}$ (MPa ^{1/2})	$\delta_{Hildebrand}$ (MPa ^{1/2})
273	905	16.55	5.32	6.14	18.43	18.45	273	760	16.18	5.28	6.08	18.07	18.21
273	900	16.55	5.32	6.14	18.43	18.44	273	755	16.16	5.27	6.08	18.06	18.2
273	895	16.53	5.32	6.13	18.42	18.43	273	750	16.14	5.27	6.08	18.04	18.19
273	890	16.51	5.32	6.13	18.40	18.43	273	745	16.13	5.27	6.07	18.02	18.18
273	885	16.51	5.32	6.13	18.40	18.42	273	740	16.11	5.27	6.07	18.00	18.17
273	880	16.49	5.32	6.13	18.38	18.41	273	735	16.11	5.27	6.07	18.00	18.16
273	875	16.48	5.31	6.13	18.36	18.4	273	730	16.09	5.26	6.07	17.99	18.15
273	870	16.46	5.31	6.12	18.35	18.39	273	725	16.07	5.26	6.07	17.97	18.14
273	865	16.46	5.31	6.12	18.35	18.39	273	720	16.06	5.26	6.06	17.95	18.13
273	860	16.44	5.31	6.12	18.33	18.38	273	715	16.04	5.26	6.06	17.93	18.12
273	855	16.42	5.31	6.12	18.31	18.37	273	710	16.02	5.26	6.06	17.92	18.11
273	850	16.41	5.31	6.12	18.30	18.36	273	705	16.02	5.26	6.06	17.92	18.1
273	845	16.41	5.31	6.12	18.30	18.35	273	700	16.00	5.25	6.06	17.90	18.09
273	840	16.39	5.30	6.11	18.28	18.35	273	695	15.99	5.25	6.05	17.88	18.08
273	835	16.37	5.30	6.11	18.26	18.34	273	690	15.97	5.25	6.05	17.87	18.07
273	830	16.35	5.30	6.11	18.24	18.33	273	685	15.95	5.25	6.05	17.85	18.06
273	825	16.35	5.30	6.11	18.24	18.32	273	680	15.94	5.24	6.05	17.83	18.05
273	820	16.34	5.30	6.11	18.23	18.31	273	675	15.92	5.24	6.04	17.81	18.03
273	815	16.32	5.29	6.10	18.21	18.31	273	670	15.92	5.24	6.04	17.81	18.02
273	810	16.30	5.29	6.10	18.19	18.3	273	665	15.90	5.24	6.04	17.80	18.01
273	805	16.30	5.29	6.10	18.19	18.29	273	660	15.88	5.24	6.04	17.78	18
273	800	16.28	5.29	6.10	18.18	18.28	273	655	15.87	5.24	6.04	17.76	17.99
273	795	16.27	5.29	6.10	18.16	18.27	273	650	15.85	5.23	6.03	17.75	17.98
273	790	16.25	5.29	6.09	18.14	18.26	273	645	15.83	5.23	6.03	17.73	17.97
273	785	16.25	5.29	6.09	18.14	18.25	273	640	15.81	5.23	6.03	17.71	17.95
273	780	16.23	5.28	6.09	18.12	18.24	273	635	15.80	5.23	6.02	17.70	17.94
273	775	16.21	5.28	6.09	18.11	18.23	273	630	15.78	5.22	6.02	17.68	17.93
273	770	16.20	5.28	6.09	18.09	18.23	273	625	15.78	5.22	6.02	17.68	17.92
273	765	16.18	5.28	6.08	18.07	18.22	273	620	15.76	5.22	6.02	17.66	17.91

T (K)	P (bar)	$\delta_d^{1/2}$ (MPa ^{1/2})	$\delta_p^{1/2}$ (MPa ^{1/2})	$\delta_h^{1/2}$ (MPa ^{1/2})	$\delta_T^{1/2}$ (MPa ^{1/2})	$\delta_{Hildebrand}$ (MPa ^{1/2})	T (K)	P (bar)	$\delta_d^{1/2}$ (MPa ^{1/2})	$\delta_p^{1/2}$ (MPa ^{1/2})	$\delta_h^{1/2}$ (MPa ^{1/2})	$\delta_T^{1/2}$ (MPa ^{1/2})	$\delta_{Hildebrand}$ (MPa ^{1/2})
273	610	15.73	5.22	6.01	17.63	17.88	273	460	15.19	5.14	5.93	17.10	17.44
273	615	15.74	5.22	6.02	17.64	17.90	273	455	15.17	5.14	5.93	17.08	17.43
273	605	15.71	5.21	6.01	17.61	17.87	273	450	15.16	5.14	5.93	17.07	17.41
273	600	15.69	5.21	6.01	17.59	17.86	273	445	15.14	5.14	5.92	17.05	17.39
273	595	15.67	5.21	6.01	17.58	17.84	273	440	15.12	5.14	5.92	17.03	17.37
273	590	15.66	5.21	6.00	17.56	17.83	273	435	15.09	5.13	5.91	17.00	17.36
273	585	15.64	5.21	6.00	17.54	17.82	273	430	15.07	5.13	5.91	16.98	17.34
273	580	15.62	5.20	6.00	17.52	17.81	273	425	15.05	5.13	5.91	16.96	17.32
273	575	15.60	5.20	6.00	17.51	17.79	273	420	15.03	5.12	5.91	16.95	17.3
273	570	15.59	5.20	5.99	17.49	17.78	273	415	15.02	5.12	5.90	16.93	17.28
273	565	15.57	5.20	5.99	17.47	17.77	273	410	15.00	5.12	5.90	16.91	17.26
273	560	15.55	5.19	5.99	17.46	17.75	273	405	14.97	5.11	5.90	16.88	17.24
273	555	15.54	5.19	5.98	17.44	17.74	273	400	14.95	5.11	5.89	16.86	17.22
273	550	15.52	5.19	5.98	17.42	17.72	273	395	14.93	5.11	5.89	16.85	17.2
273	545	15.50	5.19	5.98	17.41	17.71	273	390	14.91	5.11	5.89	16.83	17.18
273	540	15.48	5.18	5.98	17.39	17.7	273	385	14.88	5.10	5.88	16.79	17.16
273	535	15.47	5.18	5.97	17.37	17.68	273	380	14.86	5.10	5.88	16.78	17.14
273	530	15.45	5.18	5.97	17.35	17.67	273	375	14.85	5.10	5.88	16.76	17.12
273	525	15.43	5.18	5.97	17.34	17.65	273	370	14.81	5.09	5.87	16.73	17.1
273	520	15.41	5.18	5.97	17.32	17.64	273	365	14.79	5.09	5.87	16.71	17.08
273	515	15.40	5.17	5.96	17.30	17.62	273	360	14.78	5.09	5.87	16.69	17.06
273	510	15.38	5.17	5.96	17.29	17.61	273	355	14.76	5.09	5.86	16.68	17.03
273	505	15.36	5.17	5.96	17.27	17.59	273	350	14.73	5.08	5.86	16.64	17.01
273	500	15.35	5.17	5.96	17.25	17.58	273	345	14.71	5.08	5.86	16.63	16.99
273	495	15.33	5.16	5.95	17.23	17.56	273	340	14.67	5.07	5.85	16.59	16.96
273	490	15.31	5.16	5.95	17.22	17.54	273	335	14.66	5.07	5.85	16.58	16.94
273	485	15.29	5.16	5.95	17.20	17.53	273	330	14.64	5.07	5.84	16.56	16.92
273	480	15.28	5.16	5.94	17.18	17.51	273	325	14.61	5.06	5.84	16.53	16.89
273	475	15.26	5.15	5.94	17.17	17.49	273	320	14.59	5.06	5.84	16.51	16.87
273	470	15.22	5.15	5.94	17.13	17.48	273	315	14.55	5.06	5.83	16.47	16.84
273	465	15.21	5.15	5.93	17.12	17.46	273	310	14.54	5.06	5.83	16.46	16.82

T, K	P, bar	$\delta_{d_1, 1/2}$ MPa	$\delta_{p_1, 1/2}$ MPa	$\delta_{h_1, 1/2}$ MPa	$\delta_{T_1, 1/2}$ MPa	$\delta_{Hildebrand^*}$ MPa	T, K	P, bar	$\delta_{d_1, 1/2}$ MPa	$\delta_{p_1, 1/2}$ MPa	$\delta_{h_1, 1/2}$ MPa	$\delta_{T_1, 1/2}$ MPa	$\delta_{Hildebrand^*}$ MPa
273	305	14.52	5.05	5.83	16.44	16.79	273	155	13.60	4.92	5.68	15.54	15.78
273	300	14.49	5.05	5.82	16.41	16.77	273	150	13.57	4.92	5.67	15.51	15.74
273	295	14.47	5.05	5.82	16.39	16.74	273	145	13.52	4.91	5.66	15.46	15.69
273	290	14.43	5.04	5.81	16.36	16.71	273	140	13.49	4.91	5.66	15.42	15.64
273	285	14.42	5.04	5.81	16.34	16.69	273	135	13.45	4.90	5.65	15.39	15.59
273	280	14.38	5.03	5.80	16.31	16.66	273	130	13.40	4.89	5.64	15.34	15.54
273	275	14.35	5.03	5.80	16.27	16.63	273	125	13.37	4.89	5.64	15.31	15.49
273	270	14.33	5.03	5.79	16.26	16.6	273	120	13.32	4.88	5.63	15.26	15.44
273	265	14.30	5.02	5.79	16.22	16.57	273	115	13.28	4.88	5.62	15.23	15.38
273	260	14.28	5.02	5.79	16.21	16.55	273	110	13.23	4.87	5.61	15.18	15.33
273	255	14.25	5.01	5.78	16.17	16.52	273	105	13.18	4.86	5.60	15.13	15.27
273	250	14.21	5.01	5.78	16.14	16.49	273	100	13.15	4.86	5.60	15.09	15.21
273	245	14.20	5.01	5.77	16.12	16.45	273	95	13.10	4.85	5.59	15.04	15.15
273	240	14.16	5.00	5.77	16.09	16.42	273	90	13.05	4.84	5.58	15.00	15.08
273	235	14.13	5.00	5.76	16.06	16.39	273	85	13.00	4.83	5.57	14.95	15.02
273	230	14.11	5.00	5.76	16.04	16.36	273	80	12.95	4.83	5.56	14.90	14.95
273	225	14.08	4.99	5.75	16.01	16.32	273	75	12.88	4.82	5.55	14.83	14.88
273	220	14.04	4.99	5.75	15.97	16.29	273	70	12.83	4.81	5.54	14.78	14.81
273	215	14.01	4.98	5.74	15.94	16.26	273	65	12.78	4.80	5.54	14.73	14.73
273	210	13.98	4.98	5.74	15.91	16.22	273	60	12.72	4.79	5.52	14.67	14.65
273	205	13.94	4.97	5.73	15.87	16.19	273	55	12.65	4.78	5.51	14.60	14.57
273	200	13.92	4.97	5.73	15.86	16.15	273	50	12.58	4.77	5.50	14.54	14.48
273	195	13.89	4.96	5.72	15.82	16.11	273	45	12.52	4.76	5.49	14.47	14.39
273	190	13.86	4.96	5.72	15.79	16.07	273	40	1.06	1.77	2.05	2.91	2.62
273	185	13.82	4.95	5.71	15.76	16.03	273	35	0.77	1.56	1.80	2.50	2
273	180	13.79	4.95	5.71	15.72	16	273	30	0.56	1.38	1.59	2.18	1.57
273	175	13.76	4.94	5.70	15.69	15.95	273	25	0.41	1.21	1.40	1.89	1.22
273	170	13.70	4.94	5.69	15.64	15.91	273	20	0.29	1.05	1.21	1.63	0.92
273	165	13.67	4.93	5.69	15.61	15.87	273	15	0.19	0.89	1.03	1.37	0.65
273	160	13.64	4.93	5.68	15.57	15.83	273	10	0.11	0.71	0.82	1.09	0.42

T, K	P, bar	$\delta_{d1, 1/2}$ MPa	$\delta_{p1, 1/2}$ MPa	$\delta_{h1, 1/2}$ MPa	$\delta_{T1, 1/2}$ MPa	$\delta_{Hildebrand, 1/2}$ MPa	T, K	P, bar	$\delta_{d1, 1/2}$ MPa	$\delta_{p1, 1/2}$ MPa	$\delta_{h1, 1/2}$ MPa	$\delta_{T1, 1/2}$ MPa	$\delta_{Hildebrand, 1/2}$ MPa
283	905	16.16	5.27	6.00	18.03	18.04	283	755	15.74	5.22	5.94	17.62	17.75
283	900	16.16	5.27	6.00	18.03	18.03	283	750	15.73	5.22	5.94	17.60	17.74
283	895	16.14	5.27	6.00	18.01	18.02	283	745	15.71	5.21	5.93	17.58	17.73
283	890	16.13	5.27	6.00	17.99	18.01	283	740	15.71	5.21	5.93	17.58	17.72
283	885	16.11	5.27	5.99	17.98	18.00	283	735	15.69	5.21	5.93	17.57	17.71
283	880	16.11	5.27	5.99	17.98	18.00	283	730	15.67	5.21	5.93	17.55	17.70
283	875	16.09	5.26	5.99	17.96	17.99	283	725	15.66	5.21	5.92	17.53	17.69
283	870	16.07	5.26	5.99	17.94	17.98	283	720	15.64	5.21	5.92	17.51	17.68
283	865	16.06	5.26	5.98	17.93	17.97	283	715	15.62	5.20	5.92	17.50	17.66
283	860	16.04	5.26	5.98	17.91	17.96	283	710	15.60	5.20	5.92	17.48	17.65
283	855	16.04	5.26	5.98	17.91	17.95	283	705	15.59	5.20	5.91	17.46	17.64
283	850	16.02	5.26	5.98	17.89	17.94	283	700	15.57	5.20	5.91	17.45	17.63
283	845	16.00	5.25	5.98	17.87	17.93	283	695	15.55	5.19	5.91	17.43	17.62
283	840	15.99	5.25	5.97	17.86	17.92	283	690	15.55	5.19	5.91	17.43	17.60
283	835	15.97	5.25	5.97	17.84	17.91	283	685	15.54	5.19	5.91	17.41	17.59
283	830	15.97	5.25	5.97	17.84	17.90	283	680	15.52	5.19	5.90	17.40	17.58
283	825	15.95	5.25	5.97	17.82	17.89	283	675	15.50	5.19	5.90	17.38	17.57
283	820	15.94	5.24	5.97	17.81	17.89	283	670	15.48	5.18	5.90	17.36	17.55
283	815	15.92	5.24	5.96	17.79	17.88	283	665	15.47	5.18	5.90	17.34	17.54
283	810	15.90	5.24	5.96	17.77	17.87	283	660	15.45	5.18	5.89	17.33	17.53
283	805	15.90	5.24	5.96	17.77	17.86	283	655	15.43	5.18	5.89	17.31	17.52
283	800	15.88	5.24	5.96	17.75	17.85	283	650	15.41	5.18	5.89	17.29	17.50
283	795	15.87	5.24	5.96	17.74	17.84	283	645	15.40	5.17	5.89	17.28	17.49
283	790	15.85	5.23	5.95	17.72	17.83	283	640	15.38	5.17	5.88	17.26	17.48
283	785	15.83	5.23	5.95	17.70	17.82	283	635	15.36	5.17	5.88	17.24	17.46
283	780	15.81	5.23	5.95	17.69	17.81	283	630	15.35	5.17	5.88	17.23	17.45
283	775	15.81	5.23	5.95	17.69	17.79	283	625	15.33	5.16	5.87	17.21	17.44
283	770	15.80	5.23	5.95	17.67	17.79	283	620	15.31	5.16	5.87	17.19	17.42
283	765	15.78	5.22	5.94	17.65	17.77	283	615	15.29	5.16	5.87	17.17	17.41
283	760	15.76	5.22	5.94	17.63	17.76	283	610	15.28	5.16	5.87	17.16	17.39

T, K	P, bar	$\delta_{d,1/2}$ MPa	$\delta_{p,1/2}$ MPa	$\delta_{h,1/2}$ MPa	$\delta_{T,1/2}$ MPa	$\delta_{Hildebrand,1/2}$ MPa	T, K	P, bar	$\delta_{d,1/2}$ MPa	$\delta_{p,1/2}$ MPa	$\delta_{h,1/2}$ MPa	$\delta_{T,1/2}$ MPa	$\delta_{Hildebrand,1/2}$ MPa
283	605	15.26	5.15	5.86	17.14	17.38	283	455	14.67	5.07	5.77	16.57	16.87
283	600	15.24	5.15	5.86	17.12	17.36	283	450	14.66	5.07	5.77	16.55	16.85
283	595	15.22	5.15	5.86	17.11	17.35	283	445	14.64	5.07	5.77	16.53	16.83
283	590	15.21	5.15	5.86	17.09	17.34	283	440	14.61	5.06	5.76	16.50	16.81
283	585	15.19	5.14	5.85	17.07	17.32	283	435	14.59	5.06	5.76	16.48	16.79
283	580	15.17	5.14	5.85	17.06	17.31	283	430	14.57	5.06	5.76	16.46	16.77
283	575	15.16	5.14	5.85	17.04	17.29	283	425	14.55	5.06	5.75	16.45	16.75
283	570	15.14	5.14	5.85	17.02	17.28	283	420	14.52	5.05	5.75	16.41	16.72
283	565	15.12	5.14	5.84	17.00	17.26	283	415	14.50	5.05	5.75	16.40	16.70
283	560	15.10	5.13	5.84	16.99	17.24	283	410	14.47	5.05	5.74	16.36	16.68
283	555	15.09	5.13	5.84	16.97	17.23	283	405	14.45	5.04	5.74	16.35	16.66
283	550	15.05	5.13	5.83	16.94	17.21	283	400	14.43	5.04	5.74	16.33	16.64
283	545	15.03	5.12	5.83	16.92	17.20	283	395	14.40	5.04	5.73	16.30	16.61
283	540	15.02	5.12	5.83	16.90	17.18	283	390	14.38	5.03	5.73	16.28	16.59
283	535	15.00	5.12	5.82	16.89	17.16	283	385	14.37	5.03	5.72	16.26	16.56
283	530	14.98	5.12	5.82	16.87	17.15	283	380	14.33	5.03	5.72	16.23	16.54
283	525	14.97	5.11	5.82	16.85	17.13	283	375	14.32	5.02	5.72	16.21	16.52
283	520	14.95	5.11	5.82	16.84	17.11	283	370	14.28	5.02	5.71	16.18	16.49
283	515	14.93	5.11	5.81	16.82	17.09	283	365	14.26	5.02	5.71	16.16	16.47
283	510	14.90	5.11	5.81	16.78	17.08	283	360	14.23	5.01	5.70	16.13	16.44
283	505	14.88	5.10	5.81	16.77	17.06	283	355	14.21	5.01	5.70	16.11	16.41
283	500	14.86	5.10	5.80	16.75	17.04	283	350	14.18	5.01	5.69	16.08	16.39
283	495	14.85	5.10	5.80	16.73	17.02	283	345	14.16	5.00	5.69	16.06	16.36
283	490	14.83	5.10	5.80	16.72	17.01	283	340	14.13	5.00	5.69	16.03	16.34
283	485	14.81	5.09	5.79	16.70	16.99	283	335	14.11	5.00	5.68	16.01	16.31
283	480	14.78	5.09	5.79	16.67	16.97	283	330	14.08	4.99	5.68	15.98	16.28
283	475	14.76	5.09	5.79	16.65	16.95	283	325	14.04	4.99	5.67	15.95	16.25
283	470	14.74	5.08	5.78	16.63	16.93	283	320	14.03	4.98	5.67	15.93	16.22
283	465	14.73	5.08	5.78	16.62	16.91	283	315	13.99	4.98	5.66	15.90	16.19
283	460	14.69	5.08	5.78	16.58	16.89	283	310	13.96	4.97	5.66	15.86	16.16

T, K	P, bar	$\delta_{a,1/2}$ MPa	$\delta_{p,1/2}$ MPa	$\delta_{h,1/2}$ MPa	$\delta_{T,1/2}$ MPa	$\delta_{Hildebrand}, MPa^{1/2}$	T, K	P, bar	$\delta_{a,1/2}$ MPa	$\delta_{p,1/2}$ MPa	$\delta_{h,1/2}$ MPa	$\delta_{T,1/2}$ MPa	$\delta_{Hildebrand}, MPa^{1/2}$
283	305	13.94	4.97	5.66	15.85	16.13	283	155	12.87	4.81	5.48	14.79	14.89
283	300	13.91	4.97	5.65	15.81	16.10	283	150	12.82	4.81	5.47	14.74	14.83
283	295	13.87	4.96	5.64	15.78	16.07	283	145	12.77	4.80	5.46	14.69	14.77
283	290	13.86	4.96	5.64	15.76	16.04	283	140	12.72	4.79	5.45	14.64	14.71
283	285	13.82	4.95	5.64	15.73	16.01	283	135	12.67	4.78	5.44	14.59	14.65
283	280	13.79	4.95	5.63	15.70	15.97	283	130	12.62	4.78	5.43	14.54	14.58
283	275	13.76	4.94	5.63	15.66	15.94	283	125	12.55	4.77	5.42	14.48	14.51
283	270	13.72	4.94	5.62	15.63	15.91	283	120	12.50	4.76	5.41	14.43	14.44
283	265	13.69	4.94	5.61	15.60	15.87	283	115	12.45	4.75	5.41	14.38	14.37
283	260	13.67	4.93	5.61	15.58	15.84	283	110	12.38	4.74	5.39	14.32	14.29
283	255	13.64	4.93	5.61	15.55	15.80	283	105	12.32	4.73	5.38	14.25	14.21
283	250	13.60	4.92	5.60	15.51	15.76	283	100	12.25	4.72	5.37	14.19	14.13
283	245	13.57	4.92	5.60	15.48	15.73	283	95	12.18	4.71	5.36	14.12	14.04
283	240	13.54	4.91	5.59	15.45	15.69	283	90	12.12	4.70	5.35	14.06	13.95
283	235	13.50	4.91	5.58	15.41	15.65	283	85	12.05	4.69	5.34	13.99	13.85
283	230	13.47	4.90	5.58	15.38	15.61	283	80	11.97	4.68	5.32	13.91	13.75
283	225	13.43	4.90	5.57	15.35	15.57	283	75	11.91	4.67	5.31	13.85	13.65
283	220	13.38	4.89	5.56	15.30	15.53	283	70	11.81	4.65	5.29	13.75	13.53
283	215	13.35	4.89	5.56	15.26	15.49	283	65	11.72	4.64	5.28	13.67	13.41
283	210	13.32	4.88	5.55	15.23	15.44	283	60	11.63	4.62	5.26	13.57	13.28
283	205	13.28	4.88	5.55	15.20	15.40	283	55	11.53	4.61	5.24	13.48	13.15
283	200	13.23	4.87	5.54	15.15	15.35	283	50	1.68	2.13	2.43	3.64	3.56
283	195	13.20	4.86	5.53	15.12	15.31	283	45	1.14	1.83	2.08	3.00	2.67
283	190	13.17	4.86	5.53	15.08	15.26	283	40	0.86	1.63	1.86	2.62	2.14
283	185	13.12	4.85	5.52	15.03	15.21	283	35	0.66	1.47	1.67	2.32	1.74
283	180	13.08	4.85	5.51	15.00	15.16	283	30	0.50	1.32	1.50	2.06	1.40
283	175	13.03	4.84	5.51	14.95	15.11	283	25	0.38	1.17	1.33	1.81	1.11
283	170	13.00	4.83	5.50	14.92	15.06	283	20	0.27	1.03	1.17	1.58	0.84
283	165	12.95	4.83	5.49	14.87	15.00	283	15	0.18	0.86	0.98	1.32	0.61
283	160	12.90	4.82	5.48	14.82	14.95	283	10	0.10	0.69	0.79	1.06	0.39

T, K	P, bar	$\delta_{d,1/2}$ MPa	$\delta_{p,1/2}$ MPa	$\delta_{h,1/2}$ MPa	$\delta_{T,1/2}$ MPa	$\delta_{Hildebrand,1/2}$ MPa	T, K	P, bar	$\delta_{d,1/2}$ MPa	$\delta_{p,1/2}$ MPa	$\delta_{h,1/2}$ MPa	$\delta_{T,1/2}$ MPa	$\delta_{Hildebrand,1/2}$ MPa
293	905	15.78	5.22	5.87	17.63	17.63	293	755	15.35	5.17	5.80	17.20	17.31
293	900	15.78	5.22	5.87	17.63	17.62	293	750	15.33	5.16	5.80	17.18	17.30
293	895	15.76	5.22	5.86	17.61	17.62	293	745	15.31	5.16	5.79	17.17	17.29
293	890	15.74	5.22	5.86	17.59	17.61	293	740	15.29	5.16	5.79	17.15	17.28
293	885	15.73	5.22	5.86	17.57	17.60	293	735	15.28	5.16	5.79	17.13	17.26
293	880	15.71	5.21	5.85	17.56	17.59	293	730	15.26	5.15	5.79	17.11	17.25
293	875	15.71	5.21	5.85	17.56	17.58	293	725	15.24	5.15	5.78	17.10	17.24
293	870	15.69	5.21	5.85	17.54	17.57	293	720	15.22	5.15	5.78	17.08	17.23
293	865	15.67	5.21	5.85	17.52	17.56	293	715	15.21	5.15	5.78	17.06	17.21
293	860	15.66	5.21	5.85	17.51	17.55	293	710	15.19	5.14	5.78	17.05	17.20
293	855	15.64	5.21	5.84	17.49	17.54	293	705	15.17	5.14	5.77	17.03	17.19
293	850	15.62	5.20	5.84	17.47	17.53	293	700	15.16	5.14	5.77	17.01	17.17
293	845	15.62	5.20	5.84	17.47	17.52	293	695	15.14	5.14	5.77	17.00	17.16
293	840	15.60	5.20	5.84	17.45	17.51	293	690	15.12	5.14	5.77	16.98	17.15
293	835	15.59	5.20	5.84	17.44	17.49	293	685	15.10	5.13	5.76	16.96	17.13
293	830	15.57	5.20	5.83	17.42	17.48	293	680	15.09	5.13	5.76	16.94	17.12
293	825	15.55	5.19	5.83	17.40	17.47	293	675	15.07	5.13	5.76	16.93	17.10
293	820	15.54	5.19	5.83	17.39	17.46	293	670	15.05	5.13	5.76	16.91	17.09
293	815	15.52	5.19	5.83	17.37	17.45	293	665	15.03	5.12	5.75	16.89	17.08
293	810	15.52	5.19	5.83	17.37	17.44	293	660	15.02	5.12	5.75	16.88	17.06
293	805	15.50	5.19	5.82	17.35	17.43	293	655	15.00	5.12	5.75	16.86	17.05
293	800	15.48	5.18	5.82	17.34	17.42	293	650	14.98	5.12	5.74	16.84	17.03
293	795	15.47	5.18	5.82	17.32	17.41	293	645	14.97	5.11	5.74	16.83	17.02
293	790	15.45	5.18	5.82	17.30	17.40	293	640	14.95	5.11	5.74	16.81	17.00
293	785	15.43	5.18	5.81	17.28	17.38	293	635	14.93	5.11	5.74	16.79	16.99
293	780	15.41	5.18	5.81	17.27	17.37	293	630	14.91	5.11	5.73	16.78	16.97
293	775	15.40	5.17	5.81	17.25	17.36	293	625	14.90	5.11	5.73	16.76	16.96
293	770	15.38	5.17	5.81	17.23	17.35	293	620	14.88	5.10	5.73	16.74	16.94
293	765	15.36	5.17	5.80	17.22	17.34	293	615	14.85	5.10	5.72	16.71	16.92
293	760	15.36	5.17	5.80	17.22	17.33	293	610	14.83	5.10	5.72	16.69	16.91

T, K	P, bar	$\delta_{d1, 1/2}$ MPa	$\delta_{p1, 1/2}$ MPa	$\delta_{h1, 1/2}$ MPa	$\delta_{T1, 1/2}$ MPa	$\delta_{Hildebrägd1, 1/2}$ MPa	T, K	P, bar	$\delta_{d1, 1/2}$ MPa	$\delta_{p1, 1/2}$ MPa	$\delta_{h1, 1/2}$ MPa	$\delta_{T1, 1/2}$ MPa	$\delta_{Hildebrägd1, 1/2}$ MPa
293	605	14.81	5.09	5.72	16.67	16.89	293	455	14.18	5.01	5.62	16.05	16.31
293	600	14.79	5.09	5.72	16.66	16.88	293	450	14.16	5.00	5.62	16.04	16.29
293	595	14.78	5.09	5.71	16.64	16.86	293	445	14.13	5.00	5.61	16.00	16.27
293	590	14.76	5.09	5.71	16.62	16.84	293	440	14.11	5.00	5.61	15.99	16.24
293	585	14.74	5.08	5.71	16.61	16.83	293	435	14.08	4.99	5.60	15.95	16.22
293	580	14.73	5.08	5.71	16.59	16.81	293	430	14.06	4.99	5.60	15.94	16.20
293	575	14.69	5.08	5.70	16.56	16.79	293	425	14.03	4.98	5.60	15.90	16.17
293	570	14.67	5.07	5.70	16.54	16.77	293	420	14.01	4.98	5.59	15.89	16.15
293	565	14.66	5.07	5.69	16.52	16.76	293	415	13.98	4.98	5.59	15.85	16.12
293	560	14.64	5.07	5.69	16.51	16.74	293	410	13.96	4.97	5.58	15.84	16.09
293	555	14.62	5.07	5.69	16.49	16.72	293	405	13.92	4.97	5.58	15.80	16.07
293	550	14.61	5.06	5.69	16.47	16.70	293	400	13.91	4.97	5.58	15.79	16.04
293	545	14.57	5.06	5.68	16.44	16.68	293	395	13.87	4.96	5.57	15.75	16.02
293	540	14.55	5.06	5.68	16.42	16.67	293	390	13.86	4.96	5.57	15.74	15.99
293	535	14.54	5.06	5.68	16.40	16.65	293	385	13.82	4.95	5.56	15.70	15.96
293	530	14.52	5.05	5.67	16.39	16.63	293	380	13.79	4.95	5.56	15.67	15.93
293	525	14.49	5.05	5.67	16.35	16.61	293	375	13.77	4.95	5.55	15.65	15.91
293	520	14.47	5.05	5.67	16.34	16.59	293	370	13.74	4.94	5.55	15.62	15.88
293	515	14.45	5.04	5.66	16.32	16.57	293	365	13.72	4.94	5.55	15.60	15.85
293	510	14.43	5.04	5.66	16.30	16.55	293	360	13.69	4.94	5.54	15.57	15.82
293	505	14.40	5.04	5.65	16.27	16.53	293	355	13.65	4.93	5.54	15.54	15.79
293	500	14.38	5.03	5.65	16.25	16.51	293	350	13.62	4.93	5.53	15.50	15.76
293	495	14.37	5.03	5.65	16.24	16.49	293	345	13.60	4.92	5.53	15.49	15.73
293	490	14.35	5.03	5.65	16.22	16.47	293	340	13.57	4.92	5.52	15.45	15.69
293	485	14.32	5.02	5.64	16.19	16.45	293	335	13.54	4.91	5.52	15.42	15.66
293	480	14.30	5.02	5.64	16.17	16.42	293	330	13.50	4.91	5.51	15.39	15.63
293	475	14.28	5.02	5.64	16.15	16.40	293	325	13.47	4.90	5.51	15.35	15.60
293	470	14.25	5.01	5.63	16.12	16.38	293	320	13.45	4.90	5.50	15.34	15.56
293	465	14.23	5.01	5.63	16.10	16.36	293	315	13.42	4.90	5.50	15.30	15.53
293	460	14.20	5.01	5.62	16.07	16.34	293	310	13.38	4.89	5.49	15.27	15.49

T, K	P, bar	$\delta_{d,1/2}$ MPa	$\delta_{p,1/2}$ MPa	$\delta_{h,1/2}$ MPa	$\delta_{T,1/2}$ MPa	$\delta_{Hildebrand}$ MPa ^{1/2}	T, K	P, bar	$\delta_{d,1/2}$ MPa	$\delta_{p,1/2}$ MPa	$\delta_{h,1/2}$ MPa	$\delta_{T,1/2}$ MPa	$\delta_{Hildebrand}$ MPa ^{1/2}
293	305	13.35	4.89	5.49	15.24	15.46	293	155	12.05	4.69	5.27	13.96	13.93
293	300	13.32	4.88	5.48	15.21	15.42	293	150	11.99	4.68	5.25	13.90	13.85
293	295	13.28	4.88	5.47	15.17	15.39	293	145	11.92	4.67	5.24	13.84	13.77
293	290	13.25	4.87	5.47	15.14	15.35	293	140	11.86	4.66	5.23	13.77	13.69
293	285	13.22	4.87	5.46	15.11	15.31	293	135	11.79	4.65	5.22	13.71	13.60
293	280	13.18	4.86	5.46	15.07	15.27	293	130	11.72	4.64	5.21	13.64	13.51
293	275	13.15	4.86	5.45	15.04	15.23	293	125	11.64	4.63	5.19	13.56	13.41
293	270	13.10	4.85	5.44	14.99	15.19	293	120	11.56	4.61	5.18	13.48	13.31
293	265	13.07	4.84	5.44	14.96	15.15	293	115	11.48	4.60	5.16	13.40	13.21
293	260	13.03	4.84	5.43	14.93	15.11	293	110	11.40	4.59	5.15	13.32	13.10
293	255	13.00	4.83	5.43	14.89	15.06	293	105	11.32	4.57	5.13	13.24	12.98
293	250	12.95	4.83	5.42	14.84	15.02	293	100	11.22	4.56	5.12	13.15	12.86
293	245	12.92	4.82	5.41	14.81	14.97	293	95	11.12	4.54	5.10	13.05	12.73
293	240	12.88	4.82	5.41	14.78	14.93	293	90	11.01	4.52	5.08	12.94	12.58
293	235	12.83	4.81	5.40	14.73	14.88	293	85	10.90	4.50	5.06	12.83	12.43
293	230	12.80	4.80	5.39	14.70	14.83	293	80	10.77	4.48	5.03	12.70	12.26
293	225	12.75	4.80	5.39	14.65	14.78	293	75	10.62	4.46	5.01	12.56	12.07
293	220	12.72	4.79	5.38	14.61	14.73	293	70	10.48	4.43	4.98	12.42	11.86
293	215	12.67	4.78	5.37	14.57	14.68	293	65	10.29	4.40	4.94	12.23	11.62
293	210	12.62	4.78	5.36	14.52	14.63	293	60	2.61	2.54	2.86	4.63	4.67
293	205	12.57	4.77	5.35	14.47	14.57	293	50	1.19	1.86	2.09	3.04	2.68
293	200	12.53	4.76	5.35	14.43	14.52	293	45	0.94	1.69	1.90	2.71	2.24
293	195	12.48	4.76	5.34	14.39	14.46	293	40	0.75	1.54	1.73	2.44	1.87
293	190	12.43	4.75	5.33	14.34	14.40	293	35	0.59	1.40	1.58	2.19	1.55
293	185	12.38	4.74	5.32	14.29	14.34	293	30	0.46	1.27	1.42	1.96	1.27
293	180	12.33	4.73	5.31	14.24	14.27	293	25	0.35	1.14	1.28	1.75	1.02
293	175	12.27	4.72	5.30	14.17	14.21	293	20	0.26	1.00	1.13	1.53	0.78
293	170	12.22	4.72	5.29	14.13	14.14	293	15	0.17	0.85	0.95	1.29	0.57
293	165	12.17	4.71	5.29	14.08	14.07	293	10	0.10	0.68	0.76	1.02	0.37
293	160	12.10	4.70	5.27	14.01	14.00							

T, K	P, bar	$\delta_{d, 1/2}$ MPa	$\delta_{p, 1/2}$ MPa	$\delta_{h, 1/2}$ MPa	$\delta_{T, 1/2}$ MPa	$\delta_{Hildebrand, 1/2}$ MPa	T, K	P, bar	$\delta_{d, 1/2}$ MPa	$\delta_{p, 1/2}$ MPa	$\delta_{h, 1/2}$ MPa	$\delta_{T, 1/2}$ MPa	$\delta_{Hildebrand, 1/2}$ MPa
303	905	15.41	5.18	5.73	17.24	17.19	303	755	14.93	5.11	5.66	16.77	16.83
303	900	15.40	5.17	5.73	17.22	17.18	303	750	14.91	5.11	5.66	16.75	16.82
303	895	15.38	5.17	5.73	17.21	17.17	303	745	14.90	5.11	5.66	16.73	16.81
303	890	15.36	5.17	5.73	17.19	17.16	303	740	14.88	5.10	5.65	16.72	16.79
303	885	15.35	5.17	5.72	17.17	17.15	303	735	14.86	5.10	5.65	16.70	16.78
303	880	15.33	5.16	5.72	17.16	17.14	303	730	14.85	5.10	5.65	16.68	16.76
303	875	15.33	5.16	5.72	17.16	17.12	303	725	14.83	5.10	5.65	16.67	16.75
303	870	15.31	5.16	5.72	17.14	17.11	303	720	14.81	5.09	5.64	16.65	16.73
303	865	15.29	5.16	5.72	17.12	17.10	303	715	14.79	5.09	5.64	16.63	16.72
303	860	15.28	5.16	5.71	17.11	17.09	303	710	14.78	5.09	5.64	16.61	16.71
303	855	15.26	5.15	5.71	17.09	17.08	303	705	14.76	5.09	5.64	16.60	16.69
303	850	15.24	5.15	5.71	17.07	17.07	303	700	14.74	5.08	5.63	16.58	16.68
303	845	15.22	5.15	5.71	17.05	17.06	303	695	14.73	5.08	5.63	16.56	16.66
303	840	15.21	5.15	5.70	17.04	17.05	303	690	14.71	5.08	5.63	16.55	16.64
303	835	15.19	5.14	5.70	17.02	17.03	303	685	14.69	5.08	5.63	16.53	16.63
303	830	15.17	5.14	5.70	17.00	17.02	303	680	14.67	5.07	5.62	16.51	16.61
303	825	15.17	5.14	5.70	17.00	17.01	303	675	14.64	5.07	5.62	16.48	16.60
303	820	15.16	5.14	5.70	16.99	17.00	303	670	14.62	5.07	5.61	16.46	16.58
303	815	15.14	5.14	5.69	16.97	16.99	303	665	14.61	5.06	5.61	16.45	16.57
303	810	15.12	5.14	5.69	16.95	16.97	303	660	14.59	5.06	5.61	16.43	16.55
303	805	15.10	5.13	5.69	16.94	16.96	303	655	14.57	5.06	5.61	16.41	16.53
303	800	15.09	5.13	5.69	16.92	16.95	303	650	14.55	5.06	5.60	16.40	16.52
303	795	15.07	5.13	5.68	16.90	16.94	303	645	14.54	5.06	5.60	16.38	16.50
303	790	15.05	5.13	5.68	16.89	16.92	303	640	14.52	5.05	5.60	16.36	16.48
303	785	15.03	5.12	5.68	16.87	16.91	303	635	14.49	5.05	5.59	16.33	16.47
303	780	15.02	5.12	5.67	16.85	16.90	303	630	14.47	5.05	5.59	16.31	16.45
303	775	15.00	5.12	5.67	16.83	16.88	303	625	14.45	5.04	5.59	16.30	16.43
303	770	14.98	5.12	5.67	16.82	16.87	303	620	14.43	5.04	5.59	16.28	16.42
303	765	14.97	5.11	5.67	16.80	16.86	303	615	14.42	5.04	5.58	16.26	16.40
303	760	14.95	5.11	5.66	16.78	16.85	303	610	14.40	5.04	5.58	16.24	16.38

T, K	P, bar	$\delta_{d,1/2}$ MPa	$\delta_{p,1/2}$ MPa	$\delta_{H,1/2}$ MPa	$\delta_{T,1/2}$ MPa	$\delta_{Hildebrand,1/2}$ MPa	T, K	P, bar	$\delta_{d,1/2}$ MPa	$\delta_{p,1/2}$ MPa	$\delta_{H,1/2}$ MPa	$\delta_{T,1/2}$ MPa	$\delta_{Hildebrand,1/2}$ MPa
303	605	14.37	5.03	5.58	16.21	16.36	303	455	13.67	4.93	5.47	15.53	15.71
303	600	14.35	5.03	5.57	16.19	16.34	303	450	13.65	4.93	5.46	15.51	15.69
303	595	14.33	5.03	5.57	16.18	16.32	303	445	13.62	4.93	5.46	15.48	15.66
303	590	14.32	5.02	5.57	16.16	16.31	303	440	13.60	4.92	5.45	15.46	15.63
303	585	14.28	5.02	5.56	16.13	16.29	303	435	13.57	4.92	5.45	15.43	15.61
303	580	14.26	5.02	5.56	16.11	16.27	303	430	13.54	4.91	5.44	15.39	15.58
303	575	14.25	5.01	5.56	16.09	16.25	303	425	13.52	4.91	5.44	15.38	15.55
303	570	14.23	5.01	5.55	16.08	16.23	303	420	13.49	4.91	5.44	15.35	15.52
303	565	14.20	5.01	5.55	16.04	16.21	303	415	13.45	4.90	5.43	15.31	15.49
303	560	14.18	5.01	5.55	16.03	16.19	303	410	13.43	4.90	5.43	15.30	15.46
303	555	14.16	5.00	5.54	16.01	16.17	303	405	13.40	4.89	5.42	15.26	15.43
303	550	14.15	5.00	5.54	15.99	16.15	303	400	13.37	4.89	5.42	15.23	15.41
303	545	14.11	5.00	5.54	15.96	16.13	303	395	13.35	4.89	5.41	15.21	15.37
303	540	14.09	4.99	5.53	15.94	16.11	303	390	13.32	4.88	5.41	15.18	15.34
303	535	14.08	4.99	5.53	15.93	16.09	303	385	13.28	4.88	5.40	15.15	15.31
303	530	14.04	4.99	5.52	15.89	16.07	303	380	13.25	4.87	5.40	15.11	15.28
303	525	14.03	4.98	5.52	15.88	16.05	303	375	13.22	4.87	5.39	15.08	15.25
303	520	13.99	4.98	5.52	15.84	16.02	303	370	13.18	4.86	5.39	15.05	15.21
303	515	13.98	4.98	5.51	15.83	16.00	303	365	13.17	4.86	5.38	15.03	15.18
303	510	13.96	4.97	5.51	15.81	15.98	303	360	13.13	4.85	5.38	15.00	15.15
303	505	13.92	4.97	5.51	15.78	15.96	303	355	13.10	4.85	5.37	14.97	15.11
303	500	13.91	4.97	5.50	15.76	15.93	303	350	13.07	4.84	5.37	14.93	15.08
303	495	13.87	4.96	5.50	15.73	15.91	303	345	13.03	4.84	5.36	14.90	15.04
303	490	13.86	4.96	5.50	15.71	15.89	303	340	13.00	4.83	5.36	14.87	15.00
303	485	13.82	4.95	5.49	15.68	15.86	303	335	12.97	4.83	5.35	14.83	14.97
303	480	13.81	4.95	5.49	15.66	15.84	303	330	12.93	4.82	5.35	14.80	14.93
303	475	13.79	4.95	5.48	15.64	15.81	303	325	12.88	4.82	5.34	14.75	14.89
303	470	13.76	4.94	5.48	15.61	15.79	303	320	12.85	4.81	5.33	14.72	14.85
303	465	13.74	4.94	5.48	15.59	15.76	303	315	12.82	4.81	5.33	14.69	14.81
303	460	13.70	4.94	5.47	15.56	15.74	303	310	12.78	4.80	5.32	14.65	14.77

T, K	P, bar	$\delta_{d,1/2}$ MPa	$\delta_{p,1/2}$ MPa	$\delta_{H,1/2}$ MPa	$\delta_{T,1/2}$ MPa	$\delta_{H,bragg}$ MPa	T, K	P, bar	$\delta_{d,1/2}$ MPa	$\delta_{p,1/2}$ MPa	$\delta_{H,1/2}$ MPa	$\delta_{T,1/2}$ MPa	$\delta_{H,bragg}$ MPa
303	305	12.75	4.80	5.31	14.62	14.73	303	155	11.14	4.54	5.04	13.04	12.83
303	300	12.70	4.79	5.31	14.57	14.69	303	150	11.06	4.53	5.02	12.96	12.73
303	295	12.67	4.78	5.30	14.54	14.64	303	145	10.98	4.52	5.01	12.88	12.62
303	290	12.63	4.78	5.30	14.51	14.60	303	140	10.88	4.50	4.99	12.79	12.50
303	285	12.58	4.77	5.29	14.46	14.55	303	135	10.78	4.49	4.97	12.69	12.38
303	280	12.55	4.77	5.28	14.43	14.51	303	130	10.69	4.47	4.95	12.60	12.25
303	275	12.50	4.76	5.27	14.38	14.46	303	125	10.57	4.45	4.93	12.49	12.11
303	270	12.47	4.75	5.27	14.34	14.41	303	120	10.46	4.43	4.91	12.38	11.97
303	265	12.42	4.75	5.26	14.30	14.36	303	115	10.33	4.41	4.89	12.25	11.81
303	260	12.37	4.74	5.25	14.25	14.31	303	110	10.21	4.39	4.86	12.13	11.63
303	255	12.33	4.73	5.25	14.21	14.26	303	105	10.05	4.36	4.83	11.97	11.44
303	250	12.28	4.73	5.24	14.17	14.21	303	100	9.87	4.33	4.80	11.80	11.23
303	245	12.23	4.72	5.23	14.12	14.15	303	95	9.68	4.30	4.76	11.61	10.99
303	240	12.18	4.71	5.22	14.07	14.10	303	90	9.46	4.26	4.72	11.40	10.71
303	235	12.14	4.70	5.21	14.02	14.04	303	85	9.20	4.21	4.66	11.14	10.37
303	230	12.09	4.70	5.20	13.97	13.98	303	80	8.84	4.14	4.59	10.79	9.95
303	225	12.04	4.69	5.19	13.92	13.92	303	75	8.30	4.04	4.48	10.26	9.32
303	220	11.99	4.68	5.19	13.87	13.86	303	65	1.96	2.27	2.51	3.91	3.75
303	215	11.94	4.67	5.18	13.83	13.79	303	60	1.54	2.06	2.28	3.43	3.14
303	210	11.87	4.66	5.17	13.76	13.73	303	55	1.25	1.89	2.10	3.09	2.68
303	205	11.82	4.65	5.16	13.71	13.66	303	50	1.02	1.75	1.94	2.80	2.30
303	200	11.76	4.64	5.15	13.65	13.59	303	45	0.83	1.61	1.79	2.55	1.97
303	195	11.71	4.64	5.14	13.60	13.52	303	40	0.67	1.48	1.64	2.31	1.68
303	190	11.64	4.63	5.13	13.54	13.44	303	35	0.55	1.36	1.51	2.10	1.41
303	185	11.58	4.62	5.11	13.47	13.37	303	30	0.43	1.23	1.36	1.89	1.17
303	180	11.51	4.60	5.10	13.41	13.29	303	25	0.33	1.11	1.23	1.68	0.94
303	175	11.45	4.59	5.09	13.34	13.20	303	20	0.24	0.98	1.09	1.48	0.73
303	170	11.38	4.58	5.08	13.28	13.11	303	15	0.16	0.83	0.93	1.26	0.53
303	165	11.30	4.57	5.06	13.20	13.02	303	10	0.10	0.68	0.75	1.01	0.35
303	160	11.22	4.56	5.05	13.12	12.93							

T, K	P, bar	$\delta_{d, 1/2}$ MPa	$\delta_{p, 1/2}$ MPa	$\delta_{h, 1/2}$ MPa	$\delta_{T, 1/2}$ MPa	$\delta_{Hildebrand, 1/2}$ MPa	T, K	P, bar	$\delta_{d, 1/2}$ MPa	$\delta_{p, 1/2}$ MPa	$\delta_{h, 1/2}$ MPa	$\delta_{T, 1/2}$ MPa	$\delta_{Hildebrand, 1/2}$ MPa
313	905	15.03	5.12	5.60	16.84	16.84	313	755	14.54	5.06	5.53	16.35	16.45
313	900	15.02	5.12	5.60	16.83	16.83	313	750	14.52	5.05	5.53	16.34	16.43
313	895	15.00	5.12	5.60	16.81	16.82	313	745	14.50	5.05	5.52	16.32	16.42
313	890	14.98	5.12	5.60	16.79	16.81	313	740	14.47	5.05	5.52	16.29	16.40
313	885	14.98	5.12	5.60	16.79	16.80	313	735	14.45	5.04	5.52	16.27	16.39
313	880	14.97	5.11	5.59	16.78	16.79	313	730	14.43	5.04	5.51	16.25	16.37
313	875	14.95	5.11	5.59	16.76	16.77	313	725	14.42	5.04	5.51	16.24	16.35
313	870	14.93	5.11	5.59	16.74	16.76	313	720	14.40	5.04	5.51	16.22	16.34
313	865	14.91	5.11	5.58	16.72	16.75	313	715	14.38	5.03	5.50	16.20	16.32
313	860	14.90	5.11	5.58	16.71	16.74	313	710	14.37	5.03	5.50	16.19	16.31
313	855	14.88	5.10	5.58	16.69	16.72	313	705	14.35	5.03	5.50	16.17	16.29
313	850	14.86	5.10	5.58	16.67	16.71	313	700	14.33	5.03	5.50	16.15	16.27
313	845	14.85	5.10	5.57	16.66	16.70	313	695	14.30	5.02	5.49	16.12	16.26
313	840	14.83	5.10	5.57	16.64	16.69	313	690	14.28	5.02	5.49	16.10	16.24
313	835	14.81	5.09	5.57	16.62	16.67	313	685	14.26	5.02	5.49	16.09	16.22
313	830	14.79	5.09	5.57	16.61	16.66	313	680	14.25	5.01	5.48	16.07	16.21
313	825	14.78	5.09	5.56	16.59	16.65	313	675	14.23	5.01	5.48	16.05	16.19
313	820	14.76	5.09	5.56	16.57	16.63	313	670	14.21	5.01	5.48	16.04	16.17
313	815	14.74	5.08	5.56	16.56	16.62	313	665	14.18	5.01	5.47	16.00	16.15
313	810	14.73	5.08	5.56	16.54	16.60	313	660	14.16	5.00	5.47	15.99	16.14
313	805	14.71	5.08	5.55	16.52	16.59	313	655	14.15	5.00	5.47	15.97	16.12
313	800	14.69	5.08	5.55	16.51	16.58	313	650	14.13	5.00	5.47	15.95	16.10
313	795	14.67	5.07	5.55	16.49	16.56	313	645	14.11	5.00	5.46	15.94	16.08
313	790	14.66	5.07	5.55	16.47	16.55	313	640	14.08	4.99	5.46	15.90	16.06
313	785	14.64	5.07	5.54	16.45	16.54	313	635	14.06	4.99	5.45	15.88	16.04
313	780	14.62	5.07	5.54	16.44	16.52	313	630	14.04	4.99	5.45	15.87	16.02
313	775	14.61	5.06	5.54	16.42	16.51	313	625	14.01	4.98	5.45	15.83	16.00
313	770	14.59	5.06	5.54	16.40	16.49	313	620	13.99	4.98	5.44	15.82	15.99
313	765	14.57	5.06	5.53	16.39	16.48	313	615	13.98	4.98	5.44	15.80	15.97
313	760	14.55	5.06	5.53	16.37	16.46	313	610	13.96	4.97	5.44	15.78	15.95

T, K	P, bar	$\delta_{di, 1/2}$ MPa	$\delta_{pi, 1/2}$ MPa	$\delta_{hi, 1/2}$ MPa	$\delta_{T, 1/2}$ MPa	$\delta_{Hildebrand}, 1/2$ MPa	T, K	P, bar	$\delta_{di, 1/2}$ MPa	$\delta_{pi, 1/2}$ MPa	$\delta_{hi, 1/2}$ MPa	$\delta_{T, 1/2}$ MPa	$\delta_{Hildebrand}, 1/2$ MPa
313	605	13.92	4.97	5.43	15.75	15.93	313	455	13.17	4.86	5.31	15.01	15.20
313	600	13.91	4.97	5.43	15.73	15.91	313	450	13.15	4.86	5.31	14.99	15.17
313	595	13.89	4.96	5.43	15.72	15.88	313	445	13.12	4.85	5.31	14.96	15.14
313	590	13.86	4.96	5.42	15.68	15.86	313	440	13.08	4.85	5.30	14.92	15.11
313	585	13.84	4.96	5.42	15.67	15.84	313	435	13.05	4.84	5.29	14.89	15.08
313	580	13.82	4.95	5.42	15.65	15.82	313	430	13.03	4.84	5.29	14.87	15.04
313	575	13.79	4.95	5.41	15.62	15.80	313	425	13.00	4.83	5.29	14.84	15.01
313	570	13.77	4.95	5.41	15.60	15.78	313	420	12.97	4.83	5.28	14.81	14.98
313	565	13.76	4.94	5.41	15.59	15.76	313	415	12.93	4.82	5.28	14.78	14.95
313	560	13.72	4.94	5.40	15.55	15.73	313	410	12.90	4.82	5.27	14.74	14.91
313	555	13.70	4.94	5.40	15.54	15.71	313	405	12.87	4.81	5.26	14.71	14.88
313	550	13.67	4.93	5.39	15.50	15.69	313	400	12.83	4.81	5.26	14.68	14.85
313	545	13.65	4.93	5.39	15.49	15.67	313	395	12.80	4.80	5.25	14.65	14.81
313	540	13.62	4.93	5.39	15.45	15.64	313	390	12.77	4.80	5.25	14.61	14.78
313	535	13.60	4.92	5.38	15.44	15.62	313	385	12.73	4.79	5.24	14.58	14.74
313	530	13.57	4.92	5.38	15.40	15.59	313	380	12.70	4.79	5.24	14.55	14.70
313	525	13.55	4.92	5.38	15.39	15.57	313	375	12.67	4.78	5.23	14.51	14.67
313	520	13.52	4.91	5.37	15.35	15.55	313	370	12.63	4.78	5.23	14.48	14.63
313	515	13.50	4.91	5.37	15.34	15.52	313	365	12.60	4.77	5.22	14.45	14.59
313	510	13.47	4.90	5.36	15.30	15.50	313	360	12.57	4.77	5.21	14.42	14.55
313	505	13.45	4.90	5.36	15.29	15.47	313	355	12.52	4.76	5.21	14.37	14.51
313	500	13.42	4.90	5.35	15.25	15.44	313	350	12.48	4.76	5.20	14.34	14.47
313	495	13.40	4.89	5.35	15.24	15.42	313	345	12.45	4.75	5.20	14.30	14.43
313	490	13.37	4.89	5.35	15.20	15.39	313	340	12.40	4.74	5.19	14.25	14.39
313	485	13.33	4.88	5.34	15.17	15.36	313	335	12.37	4.74	5.18	14.22	14.34
313	480	13.32	4.88	5.34	15.15	15.34	313	330	12.33	4.73	5.18	14.19	14.30
313	475	13.28	4.88	5.33	15.12	15.31	313	325	12.28	4.73	5.17	14.14	14.26
313	470	13.27	4.87	5.33	15.11	15.28	313	320	12.25	4.72	5.16	14.11	14.21
313	465	13.23	4.87	5.32	15.07	15.25	313	315	12.20	4.71	5.15	14.06	14.16
313	460	13.20	4.86	5.32	15.04	15.23	313	310	12.17	4.71	5.15	14.03	14.12

T, K	P, bar	$\delta_{\theta, 1/2}$ MPa	$\delta_{p, 1/2}$ MPa	$\delta_{H, 1/2}$ MPa	$\delta_{T, 1/2}$ MPa	$\delta_{H_2O, 1/2}$ MPa	T, K	P, bar	$\delta_{\theta, 1/2}$ MPa	$\delta_{p, 1/2}$ MPa	$\delta_{H, 1/2}$ MPa	$\delta_{T, 1/2}$ MPa	$\delta_{H_2O, 1/2}$ MPa
313	305	12.12	4.70	5.14	13.98	14.07	313	155	10.13	4.37	4.78	12.02	11.69
313	300	12.07	4.69	5.13	13.93	14.02	313	150	10.00	4.35	4.76	11.90	11.55
313	295	12.04	4.69	5.13	13.90	13.97	313	145	9.87	4.33	4.74	11.77	11.39
313	290	11.99	4.68	5.12	13.85	13.91	313	140	9.75	4.31	4.71	11.65	11.23
313	285	11.94	4.67	5.11	13.80	13.86	313	135	9.59	4.28	4.68	11.50	11.05
313	280	11.89	4.66	5.10	13.75	13.81	313	130	9.43	4.25	4.65	11.34	10.85
313	275	11.84	4.66	5.09	13.70	13.75	313	125	9.24	4.22	4.61	11.16	10.63
313	270	11.79	4.65	5.08	13.66	13.69	313	120	9.04	4.18	4.57	10.96	10.39
313	265	11.74	4.64	5.08	13.61	13.63	313	115	8.81	4.14	4.52	10.73	10.11
313	260	11.69	4.63	5.07	13.56	13.57	313	110	8.53	4.08	4.47	10.46	9.79
313	255	11.64	4.63	5.06	13.51	13.51	313	105	8.18	4.02	4.39	10.12	9.41
313	250	11.58	4.62	5.05	13.45	13.45	313	100	7.74	3.93	4.30	9.68	8.92
313	245	11.53	4.61	5.04	13.40	13.38	313	95	7.07	3.79	4.14	9.03	8.26
313	240	11.46	4.60	5.03	13.33	13.32	313	90	5.89	3.52	3.85	7.87	7.23
313	235	11.41	4.59	5.02	13.29	13.25	313	80	2.89	2.65	2.90	4.88	4.76
313	230	11.35	4.58	5.01	13.22	13.17	313	75	2.26	2.40	2.63	4.22	4.04
313	225	11.28	4.57	5.00	13.16	13.10	313	70	1.84	2.21	2.42	3.75	3.51
313	220	11.22	4.56	4.98	13.10	13.03	313	65	1.52	2.05	2.24	3.40	3.07
313	215	11.15	4.55	4.97	13.03	12.95	313	60	1.28	1.91	2.09	3.11	2.69
313	210	11.09	4.54	4.96	12.97	12.87	313	55	1.08	1.79	1.96	2.86	2.36
313	205	11.01	4.52	4.95	12.89	12.78	313	50	0.90	1.66	1.82	2.62	2.06
313	200	10.94	4.51	4.93	12.83	12.69	313	45	0.76	1.55	1.70	2.42	1.79
313	195	10.86	4.50	4.92	12.75	12.60	313	40	0.62	1.43	1.56	2.21	1.54
313	190	10.78	4.49	4.91	12.67	12.51	313	35	0.50	1.32	1.44	2.01	1.31
313	185	10.70	4.47	4.89	12.59	12.41	313	30	0.40	1.20	1.31	1.82	1.09
313	180	10.62	4.46	4.88	12.51	12.30	313	25	0.31	1.09	1.19	1.64	0.88
313	175	10.53	4.44	4.86	12.41	12.19	313	20	0.23	0.96	1.05	1.43	0.69
313	170	10.43	4.43	4.84	12.32	12.08	313	15	0.15	0.82	0.90	1.23	0.51
313	165	10.33	4.41	4.82	12.23	11.96	313	10	0.09	0.66	0.72	0.98	0.33
313	160	10.24	4.39	4.80	12.13	11.83							

T, K	P, bar	$\delta_{a,1/2}$ MPa	$\delta_{p,1/2}$ MPa	$\delta_{h,1/2}$ MPa	$\delta_{T,1/2}$ MPa	$\delta_{Hildebrand,1/2}$ MPa	T, K	P, bar	$\delta_{a,1/2}$ MPa	$\delta_{p,1/2}$ MPa	$\delta_{h,1/2}$ MPa	$\delta_{T,1/2}$ MPa	$\delta_{Hildebrand,1/2}$ MPa
323	905	14.67	5.07	5.48	16.46	16.46	323	755	14.13	5.00	5.39	15.93	16.02
323	900	14.66	5.07	5.47	16.45	16.44	323	750	14.11	5.00	5.39	15.91	16.01
323	895	14.64	5.07	5.47	16.43	16.43	323	745	14.09	4.99	5.39	15.89	15.99
323	890	14.62	5.07	5.47	16.41	16.42	323	740	14.08	4.99	5.39	15.88	15.97
323	885	14.61	5.06	5.47	16.40	16.41	323	735	14.06	4.99	5.38	15.86	15.95
323	880	14.59	5.06	5.46	16.38	16.39	323	730	14.04	4.99	5.38	15.84	15.94
323	875	14.57	5.06	5.46	16.36	16.38	323	725	14.01	4.98	5.38	15.81	15.92
323	870	14.55	5.06	5.46	16.35	16.36	323	720	13.99	4.98	5.37	15.79	15.90
323	865	14.54	5.06	5.46	16.33	16.35	323	715	13.98	4.98	5.37	15.78	15.89
323	860	14.52	5.05	5.45	16.31	16.34	323	710	13.96	4.97	5.37	15.76	15.87
323	855	14.50	5.05	5.45	16.30	16.32	323	705	13.94	4.97	5.37	15.74	15.85
323	850	14.49	5.05	5.45	16.28	16.31	323	700	13.91	4.97	5.36	15.71	15.83
323	845	14.47	5.05	5.45	16.26	16.30	323	695	13.89	4.96	5.36	15.69	15.81
323	840	14.45	5.04	5.44	16.25	16.28	323	690	13.87	4.96	5.35	15.68	15.79
323	835	14.43	5.04	5.44	16.23	16.27	323	685	13.86	4.96	5.35	15.66	15.77
323	830	14.42	5.04	5.44	16.21	16.25	323	680	13.82	4.95	5.35	15.63	15.76
323	825	14.40	5.04	5.44	16.20	16.24	323	675	13.81	4.95	5.34	15.61	15.74
323	820	14.38	5.03	5.43	16.18	16.22	323	670	13.79	4.95	5.34	15.59	15.72
323	815	14.37	5.03	5.43	16.16	16.21	323	665	13.77	4.95	5.34	15.58	15.70
323	810	14.35	5.03	5.43	16.14	16.19	323	660	13.74	4.94	5.33	15.54	15.68
323	805	14.32	5.02	5.42	16.11	16.18	323	655	13.72	4.94	5.33	15.53	15.66
323	800	14.30	5.02	5.42	16.09	16.17	323	650	13.70	4.94	5.33	15.51	15.64
323	795	14.28	5.02	5.42	16.08	16.15	323	645	13.67	4.93	5.32	15.48	15.62
323	790	14.26	5.02	5.41	16.06	16.13	323	640	13.65	4.93	5.32	15.46	15.60
323	785	14.25	5.01	5.41	16.04	16.12	323	635	13.64	4.93	5.32	15.44	15.58
323	780	14.23	5.01	5.41	16.03	16.10	323	630	13.60	4.92	5.31	15.41	15.55
323	775	14.21	5.01	5.41	16.01	16.09	323	625	13.59	4.92	5.31	15.39	15.53
323	770	14.20	5.01	5.40	15.99	16.07	323	620	13.57	4.92	5.31	15.38	15.51
323	765	14.18	5.01	5.40	15.98	16.05	323	615	13.54	4.91	5.30	15.35	15.49
323	760	14.16	5.00	5.40	15.96	16.04	323	610	13.52	4.91	5.30	15.33	15.47

T, K	P, bar	$\delta_{d_1, 1/2}$ MPa	$\delta_{p_1, 1/2}$ MPa	$\delta_{H_1, 1/2}$ MPa	$\delta_{T_1, 1/2}$ MPa	$\delta_{H_{H_2}Br_{H_2}d_1}$ MPa	T, K	P, bar	$\delta_{d_1, 1/2}$ MPa	$\delta_{p_1, 1/2}$ MPa	$\delta_{H_1, 1/2}$ MPa	$\delta_{T_1, 1/2}$ MPa	$\delta_{H_{H_2}Br_{H_2}d_1}$ MPa
323	605	13.49	4.91	5.29	15.30	15.45	323	455	12.67	4.78	5.16	14.49	14.64
323	600	13.47	4.90	5.29	15.28	15.42	323	450	12.63	4.78	5.16	14.46	14.60
323	595	13.43	4.90	5.29	15.25	15.40	323	445	12.60	4.77	5.15	14.42	14.57
323	590	13.42	4.90	5.28	15.23	15.38	323	440	12.57	4.77	5.15	14.39	14.54
323	585	13.40	4.89	5.28	15.21	15.36	323	435	12.53	4.76	5.14	14.36	14.50
323	580	13.37	4.89	5.28	15.18	15.33	323	430	12.50	4.76	5.14	14.33	14.47
323	575	13.35	4.89	5.27	15.16	15.31	323	425	12.47	4.75	5.13	14.29	14.43
323	570	13.32	4.88	5.27	15.13	15.28	323	420	12.43	4.75	5.12	14.26	14.40
323	565	13.30	4.88	5.26	15.11	15.26	323	415	12.40	4.74	5.12	14.23	14.36
323	560	13.27	4.87	5.26	15.08	15.24	323	410	12.37	4.74	5.11	14.20	14.32
323	555	13.23	4.87	5.25	15.05	15.21	323	405	12.33	4.73	5.11	14.16	14.28
323	550	13.22	4.87	5.25	15.03	15.19	323	400	12.28	4.73	5.10	14.12	14.24
323	545	13.18	4.86	5.25	15.00	15.16	323	395	12.25	4.72	5.09	14.08	14.21
323	540	13.17	4.86	5.24	14.98	15.13	323	390	12.22	4.72	5.09	14.05	14.17
323	535	13.13	4.85	5.24	14.95	15.11	323	385	12.18	4.71	5.08	14.02	14.12
323	530	13.12	4.85	5.24	14.93	15.08	323	380	12.14	4.70	5.08	13.97	14.08
323	525	13.08	4.85	5.23	14.90	15.05	323	375	12.10	4.70	5.07	13.94	14.04
323	520	13.05	4.84	5.22	14.87	15.03	323	370	12.07	4.69	5.06	13.90	14.00
323	515	13.03	4.84	5.22	14.85	15.00	323	365	12.02	4.69	5.06	13.86	13.96
323	510	13.00	4.83	5.22	14.82	14.97	323	360	11.99	4.68	5.05	13.82	13.91
323	505	12.97	4.83	5.21	14.78	14.94	323	355	11.94	4.67	5.04	13.78	13.87
323	500	12.93	4.82	5.21	14.75	14.91	323	350	11.91	4.67	5.04	13.74	13.82
323	495	12.92	4.82	5.20	14.74	14.89	323	345	11.86	4.66	5.03	13.70	13.77
323	490	12.88	4.82	5.20	14.70	14.86	323	340	11.81	4.65	5.02	13.65	13.72
323	485	12.85	4.81	5.19	14.67	14.83	323	335	11.77	4.65	5.01	13.61	13.67
323	480	12.82	4.81	5.19	14.64	14.80	323	330	11.72	4.64	5.01	13.57	13.62
323	475	12.80	4.80	5.18	14.62	14.76	323	325	11.68	4.63	5.00	13.52	13.57
323	470	12.77	4.80	5.18	14.59	14.73	323	320	11.63	4.62	4.99	13.47	13.52
323	465	12.73	4.79	5.17	14.56	14.70	323	315	11.58	4.62	4.98	13.42	13.47
323	460	12.70	4.79	5.17	14.52	14.67	323	310	11.53	4.61	4.97	13.37	13.41

T, K	P, bar	$\delta_{d, 1/2}$ MPa	$\delta_{p, 1/2}$ MPa	$\delta_{h, 1/2}$ MPa	$\delta_{r, 1/2}$ MPa	$\delta_{Hildebragg, 1/2}$ MPa	T, K	P, bar	$\delta_{d, 1/2}$ MPa	$\delta_{p, 1/2}$ MPa	$\delta_{h, 1/2}$ MPa	$\delta_{r, 1/2}$ MPa	$\delta_{Hildebragg, 1/2}$ MPa
323	305	11.48	4.60	4.96	13.33	13.35	323	155	8.93	4.16	4.49	10.83	10.39
323	300	11.43	4.59	4.96	13.28	13.30	323	150	8.76	4.13	4.46	10.66	10.19
323	295	11.38	4.58	4.95	13.23	13.24	323	145	8.56	4.09	4.41	10.47	9.97
323	290	11.32	4.57	4.94	13.17	13.18	323	140	8.35	4.05	4.37	10.26	9.73
323	285	11.27	4.57	4.93	13.12	13.11	323	135	8.10	4.00	4.32	10.02	9.45
323	280	11.22	4.56	4.92	13.07	13.05	323	130	7.82	3.94	4.26	9.73	9.15
323	275	11.15	4.55	4.91	13.01	12.99	323	125	7.48	3.88	4.18	9.41	8.80
323	270	11.09	4.54	4.90	12.94	12.92	323	120	7.08	3.79	4.09	9.02	8.40
323	265	11.04	4.53	4.89	12.90	12.85	323	115	6.58	3.68	3.97	8.53	7.92
323	260	10.98	4.52	4.88	12.83	12.78	323	110	5.95	3.54	3.82	7.90	7.36
323	255	10.91	4.51	4.86	12.77	12.70	323	105	5.19	3.35	3.61	7.15	6.72
323	250	10.85	4.50	4.85	12.71	12.63	323	100	4.34	3.12	3.36	6.31	6.02
323	245	10.78	4.49	4.84	12.64	12.55	323	95	3.56	2.88	3.11	5.54	5.34
323	240	10.70	4.47	4.83	12.56	12.47	323	90	2.93	2.66	2.87	4.89	4.73
323	235	10.64	4.46	4.81	12.50	12.39	323	85	2.45	2.48	2.68	4.40	4.20
323	230	10.56	4.45	4.80	12.42	12.30	323	80	2.09	2.33	2.51	4.01	3.75
323	225	10.49	4.44	4.79	12.36	12.21	323	75	1.78	2.18	2.35	3.67	3.36
323	220	10.41	4.42	4.77	12.28	12.12	323	70	1.54	2.06	2.22	3.39	3.00
323	215	10.33	4.41	4.76	12.20	12.02	323	65	1.32	1.94	2.09	3.14	2.69
323	210	10.24	4.39	4.74	12.11	11.92	323	60	1.13	1.82	1.97	2.91	2.40
323	205	10.16	4.38	4.73	12.03	11.81	323	55	0.97	1.71	1.85	2.70	2.13
323	200	10.06	4.36	4.71	11.94	11.70	323	50	0.82	1.60	1.73	2.50	1.88
323	195	9.95	4.34	4.69	11.83	11.59	323	45	0.69	1.50	1.61	2.31	1.64
323	190	9.86	4.33	4.67	11.73	11.47	323	40	0.57	1.39	1.50	2.12	1.42
323	185	9.75	4.31	4.65	11.63	11.34	323	35	0.47	1.28	1.38	1.94	1.22
323	180	9.64	4.29	4.63	11.52	11.21	323	30	0.38	1.17	1.26	1.76	1.02
323	175	9.51	4.27	4.60	11.39	11.06	323	25	0.29	1.05	1.13	1.57	0.83
323	170	9.38	4.24	4.58	11.27	10.91	323	20	0.21	0.93	1.00	1.38	0.65
323	165	9.24	4.22	4.55	11.13	10.75	323	15	0.15	0.81	0.87	1.19	0.48
323	160	9.10	4.19	4.52	11.00	10.58	323	10	0.08	0.64	0.69	0.94	0.31

T, K	P, bar	$\delta_{d,1/2}$ MPa	$\delta_{p,1/2}$ MPa	$\delta_{H,1/2}$ MPa	$\delta_{T,1/2}$ MPa	$\delta_{H,bragg}$ MPa ^{1/2}	T, K	P, bar	$\delta_{d,1/2}$ MPa	$\delta_{p,1/2}$ MPa	$\delta_{H,1/2}$ MPa	$\delta_{T,1/2}$ MPa	$\delta_{H,bragg}$ MPa ^{1/2}
333	905	14.32	5.02	5.35	16.09	16.07	333	755	13.74	4.94	5.26	15.52	15.60
333	900	14.30	5.02	5.35	16.07	16.06	333	750	13.72	4.94	5.26	15.50	15.58
333	895	14.28	5.02	5.35	16.05	16.05	333	745	13.70	4.94	5.26	15.49	15.56
333	890	14.25	5.01	5.34	16.02	16.03	333	740	13.69	4.94	5.26	15.47	15.55
333	885	14.23	5.01	5.34	16.00	16.02	333	735	13.65	4.93	5.25	15.44	15.53
333	880	14.21	5.01	5.34	15.99	16.00	333	730	13.64	4.93	5.25	15.42	15.51
333	875	14.20	5.01	5.33	15.97	15.99	333	725	13.62	4.93	5.25	15.40	15.49
333	870	14.18	5.01	5.33	15.95	15.97	333	720	13.59	4.92	5.24	15.37	15.47
333	865	14.16	5.00	5.33	15.94	15.96	333	715	13.57	4.92	5.24	15.35	15.45
333	860	14.15	5.00	5.33	15.92	15.94	333	710	13.55	4.92	5.24	15.34	15.43
333	855	14.13	5.00	5.32	15.90	15.93	333	705	13.54	4.91	5.23	15.32	15.41
333	850	14.11	5.00	5.32	15.89	15.91	333	700	13.50	4.91	5.23	15.29	15.39
333	845	14.09	4.99	5.32	15.87	15.90	333	695	13.49	4.91	5.22	15.27	15.37
333	840	14.08	4.99	5.32	15.85	15.88	333	690	13.47	4.90	5.22	15.26	15.35
333	835	14.06	4.99	5.31	15.84	15.87	333	685	13.43	4.90	5.22	15.22	15.33
333	830	14.04	4.99	5.31	15.82	15.85	333	680	13.42	4.90	5.21	15.21	15.31
333	825	14.03	4.98	5.31	15.80	15.84	333	675	13.40	4.89	5.21	15.19	15.29
333	820	13.99	4.98	5.30	15.77	15.82	333	670	13.37	4.89	5.21	15.16	15.27
333	815	13.98	4.98	5.30	15.75	15.80	333	665	13.35	4.89	5.20	15.14	15.25
333	810	13.96	4.97	5.30	15.74	15.79	333	660	13.32	4.88	5.20	15.11	15.23
333	805	13.94	4.97	5.29	15.72	15.77	333	655	13.30	4.88	5.20	15.09	15.20
333	800	13.92	4.97	5.29	15.70	15.75	333	650	13.28	4.88	5.19	15.07	15.18
333	795	13.91	4.97	5.29	15.69	15.74	333	645	13.25	4.87	5.19	15.04	15.16
333	790	13.89	4.96	5.29	15.67	15.72	333	640	13.23	4.87	5.19	15.02	15.14
333	785	13.86	4.96	5.28	15.64	15.70	333	635	13.20	4.86	5.18	14.99	15.11
333	780	13.84	4.96	5.28	15.62	15.69	333	630	13.18	4.86	5.18	14.97	15.09
333	775	13.82	4.95	5.28	15.60	15.67	333	625	13.15	4.86	5.17	14.94	15.07
333	770	13.81	4.95	5.27	15.59	15.65	333	620	13.13	4.85	5.17	14.92	15.04
333	765	13.79	4.95	5.27	15.57	15.64	333	615	13.10	4.85	5.16	14.89	15.02
333	760	13.76	4.94	5.27	15.54	15.62	333	610	13.08	4.85	5.16	14.88	15.00

T, K	P, bar	$\delta_{d,1/2}$ MPa	$\delta_{p,1/2}$ MPa	$\delta_{H_2,1/2}$ MPa	$\delta_{T,1/2}$ MPa	$\delta_{H_2,brg}$ MPa	T, K	P, bar	$\delta_{d,1/2}$ MPa	$\delta_{p,1/2}$ MPa	$\delta_{H_2,1/2}$ MPa	$\delta_{T,1/2}$ MPa	$\delta_{H_2,brg}$ MPa
333	605	13.05	4.84	5.16	14.84	14.97	333	455	12.17	4.71	5.01	13.98	14.08
333	600	13.03	4.84	5.15	14.83	14.95	333	450	12.12	4.70	5.01	13.93	14.04
333	595	13.00	4.83	5.15	14.79	14.92	333	445	12.09	4.70	5.00	13.90	14.01
333	590	12.98	4.83	5.15	14.78	14.90	333	440	12.05	4.69	5.00	13.86	13.97
333	585	12.95	4.83	5.14	14.74	14.87	333	435	12.02	4.69	4.99	13.83	13.93
333	580	12.92	4.82	5.14	14.71	14.85	333	430	11.99	4.68	4.98	13.80	13.89
333	575	12.90	4.82	5.13	14.69	14.82	333	425	11.94	4.67	4.98	13.75	13.85
333	570	12.87	4.81	5.13	14.66	14.79	333	420	11.91	4.67	4.97	13.72	13.81
333	565	12.85	4.81	5.12	14.65	14.77	333	415	11.87	4.66	4.97	13.69	13.77
333	560	12.82	4.81	5.12	14.61	14.74	333	410	11.82	4.65	4.96	13.64	13.73
333	555	12.78	4.80	5.11	14.58	14.71	333	405	11.79	4.65	4.95	13.61	13.69
333	550	12.77	4.80	5.11	14.56	14.68	333	400	11.74	4.64	4.94	13.56	13.64
333	545	12.73	4.79	5.11	14.53	14.66	333	395	11.71	4.64	4.94	13.53	13.60
333	540	12.70	4.79	5.10	14.50	14.63	333	390	11.66	4.63	4.93	13.48	13.56
333	535	12.67	4.78	5.10	14.47	14.60	333	385	11.63	4.62	4.92	13.45	13.51
333	530	12.65	4.78	5.09	14.45	14.57	333	380	11.58	4.62	4.92	13.40	13.46
333	525	12.62	4.78	5.09	14.42	14.54	333	375	11.53	4.61	4.91	13.35	13.42
333	520	12.58	4.77	5.08	14.38	14.51	333	370	11.50	4.60	4.90	13.32	13.37
333	515	12.55	4.77	5.08	14.35	14.48	333	365	11.45	4.59	4.89	13.27	13.32
333	510	12.52	4.76	5.07	14.32	14.45	333	360	11.40	4.59	4.88	13.22	13.27
333	505	12.48	4.76	5.07	14.29	14.42	333	355	11.35	4.58	4.88	13.17	13.22
333	500	12.47	4.75	5.06	14.27	14.39	333	350	11.30	4.57	4.87	13.13	13.16
333	495	12.43	4.75	5.06	14.24	14.35	333	345	11.25	4.56	4.86	13.08	13.11
333	490	12.40	4.74	5.05	14.21	14.32	333	340	11.20	4.55	4.85	13.03	13.06
333	485	12.37	4.74	5.05	14.17	14.29	333	335	11.15	4.55	4.84	12.98	13.00
333	480	12.33	4.73	5.04	14.14	14.26	333	330	11.11	4.54	4.83	12.93	12.94
333	475	12.30	4.73	5.04	14.11	14.22	333	325	11.06	4.53	4.83	12.89	12.88
333	470	12.27	4.72	5.03	14.08	14.19	333	320	10.99	4.52	4.81	12.82	12.82
333	465	12.23	4.72	5.03	14.04	14.15	333	315	10.94	4.51	4.81	12.78	12.76
333	460	12.20	4.71	5.02	14.01	14.12	333	310	10.88	4.50	4.79	12.71	12.70

T, K	P, bar	$\delta_{d,1/2}$ MPa	$\delta_{p,1/2}$ MPa	$\delta_{h,1/2}$ MPa	$\delta_{T,1/2}$ MPa	$\delta_{Hildebrand,1/2}$ MPa	T, K	P, bar	$\delta_{d,1/2}$ MPa	$\delta_{p,1/2}$ MPa	$\delta_{h,1/2}$ MPa	$\delta_{T,1/2}$ MPa	$\delta_{Hildebrand,1/2}$ MPa
333	305	10.83	4.49	4.79	12.67	12.64	333	155	7.59	3.90	4.15	9.49	9.02
333	300	10.77	4.48	4.77	12.60	12.57	333	150	7.34	3.85	4.10	9.24	8.75
333	295	10.70	4.47	4.76	12.54	12.50	333	145	7.05	3.79	4.03	8.96	8.46
333	290	10.65	4.46	4.75	12.49	12.43	333	140	6.73	3.71	3.96	8.64	8.15
333	285	10.59	4.45	4.74	12.43	12.36	333	135	6.35	3.63	3.87	8.27	7.80
333	280	10.53	4.44	4.73	12.37	12.29	333	130	5.95	3.54	3.77	7.88	7.42
333	275	10.45	4.43	4.72	12.29	12.21	333	125	5.48	3.42	3.64	7.42	7.00
333	270	10.38	4.42	4.71	12.22	12.13	333	120	4.96	3.29	3.50	6.91	6.55
333	265	10.32	4.41	4.69	12.16	12.05	333	115	4.43	3.14	3.35	6.38	6.08
333	260	10.24	4.39	4.68	12.08	11.97	333	110	3.90	2.99	3.18	5.85	5.61
333	255	10.16	4.38	4.66	12.01	11.88	333	105	3.41	2.83	3.01	5.36	5.15
333	250	10.08	4.37	4.65	11.93	11.79	333	100	2.98	2.68	2.86	4.92	4.71
333	245	10.00	4.35	4.64	11.85	11.70	333	95	2.60	2.54	2.70	4.53	4.30
333	240	9.92	4.34	4.62	11.77	11.61	333	90	2.27	2.41	2.56	4.19	3.92
333	235	9.84	4.32	4.61	11.69	11.51	333	85	1.99	2.28	2.43	3.89	3.57
333	230	9.75	4.31	4.59	11.60	11.40	333	80	1.75	2.17	2.31	3.61	3.25
333	225	9.65	4.29	4.57	11.51	11.30	333	75	1.54	2.06	2.19	3.37	2.96
333	220	9.56	4.27	4.55	11.42	11.18	333	70	1.34	1.95	2.08	3.15	2.68
333	215	9.45	4.25	4.53	11.31	11.07	333	65	1.17	1.85	1.97	2.94	2.42
333	210	9.34	4.23	4.51	11.20	10.94	333	60	1.02	1.75	1.86	2.75	2.18
333	205	9.23	4.22	4.49	11.09	10.82	333	55	0.88	1.65	1.76	2.56	1.95
333	200	9.10	4.19	4.46	10.97	10.68	333	50	0.76	1.55	1.65	2.39	1.74
333	195	8.98	4.17	4.44	10.85	10.54	333	45	0.65	1.45	1.55	2.22	1.53
333	190	8.86	4.15	4.42	10.73	10.39	333	40	0.54	1.35	1.44	2.05	1.33
333	185	8.72	4.12	4.39	10.59	10.23	333	35	0.44	1.25	1.33	1.88	1.14
333	180	8.56	4.09	4.36	10.44	10.06	333	30	0.35	1.14	1.21	1.70	0.96
333	175	8.39	4.06	4.32	10.28	9.88	333	25	0.27	1.03	1.10	1.53	0.79
333	170	8.23	4.03	4.29	10.11	9.69	333	20	0.20	0.92	0.98	1.36	0.62
333	165	8.03	3.99	4.25	9.92	9.48	333	15	0.14	0.79	0.84	1.16	0.46
333	160	7.82	3.94	4.20	9.71	9.26	333	10	0.08	0.64	0.68	0.94	0.30

T, K	P, bar	$\delta_{d, 1/2}$ MPa	$\delta_{p, 1/2}$ MPa	$\delta_{h, 1/2}$ MPa	$\delta_{T, 1/2}$ MPa	$\delta_{Hildebrand, 1/2}$ MPa	T, K	P, bar	$\delta_{d, 1/2}$ MPa	$\delta_{p, 1/2}$ MPa	$\delta_{h, 1/2}$ MPa	$\delta_{T, 1/2}$ MPa	$\delta_{Hildebrand, 1/2}$ MPa
343	905	13.96	4.97	5.23	15.71	15.69	343	755	13.35	4.89	5.14	15.12	15.18
343	900	13.92	4.97	5.22	15.68	15.68	343	750	13.33	4.88	5.13	15.10	15.16
343	895	13.91	4.97	5.22	15.66	15.66	343	745	13.32	4.88	5.13	15.08	15.14
343	890	13.89	4.96	5.22	15.65	15.65	343	740	13.28	4.88	5.13	15.05	15.12
343	885	13.87	4.96	5.22	15.63	15.63	343	735	13.27	4.87	5.12	15.03	15.10
343	880	13.86	4.96	5.21	15.61	15.62	343	730	13.25	4.87	5.12	15.02	15.08
343	875	13.84	4.96	5.21	15.60	15.60	343	725	13.22	4.87	5.11	14.98	15.06
343	870	13.82	4.95	5.21	15.58	15.59	343	720	13.20	4.86	5.11	14.97	15.04
343	865	13.81	4.95	5.20	15.56	15.57	343	715	13.18	4.86	5.11	14.95	15.02
343	860	13.79	4.95	5.20	15.55	15.55	343	710	13.15	4.86	5.10	14.92	15.00
343	855	13.77	4.95	5.20	15.53	15.54	343	705	13.13	4.85	5.10	14.90	14.98
343	850	13.74	4.94	5.19	15.50	15.52	343	700	13.10	4.85	5.10	14.87	14.96
343	845	13.72	4.94	5.19	15.48	15.51	343	695	13.08	4.85	5.09	14.85	14.94
343	840	13.70	4.94	5.19	15.46	15.49	343	690	13.07	4.84	5.09	14.84	14.91
343	835	13.69	4.94	5.19	15.45	15.47	343	685	13.03	4.84	5.09	14.80	14.89
343	830	13.67	4.93	5.18	15.43	15.46	343	680	13.02	4.84	5.08	14.79	14.87
343	825	13.65	4.93	5.18	15.41	15.44	343	675	12.98	4.83	5.08	14.75	14.85
343	820	13.62	4.93	5.18	15.38	15.42	343	670	12.97	4.83	5.08	14.74	14.82
343	815	13.60	4.92	5.17	15.36	15.40	343	665	12.93	4.82	5.07	14.70	14.80
343	810	13.59	4.92	5.17	15.35	15.39	343	660	12.92	4.82	5.07	14.69	14.78
343	805	13.57	4.92	5.17	15.33	15.37	343	655	12.88	4.82	5.06	14.66	14.75
343	800	13.55	4.92	5.17	15.31	15.35	343	650	12.87	4.81	5.06	14.64	14.73
343	795	13.52	4.91	5.16	15.28	15.33	343	645	12.83	4.81	5.05	14.61	14.70
343	790	13.50	4.91	5.16	15.26	15.31	343	640	12.82	4.81	5.05	14.59	14.68
343	785	13.49	4.91	5.16	15.25	15.30	343	635	12.78	4.80	5.05	14.56	14.66
343	780	13.47	4.90	5.15	15.23	15.28	343	630	12.75	4.80	5.04	14.52	14.63
343	775	13.43	4.90	5.15	15.20	15.26	343	625	12.73	4.79	5.04	14.51	14.61
343	770	13.42	4.90	5.15	15.18	15.24	343	620	12.70	4.79	5.03	14.48	14.58
343	765	13.40	4.89	5.14	15.17	15.22	343	615	12.68	4.79	5.03	14.46	14.55
343	760	13.38	4.89	5.14	15.15	15.20	343	610	12.65	4.78	5.03	14.43	14.53

T, K	P, bar	$\delta_{d,1/2}$ MPa ^{1/2}	$\delta_{p,1/2}$ MPa ^{1/2}	$\delta_{th,1/2}$ MPa ^{1/2}	$\delta_{T,1/2}$ MPa ^{1/2}	$\delta_{Hildebrand^p}$ MPa ^{1/2}	T, K	P, bar	$\delta_{d,1/2}$ MPa ^{1/2}	$\delta_{p,1/2}$ MPa ^{1/2}	$\delta_{th,1/2}$ MPa ^{1/2}	$\delta_{T,1/2}$ MPa ^{1/2}	$\delta_{Hildebrand^p}$ MPa ^{1/2}
343	605	12.62	4.78	5.02	14.39	14.50	343	455	11.66	4.63	4.86	13.45	13.53
343	600	12.60	4.77	5.02	14.38	14.48	343	450	11.61	4.62	4.86	13.41	13.49
343	595	12.57	4.77	5.01	14.34	14.45	343	445	11.58	4.62	4.85	13.37	13.45
343	590	12.53	4.76	5.01	14.31	14.42	343	440	11.54	4.61	4.85	13.34	13.40
343	585	12.52	4.76	5.00	14.30	14.39	343	435	11.50	4.60	4.84	13.29	13.36
343	580	12.48	4.76	5.00	14.26	14.36	343	430	11.46	4.60	4.83	13.26	13.32
343	575	12.45	4.75	4.99	14.23	14.34	343	425	11.41	4.59	4.82	13.21	13.28
343	570	12.42	4.75	4.99	14.20	14.31	343	420	11.37	4.58	4.82	13.17	13.23
343	565	12.40	4.74	4.99	14.18	14.28	343	415	11.33	4.58	4.81	13.13	13.19
343	560	12.37	4.74	4.98	14.15	14.25	343	410	11.28	4.57	4.80	13.09	13.14
343	555	12.33	4.73	4.98	14.12	14.22	343	405	11.25	4.56	4.80	13.05	13.09
343	550	12.30	4.73	4.97	14.08	14.19	343	400	11.20	4.55	4.79	13.01	13.05
343	545	12.27	4.72	4.96	14.05	14.16	343	395	11.15	4.55	4.78	12.96	13.00
343	540	12.23	4.72	4.96	14.02	14.13	343	390	11.11	4.54	4.77	12.91	12.95
343	535	12.20	4.71	4.95	13.99	14.10	343	385	11.06	4.53	4.76	12.86	12.90
343	530	12.18	4.71	4.95	13.97	14.06	343	380	11.01	4.52	4.75	12.82	12.85
343	525	12.15	4.71	4.95	13.94	14.03	343	375	10.96	4.52	4.75	12.77	12.79
343	520	12.12	4.70	4.94	13.91	14.00	343	370	10.91	4.51	4.74	12.72	12.74
343	515	12.09	4.70	4.94	13.87	13.97	343	365	10.86	4.50	4.73	12.67	12.68
343	510	12.05	4.69	4.93	13.84	13.93	343	360	10.81	4.49	4.72	12.63	12.63
343	505	12.02	4.69	4.92	13.81	13.90	343	355	10.77	4.48	4.71	12.58	12.57
343	500	11.99	4.68	4.92	13.78	13.86	343	350	10.70	4.47	4.70	12.52	12.51
343	495	11.94	4.67	4.91	13.73	13.83	343	345	10.65	4.46	4.69	12.47	12.45
343	490	11.91	4.67	4.91	13.70	13.79	343	340	10.59	4.45	4.68	12.41	12.39
343	485	11.87	4.66	4.90	13.66	13.76	343	335	10.54	4.45	4.67	12.36	12.33
343	480	11.84	4.66	4.89	13.63	13.72	343	330	10.48	4.43	4.66	12.30	12.27
343	475	11.81	4.65	4.89	13.60	13.68	343	325	10.41	4.42	4.65	12.23	12.20
343	470	11.77	4.65	4.88	13.57	13.65	343	320	10.37	4.42	4.64	12.19	12.13
343	465	11.72	4.64	4.88	13.52	13.61	343	315	10.30	4.40	4.63	12.12	12.06
343	460	11.69	4.63	4.87	13.49	13.57	343	310	10.24	4.39	4.62	12.06	11.99

T, K	P, bar	$\delta_{a1, 1/2}$ MPa	$\delta_{p1, 1/2}$ MPa	$\delta_{h1, 1/2}$ MPa	$\delta_{T1, 1/2}$ MPa	$\delta_{Hildebrandt, 1/2}$ MPa	T, K	P, bar	$\delta_{a1, 1/2}$ MPa	$\delta_{p1, 1/2}$ MPa	$\delta_{h1, 1/2}$ MPa	$\delta_{T1, 1/2}$ MPa	$\delta_{Hildebrandt, 1/2}$ MPa
343	305	10.17	4.38	4.61	12.00	11.92	343	155	6.23	3.60	3.79	8.14	7.73
343	300	10.09	4.37	4.59	11.92	11.84	343	150	5.92	3.53	3.71	7.83	7.44
343	295	10.03	4.36	4.58	11.86	11.77	343	145	5.59	3.45	3.63	7.50	7.13
343	290	9.97	4.35	4.57	11.80	11.69	343	140	5.24	3.36	3.53	7.16	6.81
343	285	9.89	4.33	4.55	11.72	11.61	343	135	4.85	3.26	3.43	6.78	6.47
343	280	9.81	4.32	4.54	11.64	11.52	343	130	4.47	3.15	3.32	6.40	6.11
343	275	9.73	4.31	4.53	11.56	11.44	343	125	4.08	3.04	3.20	6.01	5.75
343	270	9.65	4.29	4.51	11.49	11.35	343	120	3.70	2.93	3.07	5.63	5.39
343	265	9.57	4.28	4.50	11.41	11.25	343	115	3.34	2.81	2.95	5.27	5.04
343	260	9.48	4.26	4.48	11.32	11.16	343	110	3.00	2.69	2.83	4.92	4.69
343	255	9.40	4.25	4.46	11.24	11.06	343	105	2.69	2.58	2.71	4.61	4.35
343	250	9.31	4.23	4.45	11.15	10.96	343	100	2.42	2.47	2.59	4.32	4.04
343	245	9.21	4.21	4.43	11.06	10.85	343	95	2.17	2.36	2.48	4.05	3.73
343	240	9.10	4.19	4.41	10.95	10.74	343	90	1.94	2.26	2.37	3.81	3.45
343	235	9.01	4.17	4.39	10.86	10.63	343	85	1.73	2.16	2.27	3.58	3.18
343	230	8.90	4.15	4.37	10.75	10.51	343	80	1.55	2.06	2.17	3.37	2.92
343	225	8.79	4.13	4.35	10.64	10.38	343	75	1.37	1.97	2.07	3.17	2.68
343	220	8.67	4.11	4.32	10.52	10.25	343	70	1.22	1.87	1.97	2.98	2.45
343	215	8.55	4.09	4.30	10.40	10.11	343	65	1.07	1.78	1.87	2.80	2.23
343	210	8.41	4.06	4.27	10.27	9.97	343	60	0.94	1.69	1.78	2.63	2.01
343	205	8.27	4.03	4.24	10.13	9.82	343	55	0.81	1.60	1.68	2.46	1.81
343	200	8.12	4.00	4.21	9.98	9.66	343	50	0.70	1.50	1.58	2.29	1.62
343	195	7.97	3.97	4.18	9.83	9.50	343	45	0.60	1.41	1.48	2.14	1.43
343	190	7.80	3.94	4.14	9.67	9.32	343	40	0.50	1.32	1.38	1.97	1.25
343	185	7.62	3.90	4.10	9.49	9.13	343	35	0.42	1.22	1.28	1.82	1.08
343	180	7.44	3.87	4.06	9.32	8.94	343	30	0.33	1.12	1.18	1.66	0.91
343	175	7.23	3.82	4.02	9.11	8.72	343	25	0.26	1.02	1.07	1.50	0.75
343	170	7.01	3.78	3.97	8.90	8.50	343	20	0.19	0.89	0.94	1.31	0.59
343	165	6.77	3.72	3.91	8.66	8.26	343	15	0.13	0.78	0.81	1.13	0.44
343	160	6.51	3.67	3.85	8.41	8.01	343	10	0.08	0.62	0.65	0.90	0.29

T, K	P, bar	$\delta_{d, 1/2}$ MPa	$\delta_{p, 1/2}$ MPa	$\delta_{H, 1/2}$ MPa	$\delta_{T, 1/2}$ MPa	$\delta_{Hildebrand, 1/2}$ MPa	T, K	P, bar	$\delta_{d, 1/2}$ MPa	$\delta_{p, 1/2}$ MPa	$\delta_{H, 1/2}$ MPa	$\delta_{T, 1/2}$ MPa	$\delta_{Hildebrand, 1/2}$ MPa
353	905	13.60	4.92	5.11	15.34	15.32	353	755	12.97	4.83	5.01	14.71	14.77
353	900	13.59	4.92	5.10	15.32	15.30	353	750	12.95	4.83	5.01	14.70	14.75
353	895	13.57	4.92	5.10	15.31	15.29	353	745	12.93	4.82	5.00	14.68	14.73
353	890	13.54	4.91	5.10	15.28	15.27	353	740	12.90	4.82	5.00	14.65	14.71
353	885	13.52	4.91	5.09	15.26	15.25	353	735	12.88	4.82	5.00	14.63	14.68
353	880	13.50	4.91	5.09	15.24	15.24	353	730	12.85	4.81	4.99	14.60	14.66
353	875	13.49	4.91	5.09	15.23	15.22	353	725	12.83	4.81	4.99	14.58	14.64
353	870	13.47	4.90	5.09	15.21	15.20	353	720	12.80	4.80	4.98	14.55	14.62
353	865	13.45	4.90	5.08	15.19	15.19	353	715	12.78	4.80	4.98	14.53	14.60
353	860	13.42	4.90	5.08	15.16	15.17	353	710	12.77	4.80	4.98	14.52	14.57
353	855	13.40	4.89	5.08	15.14	15.15	353	705	12.73	4.79	4.97	14.49	14.55
353	850	13.38	4.89	5.07	15.13	15.14	353	700	12.72	4.79	4.97	14.47	14.53
353	845	13.37	4.89	5.07	15.11	15.12	353	695	12.68	4.79	4.97	14.44	14.50
353	840	13.33	4.88	5.07	15.08	15.10	353	690	12.67	4.78	4.96	14.42	14.48
353	835	13.32	4.88	5.06	15.06	15.08	353	685	12.63	4.78	4.96	14.39	14.46
353	830	13.30	4.88	5.06	15.04	15.06	353	680	12.60	4.77	4.95	14.35	14.43
353	825	13.28	4.88	5.06	15.03	15.04	353	675	12.58	4.77	4.95	14.34	14.41
353	820	13.25	4.87	5.05	14.99	15.03	353	670	12.55	4.77	4.94	14.31	14.38
353	815	13.23	4.87	5.05	14.98	15.01	353	665	12.53	4.76	4.94	14.29	14.36
353	810	13.22	4.87	5.05	14.96	14.99	353	660	12.50	4.76	4.94	14.26	14.33
353	805	13.20	4.86	5.05	14.94	14.97	353	655	12.48	4.76	4.93	14.24	14.31
353	800	13.17	4.86	5.04	14.91	14.95	353	650	12.45	4.75	4.93	14.21	14.28
353	795	13.15	4.86	5.04	14.90	14.93	353	645	12.42	4.75	4.92	14.18	14.26
353	790	13.13	4.85	5.03	14.88	14.91	353	640	12.40	4.74	4.92	14.16	14.23
353	785	13.10	4.85	5.03	14.85	14.89	353	635	12.37	4.74	4.92	14.13	14.20
353	780	13.08	4.85	5.03	14.83	14.87	353	630	12.33	4.73	4.91	14.09	14.18
353	775	13.07	4.84	5.02	14.81	14.85	353	625	12.32	4.73	4.91	14.08	14.15
353	770	13.03	4.84	5.02	14.78	14.83	353	620	12.28	4.73	4.90	14.05	14.12
353	765	13.02	4.84	5.02	14.76	14.81	353	615	12.25	4.72	4.90	14.01	14.09
353	760	13.00	4.83	5.01	14.75	14.79	353	610	12.22	4.72	4.89	13.98	14.07

T, K	P, bar	δ_{d1} , MPa ^{1/2}	δ_{p1} , MPa ^{1/2}	δ_{h1} , MPa ^{1/2}	δ_{T1} , MPa ^{1/2}	$\delta_{Hildebrand1}$, MPa ^{1/2}	T, K	P, bar	δ_{d1} , MPa ^{1/2}	δ_{p1} , MPa ^{1/2}	δ_{h1} , MPa ^{1/2}	δ_{T1} , MPa ^{1/2}	$\delta_{Hildebrand1}$, MPa ^{1/2}
353	605	12.20	4.71	4.89	13.96	14.04	353	455	11.15	4.55	4.72	12.94	12.98
353	600	12.17	4.71	4.88	13.93	14.01	353	450	11.11	4.54	4.71	12.89	12.94
353	595	12.14	4.70	4.88	13.90	13.98	353	445	11.07	4.53	4.70	12.86	12.89
353	590	12.10	4.70	4.87	13.87	13.95	353	440	11.02	4.53	4.69	12.81	12.85
353	585	12.07	4.69	4.87	13.83	13.92	353	435	10.98	4.52	4.69	12.76	12.80
353	580	12.04	4.69	4.86	13.80	13.89	353	430	10.94	4.51	4.68	12.73	12.76
353	575	12.02	4.69	4.86	13.79	13.86	353	425	10.90	4.50	4.67	12.68	12.71
353	570	11.99	4.68	4.85	13.75	13.83	353	420	10.85	4.50	4.66	12.63	12.66
353	565	11.95	4.67	4.85	13.72	13.80	353	415	10.80	4.49	4.66	12.59	12.61
353	560	11.92	4.67	4.84	13.69	13.76	353	410	10.75	4.48	4.65	12.54	12.56
353	555	11.89	4.66	4.84	13.66	13.73	353	405	10.70	4.47	4.64	12.49	12.51
353	550	11.86	4.66	4.83	13.62	13.70	353	400	10.65	4.46	4.63	12.45	12.46
353	545	11.82	4.65	4.83	13.59	13.67	353	395	10.61	4.46	4.62	12.40	12.40
353	540	11.79	4.65	4.82	13.56	13.63	353	390	10.56	4.45	4.61	12.35	12.35
353	535	11.76	4.64	4.82	13.53	13.60	353	385	10.51	4.44	4.61	12.30	12.29
353	530	11.72	4.64	4.81	13.50	13.56	353	380	10.45	4.43	4.59	12.24	12.24
353	525	11.69	4.63	4.81	13.46	13.53	353	375	10.40	4.42	4.59	12.19	12.18
353	520	11.64	4.63	4.80	13.42	13.49	353	370	10.35	4.41	4.58	12.15	12.12
353	515	11.61	4.62	4.79	13.38	13.46	353	365	10.29	4.40	4.57	12.08	12.06
353	510	11.58	4.62	4.79	13.35	13.42	353	360	10.22	4.39	4.55	12.02	12.00
353	505	11.54	4.61	4.78	13.32	13.38	353	355	10.17	4.38	4.55	11.97	11.93
353	500	11.51	4.60	4.78	13.29	13.35	353	350	10.11	4.37	4.53	11.91	11.87
353	495	11.46	4.60	4.77	13.24	13.31	353	345	10.05	4.36	4.52	11.85	11.80
353	490	11.43	4.59	4.76	13.21	13.27	353	340	9.98	4.35	4.51	11.79	11.74
353	485	11.40	4.59	4.76	13.18	13.23	353	335	9.92	4.34	4.50	11.73	11.67
353	480	11.35	4.58	4.75	13.13	13.19	353	330	9.86	4.33	4.49	11.66	11.60
353	475	11.32	4.57	4.74	13.10	13.15	353	325	9.79	4.32	4.48	11.60	11.52
353	470	11.27	4.57	4.74	13.05	13.11	353	320	9.73	4.31	4.47	11.54	11.45
353	465	11.24	4.56	4.73	13.02	13.07	353	315	9.65	4.29	4.45	11.46	11.37
353	460	11.19	4.55	4.72	12.97	13.02	353	310	9.59	4.28	4.44	11.40	11.29

T, K	P, bar	$\delta_{d1, 1/2}$ MPa	$\delta_{p1, 1/2}$ MPa	$\delta_{h1, 1/2}$ MPa	$\delta_{T, 1/2}$ MPa	$\delta_{Hildebrand, 1/2}$ MPa	T, K	P, bar	$\delta_{d1, 1/2}$ MPa	$\delta_{p1, 1/2}$ MPa	$\delta_{h1, 1/2}$ MPa	$\delta_{T, 1/2}$ MPa	$\delta_{Hildebrand, 1/2}$ MPa
353	305	9.51	4.27	4.43	11.32	11.21	353	160	5.38	3.40	3.52	7.27	6.96
353	300	9.43	4.25	4.41	11.25	11.13	353	155	5.10	3.33	3.45	7.00	6.69
353	295	9.35	4.24	4.40	11.17	11.04	353	150	4.80	3.25	3.37	6.70	6.41
353	290	9.28	4.22	4.38	11.09	10.96	353	145	4.50	3.16	3.28	6.40	6.13
353	285	9.20	4.21	4.37	11.02	10.87	353	140	4.20	3.08	3.19	6.11	5.84
353	280	9.10	4.19	4.35	10.93	10.77	353	135	3.90	2.99	3.10	5.81	5.55
353	275	9.01	4.17	4.33	10.83	10.68	353	130	3.60	2.89	3.00	5.51	5.25
353	270	8.93	4.16	4.32	10.76	10.58	353	125	3.31	2.80	2.90	5.21	4.96
353	265	8.82	4.14	4.29	10.65	10.47	353	120	3.03	2.70	2.80	4.93	4.67
353	260	8.73	4.12	4.28	10.56	10.37	353	115	2.77	2.60	2.70	4.66	4.39
353	255	8.62	4.10	4.26	10.45	10.26	353	110	2.54	2.51	2.61	4.42	4.12
353	250	8.53	4.08	4.24	10.36	10.14	353	105	2.31	2.42	2.51	4.18	3.86
353	245	8.41	4.06	4.21	10.24	10.02	353	100	2.10	2.33	2.42	3.96	3.60
353	240	8.30	4.04	4.19	10.14	9.90	353	95	1.90	2.24	2.33	3.75	3.36
353	235	8.18	4.02	4.17	10.02	9.77	353	90	1.72	2.15	2.23	3.55	3.12
353	230	8.06	3.99	4.14	9.90	9.64	353	85	1.55	2.06	2.14	3.35	2.89
353	225	7.92	3.97	4.11	9.77	9.50	353	80	1.39	1.98	2.05	3.18	2.67
353	220	7.79	3.94	4.08	9.63	9.35	353	75	1.25	1.89	1.96	3.00	2.46
353	215	7.63	3.91	4.05	9.49	9.20	353	70	1.11	1.81	1.88	2.83	2.26
353	210	7.48	3.88	4.02	9.34	9.04	353	65	0.99	1.73	1.79	2.68	2.07
353	205	7.34	3.85	3.99	9.19	8.88	353	60	0.87	1.64	1.70	2.52	1.88
353	200	7.16	3.81	3.95	9.02	8.70	353	55	0.77	1.56	1.62	2.37	1.70
353	195	6.98	3.77	3.91	8.84	8.52	353	50	0.66	1.47	1.53	2.22	1.52
353	195	6.98	3.77	3.91	8.84	8.52	353	45	0.56	1.38	1.43	2.06	1.35
353	190	6.79	3.73	3.87	8.66	8.33	353	40	0.48	1.29	1.34	1.92	1.18
353	185	6.58	3.68	3.82	8.45	8.12	353	35	0.39	1.19	1.24	1.76	1.02
353	180	6.38	3.64	3.77	8.26	7.91	353	30	0.32	1.10	1.14	1.61	0.86
353	175	6.15	3.58	3.72	8.03	7.69	353	25	0.25	0.99	1.03	1.45	0.71
353	170	5.90	3.53	3.66	7.79	7.46	353	20	0.18	0.88	0.91	1.28	0.56
353	165	5.65	3.46	3.59	7.54	7.21	353	15	0.13	0.76	0.79	1.10	0.42

T, K	P, bar	$\delta_{d, 1/2}$ MPa	$\delta_{p, 1/2}$ MPa	$\delta_{h, 1/2}$ MPa	$\delta_{T, 1/2}$ MPa	$\delta_{Hildebrand, 1/2}$ MPa	T, K	P, bar	$\delta_{d, 1/2}$ MPa	$\delta_{p, 1/2}$ MPa	$\delta_{h, 1/2}$ MPa	$\delta_{T, 1/2}$ MPa	$\delta_{Hildebrand, 1/2}$ MPa
363	905	13.25	4.87	4.99	14.97	14.95	363	755	12.60	4.77	4.89	14.33	14.36
363	900	13.23	4.87	4.98	14.96	14.93	363	750	12.57	4.77	4.88	14.30	14.34
363	895	13.22	4.87	4.98	14.94	14.92	363	745	12.55	4.77	4.88	14.28	14.32
363	890	13.20	4.86	4.98	14.92	14.90	363	740	12.52	4.76	4.87	14.25	14.30
363	885	13.17	4.86	4.97	14.89	14.88	363	735	12.50	4.76	4.87	14.23	14.27
363	880	13.15	4.86	4.97	14.87	14.86	363	730	12.47	4.75	4.87	14.20	14.25
363	875	13.13	4.85	4.97	14.86	14.84	363	725	12.45	4.75	4.86	14.19	14.23
363	870	13.12	4.85	4.97	14.84	14.83	363	720	12.42	4.75	4.86	14.15	14.20
363	865	13.08	4.85	4.96	14.81	14.81	363	715	12.40	4.74	4.86	14.14	14.18
363	860	13.07	4.84	4.96	14.79	14.79	363	710	12.37	4.74	4.85	14.10	14.15
363	855	13.05	4.84	4.96	14.77	14.77	363	705	12.35	4.74	4.85	14.09	14.13
363	850	13.03	4.84	4.95	14.76	14.75	363	700	12.32	4.73	4.84	14.06	14.10
363	845	13.00	4.83	4.95	14.73	14.73	363	695	12.28	4.73	4.84	14.02	14.08
363	840	12.98	4.83	4.95	14.71	14.72	363	690	12.27	4.72	4.84	14.01	14.05
363	835	12.97	4.83	4.94	14.69	14.70	363	685	12.23	4.72	4.83	13.97	14.03
363	830	12.95	4.83	4.94	14.68	14.68	363	680	12.22	4.72	4.83	13.96	14.00
363	825	12.92	4.82	4.94	14.64	14.66	363	675	12.18	4.71	4.82	13.93	13.98
363	820	12.90	4.82	4.93	14.63	14.64	363	670	12.15	4.71	4.82	13.89	13.95
363	815	12.88	4.82	4.93	14.61	14.62	363	665	12.14	4.70	4.81	13.88	13.92
363	810	12.85	4.81	4.93	14.58	14.60	363	660	12.10	4.70	4.81	13.84	13.90
363	805	12.83	4.81	4.92	14.56	14.58	363	655	12.07	4.69	4.80	13.81	13.87
363	800	12.82	4.81	4.92	14.54	14.56	363	650	12.04	4.69	4.80	13.78	13.84
363	795	12.78	4.80	4.92	14.51	14.54	363	645	12.02	4.69	4.80	13.76	13.81
363	790	12.77	4.80	4.91	14.50	14.52	363	640	11.99	4.68	4.79	13.73	13.79
363	785	12.73	4.79	4.91	14.46	14.49	363	635	11.95	4.67	4.79	13.70	13.76
363	780	12.72	4.79	4.91	14.45	14.47	363	630	11.92	4.67	4.78	13.67	13.73
363	775	12.70	4.79	4.90	14.43	14.45	363	625	11.89	4.66	4.77	13.63	13.70
363	770	12.67	4.78	4.90	14.40	14.43	363	620	11.87	4.66	4.77	13.62	13.67
363	765	12.65	4.78	4.89	14.38	14.41	363	615	11.84	4.66	4.77	13.59	13.64
363	760	12.62	4.78	4.89	14.35	14.39	363	610	11.81	4.65	4.76	13.55	13.61

T _i , K	P _i , bar	$\delta_{d,i,1/2}$ MPa	$\delta_{p,i,1/2}$ MPa	$\delta_{h,i,1/2}$ MPa	$\delta_{T,i,1/2}$ MPa	$\delta_{Hildebrg,i}$ MPa ^{1/2}	T _i , K	P _i , bar	$\delta_{d,i,1/2}$ MPa	$\delta_{p,i,1/2}$ MPa	$\delta_{h,i,1/2}$ MPa	$\delta_{T,i,1/2}$ MPa	$\delta_{Hildebrg,i}$ MPa ^{1/2}
363	605	11.77	4.65	4.76	13.52	13.58	363	455	10.65	4.46	4.57	12.42	12.45
363	600	11.74	4.64	4.75	13.49	13.55	363	450	10.61	4.46	4.56	12.38	12.40
363	595	11.71	4.64	4.75	13.46	13.52	363	445	10.57	4.45	4.56	12.34	12.35
363	590	11.68	4.63	4.74	13.43	13.49	363	440	10.53	4.44	4.55	12.30	12.30
363	585	11.64	4.63	4.74	13.39	13.45	363	435	10.48	4.43	4.54	12.25	12.25
363	580	11.61	4.62	4.73	13.36	13.42	363	430	10.43	4.43	4.53	12.20	12.20
363	575	11.58	4.62	4.72	13.33	13.39	363	425	10.38	4.42	4.52	12.16	12.15
363	570	11.54	4.61	4.72	13.30	13.36	363	420	10.33	4.41	4.51	12.11	12.10
363	565	11.51	4.60	4.71	13.26	13.32	363	415	10.27	4.40	4.50	12.05	12.04
363	560	11.48	4.60	4.71	13.23	13.29	363	410	10.22	4.39	4.50	12.00	11.99
363	555	11.45	4.59	4.70	13.20	13.25	363	405	10.17	4.38	4.49	11.95	11.93
363	550	11.41	4.59	4.70	13.17	13.22	363	400	10.13	4.37	4.48	11.91	11.88
363	545	11.38	4.58	4.69	13.14	13.18	363	395	10.06	4.36	4.47	11.84	11.82
363	540	11.33	4.58	4.68	13.09	13.15	363	390	10.02	4.36	4.46	11.80	11.76
363	535	11.30	4.57	4.68	13.06	13.11	363	385	9.95	4.34	4.45	11.73	11.70
363	530	11.27	4.57	4.67	13.03	13.07	363	380	9.89	4.33	4.44	11.67	11.64
363	525	11.24	4.56	4.67	12.99	13.04	363	375	9.84	4.32	4.43	11.63	11.58
363	520	11.19	4.55	4.66	12.95	13.00	363	370	9.78	4.31	4.42	11.56	11.51
363	515	11.15	4.55	4.65	12.91	12.96	363	365	9.71	4.30	4.40	11.50	11.45
363	510	11.12	4.54	4.65	12.88	12.92	363	360	9.65	4.29	4.39	11.44	11.38
363	505	11.07	4.53	4.64	12.83	12.88	363	355	9.59	4.28	4.38	11.38	11.31
363	500	11.04	4.53	4.64	12.80	12.84	363	350	9.53	4.27	4.37	11.32	11.24
363	495	10.99	4.52	4.63	12.75	12.80	363	345	9.46	4.26	4.36	11.26	11.17
363	490	10.96	4.52	4.62	12.72	12.76	363	340	9.38	4.24	4.34	11.18	11.10
363	485	10.91	4.51	4.61	12.68	12.71	363	335	9.32	4.23	4.33	11.12	11.02
363	480	10.88	4.50	4.61	12.64	12.67	363	330	9.24	4.22	4.32	11.04	10.95
363	475	10.83	4.49	4.60	12.60	12.63	363	325	9.18	4.21	4.31	10.98	10.87
363	470	10.78	4.49	4.59	12.55	12.58	363	320	9.10	4.19	4.29	10.90	10.79
363	465	10.75	4.48	4.59	12.52	12.54	363	315	9.03	4.18	4.28	10.83	10.70
363	460	10.70	4.47	4.58	12.47	12.49	363	310	8.95	4.16	4.26	10.75	10.62

T_1 K	P_1 bar	$\delta_{d1,1/2}$ MPa ^{1/2}	$\delta_{p1,1/2}$ MPa ^{1/2}	$\delta_{h1,1/2}$ MPa ^{1/2}	$\delta_{T1,1/2}$ MPa ^{1/2}	$\delta_{Hildebergp1}$ MPa ^{1/2}	T_1 K	P_1 bar	$\delta_{d1,1/2}$ MPa ^{1/2}	$\delta_{p1,1/2}$ MPa ^{1/2}	$\delta_{h1,1/2}$ MPa ^{1/2}	$\delta_{T1,1/2}$ MPa ^{1/2}	$\delta_{Hildebergp1}$ MPa ^{1/2}
363	305	8.86	4.15	4.24	10.66	10.53	363	170	5.01	3.30	3.38	6.88	6.61
363	300	8.78	4.13	4.23	10.58	10.44	363	165	4.77	3.24	3.31	6.65	6.38
363	295	8.69	4.11	4.21	10.49	10.35	363	160	4.53	3.17	3.25	6.41	6.14
363	290	8.59	4.10	4.19	10.40	10.25	363	155	4.27	3.10	3.17	6.16	5.90
363	285	8.50	4.08	4.18	10.31	10.15	363	150	4.02	3.02	3.09	5.90	5.65
363	280	8.41	4.06	4.16	10.22	10.05	363	145	3.78	2.95	3.02	5.67	5.41
363	275	8.32	4.04	4.14	10.13	9.95	363	140	3.54	2.87	2.94	5.42	5.16
363	270	8.21	4.02	4.12	10.03	9.84	363	135	3.29	2.79	2.86	5.18	4.91
363	265	8.10	4.00	4.10	9.92	9.73	363	130	3.05	2.71	2.77	4.93	4.66
363	260	8.00	3.98	4.07	9.82	9.61	363	125	2.83	2.63	2.69	4.70	4.42
363	255	7.89	3.96	4.05	9.71	9.49	363	120	2.62	2.55	2.61	4.49	4.18
363	250	7.77	3.93	4.03	9.60	9.37	363	115	2.42	2.47	2.52	4.28	3.95
363	245	7.65	3.91	4.00	9.48	9.24	363	110	2.23	2.39	2.44	4.08	3.72
363	245	7.65	3.91	4.00	9.48	9.24	363	105	2.04	2.31	2.36	3.88	3.50
363	240	7.51	3.88	3.97	9.35	9.11	363	100	1.87	2.23	2.28	3.69	3.28
363	240	7.51	3.88	3.97	9.35	9.11	363	95	1.71	2.15	2.20	3.52	3.07
363	235	7.38	3.85	3.95	9.21	8.97	363	90	1.56	2.07	2.12	3.34	2.87
363	235	7.38	3.85	3.95	9.21	8.97	363	85	1.42	1.99	2.04	3.18	2.67
363	230	7.25	3.83	3.92	9.08	8.83	363	80	1.28	1.91	1.96	3.02	2.48
363	225	7.10	3.79	3.88	8.94	8.68	363	75	1.15	1.83	1.88	2.87	2.29
363	220	6.95	3.76	3.85	8.79	8.53	363	70	1.03	1.75	1.80	2.71	2.11
363	215	6.79	3.73	3.82	8.63	8.36	363	65	0.92	1.68	1.72	2.57	1.94
363	210	6.63	3.69	3.78	8.48	8.20	363	60	0.81	1.60	1.63	2.43	1.76
363	205	6.45	3.65	3.74	8.30	8.03	363	55	0.72	1.52	1.56	2.29	1.60
363	200	6.28	3.61	3.70	8.13	7.84	363	50	0.63	1.44	1.47	2.15	1.43
363	195	6.09	3.57	3.65	7.95	7.66	363	45	0.54	1.35	1.38	2.01	1.28
363	190	5.89	3.52	3.61	7.75	7.46	363	40	0.45	1.26	1.29	1.86	1.12
363	185	5.68	3.47	3.55	7.54	7.26	363	35	0.38	1.17	1.20	1.72	0.97
363	180	5.47	3.42	3.50	7.33	7.05	363	30	0.30	1.07	1.10	1.57	0.82
363	175	5.24	3.36	3.44	7.11	6.83	363	25	0.24	0.98	1.00	1.42	0.68

T, K	P, bar	$\delta_{d1,1/2}$ MPa	$\delta_{p1,1/2}$ MPa	$\delta_{h1,1/2}$ MPa	$\delta_{T,1/2}$ MPa	$\delta_{Hildebragg1}$ MPa ^{1/2}	T, K	P, bar	$\delta_{d1,1/2}$ MPa	$\delta_{p1,1/2}$ MPa	$\delta_{h1,1/2}$ MPa	$\delta_{T,1/2}$ MPa	$\delta_{Hildebragg1}$ MPa ^{1/2}
373	905	12.92	4.82	4.87	14.62	14.59	373	755	12.23	4.72	4.77	13.95	13.96
373	900	12.90	4.82	4.87	14.60	14.57	373	750	12.20	4.71	4.76	13.92	13.94
373	895	12.87	4.81	4.86	14.57	14.55	373	745	12.17	4.71	4.76	13.89	13.92
373	890	12.85	4.81	4.86	14.56	14.53	373	740	12.15	4.71	4.75	13.87	13.89
373	885	12.83	4.81	4.86	14.54	14.51	373	735	12.12	4.70	4.75	13.84	13.87
373	880	12.82	4.81	4.86	14.52	14.49	373	730	12.10	4.70	4.75	13.82	13.84
373	875	12.78	4.80	4.85	14.49	14.47	373	725	12.07	4.69	4.74	13.79	13.82
373	870	12.77	4.80	4.85	14.47	14.46	373	720	12.04	4.69	4.74	13.76	13.79
373	865	12.75	4.80	4.85	14.46	14.44	373	715	12.02	4.69	4.73	13.74	13.77
373	860	12.72	4.79	4.84	14.42	14.42	373	710	11.99	4.68	4.73	13.71	13.74
373	855	12.70	4.79	4.84	14.41	14.40	373	705	11.95	4.67	4.72	13.68	13.71
373	850	12.68	4.79	4.84	14.39	14.38	373	700	11.94	4.67	4.72	13.66	13.69
373	845	12.65	4.78	4.83	14.36	14.36	373	695	11.91	4.67	4.71	13.63	13.66
373	840	12.63	4.78	4.83	14.34	14.34	373	690	11.87	4.66	4.71	13.60	13.63
373	835	12.62	4.78	4.83	14.33	14.32	373	685	11.86	4.66	4.71	13.58	13.61
373	830	12.58	4.77	4.82	14.29	14.30	373	680	11.82	4.65	4.70	13.55	13.58
373	825	12.57	4.77	4.82	14.28	14.27	373	675	11.79	4.65	4.70	13.52	13.55
373	820	12.55	4.77	4.82	14.26	14.25	373	670	11.76	4.64	4.69	13.48	13.52
373	815	12.52	4.76	4.81	14.23	14.23	373	665	11.74	4.64	4.69	13.47	13.50
373	810	12.50	4.76	4.81	14.21	14.21	373	660	11.71	4.64	4.68	13.44	13.47
373	805	12.47	4.75	4.80	14.18	14.19	373	655	11.68	4.63	4.68	13.40	13.44
373	800	12.45	4.75	4.80	14.16	14.17	373	650	11.64	4.63	4.67	13.37	13.41
373	795	12.42	4.75	4.79	14.13	14.15	373	645	11.61	4.62	4.67	13.34	13.38
373	790	12.40	4.74	4.79	14.11	14.13	373	640	11.58	4.62	4.66	13.31	13.35
373	785	12.38	4.74	4.79	14.10	14.10	373	635	11.54	4.61	4.66	13.28	13.32
373	780	12.35	4.74	4.78	14.07	14.08	373	630	11.53	4.61	4.65	13.26	13.29
373	775	12.33	4.73	4.78	14.05	14.06	373	625	11.50	4.60	4.65	13.23	13.26
373	770	12.30	4.73	4.78	14.02	14.03	373	620	11.46	4.60	4.64	13.19	13.23
373	765	12.28	4.73	4.77	14.00	14.01	373	615	11.43	4.59	4.64	13.16	13.20
373	760	12.25	4.72	4.77	13.97	13.99	373	610	11.40	4.59	4.63	13.13	13.16

T_i K	P_i bar	$\delta_{d_i, 1/2}$ MPa	$\delta_{p_i, 1/2}$ MPa	$\delta_{h_i, 1/2}$ MPa	$\delta_{T_i, 1/2}$ MPa	$\delta_{Hildebrand, 1/2}$ MPa	T_i K	P_i bar	$\delta_{d_i, 1/2}$ MPa	$\delta_{p_i, 1/2}$ MPa	$\delta_{h_i, 1/2}$ MPa	$\delta_{T_i, 1/2}$ MPa	$\delta_{Hildebrand, 1/2}$ MPa
373	605	11.37	4.58	4.63	13.10	13.13	373	455	10.17	4.38	4.43	11.93	11.92
373	600	11.33	4.58	4.62	13.07	13.10	373	450	10.13	4.37	4.42	11.88	11.87
373	595	11.30	4.57	4.62	13.04	13.06	373	445	10.08	4.37	4.41	11.84	11.82
373	590	11.25	4.56	4.61	12.99	13.03	373	440	10.03	4.36	4.40	11.79	11.77
373	585	11.22	4.56	4.60	12.96	13.00	373	435	9.97	4.35	4.39	11.73	11.72
373	580	11.19	4.55	4.60	12.92	12.96	373	430	9.92	4.34	4.38	11.68	11.66
373	575	11.15	4.55	4.59	12.89	12.93	373	425	9.87	4.33	4.37	11.63	11.61
373	570	11.12	4.54	4.59	12.86	12.89	373	420	9.83	4.32	4.37	11.59	11.55
373	565	11.09	4.54	4.58	12.83	12.86	373	415	9.76	4.31	4.36	11.53	11.49
373	560	11.04	4.53	4.57	12.78	12.82	373	410	9.71	4.30	4.35	11.48	11.44
373	555	11.01	4.52	4.57	12.75	12.78	373	405	9.65	4.29	4.34	11.42	11.38
373	550	10.98	4.52	4.56	12.72	12.75	373	400	9.59	4.28	4.32	11.36	11.32
373	545	10.94	4.51	4.56	12.69	12.71	373	395	9.54	4.27	4.32	11.31	11.26
373	540	10.90	4.50	4.55	12.64	12.67	373	390	9.48	4.26	4.30	11.25	11.19
373	535	10.86	4.50	4.55	12.61	12.63	373	385	9.42	4.25	4.29	11.19	11.13
373	530	10.81	4.49	4.54	12.56	12.59	373	380	9.35	4.24	4.28	11.13	11.06
373	525	10.78	4.49	4.53	12.53	12.55	373	375	9.29	4.23	4.27	11.06	11.00
373	520	10.75	4.48	4.53	12.50	12.51	373	370	9.23	4.22	4.26	11.00	10.93
373	515	10.70	4.47	4.52	12.45	12.47	373	365	9.17	4.20	4.25	10.94	10.86
373	510	10.65	4.46	4.51	12.40	12.43	373	360	9.09	4.19	4.23	10.87	10.79
373	505	10.62	4.46	4.50	12.37	12.39	373	355	9.03	4.18	4.22	10.80	10.71
373	500	10.57	4.45	4.50	12.32	12.34	373	350	8.95	4.16	4.21	10.73	10.64
373	495	10.54	4.45	4.49	12.29	12.30	373	345	8.89	4.15	4.19	10.67	10.56
373	490	10.49	4.44	4.48	12.24	12.25	373	340	8.81	4.14	4.18	10.59	10.48
373	485	10.45	4.43	4.47	12.20	12.21	373	335	8.73	4.12	4.17	10.52	10.40
373	480	10.40	4.42	4.47	12.15	12.16	373	330	8.65	4.11	4.15	10.44	10.32
373	475	10.37	4.42	4.46	12.12	12.12	373	325	8.58	4.09	4.14	10.37	10.24
373	470	10.32	4.41	4.45	12.07	12.07	373	320	8.49	4.08	4.12	10.27	10.15
373	465	10.27	4.40	4.44	12.02	12.02	373	315	8.41	4.06	4.10	10.20	10.06
373	460	10.22	4.39	4.44	11.98	11.97	373	310	8.32	4.04	4.08	10.11	9.97

T, K	P, bar	$\delta_{dt,1/2}$ MPa ^{1/2}	$\delta_{pr,1/2}$ MPa ^{1/2}	$\delta_{ht,1/2}$ MPa ^{1/2}	$\delta_{T,1/2}$ MPa ^{1/2}	$\delta_{Hildebragg}$ MPa ^{1/2}	T, K	P, bar	$\delta_{dt,1/2}$ MPa ^{1/2}	$\delta_{pr,1/2}$ MPa ^{1/2}	$\delta_{ht,1/2}$ MPa ^{1/2}	$\delta_{T,1/2}$ MPa ^{1/2}	$\delta_{Hildebragg}$ MPa ^{1/2}
373	305	8.23	4.03	4.07	10.02	9.88	373	175	4.54	3.17	3.21	6.40	6.14
373	300	8.15	4.01	4.05	9.95	9.78	373	170	4.32	3.11	3.14	6.19	5.94
373	300	8.15	4.01	4.05	9.95	9.78	373	165	4.11	3.05	3.08	5.98	5.73
373	295	8.04	3.99	4.03	9.84	9.69	373	160	3.91	2.99	3.02	5.78	5.51
373	295	8.04	3.99	4.03	9.84	9.69	373	155	3.69	2.92	2.95	5.56	5.30
373	290	7.95	3.97	4.01	9.75	9.58	373	150	3.48	2.85	2.88	5.35	5.08
373	290	7.95	3.97	4.01	9.75	9.58	373	145	3.28	2.79	2.82	5.14	4.87
373	285	7.85	3.95	3.99	9.65	9.48	373	140	3.08	2.72	2.74	4.94	4.65
373	285	7.85	3.95	3.99	9.65	9.48	373	135	2.88	2.65	2.67	4.74	4.44
373	280	7.76	3.93	3.97	9.56	9.37	373	130	2.69	2.58	2.60	4.55	4.23
373	275	7.65	3.91	3.95	9.46	9.37	373	125	2.51	2.50	2.53	4.36	4.02
373	270	7.53	3.89	3.93	9.34	9.26	373	120	2.33	2.43	2.46	4.17	3.82
373	265	7.42	3.86	3.90	9.24	9.15	373	115	2.17	2.36	2.39	4.00	3.62
373	260	7.31	3.84	3.88	9.12	9.03	373	110	2.01	2.29	2.31	3.82	3.42
373	255	7.19	3.81	3.85	9.00	8.91	373	105	1.86	2.22	2.24	3.66	3.22
373	250	7.05	3.79	3.82	8.87	8.79	373	100	1.71	2.15	2.17	3.50	3.04
373	245	6.93	3.76	3.80	8.76	8.66	373	95	1.57	2.07	2.10	3.34	2.85
373	240	6.79	3.73	3.77	8.61	8.52	373	90	1.44	2.00	2.02	3.19	2.67
373	235	6.66	3.70	3.74	8.48	8.39	373	85	1.31	1.93	1.95	3.04	2.49
373	230	6.51	3.67	3.70	8.34	8.24	373	80	1.18	1.85	1.87	2.89	2.32
373	225	6.36	3.63	3.67	8.20	8.10	373	75	1.07	1.78	1.80	2.75	2.15
373	220	6.21	3.60	3.63	8.04	7.95	373	70	0.97	1.71	1.73	2.62	1.99
373	215	6.05	3.56	3.60	7.89	7.79	373	65	0.86	1.63	1.65	2.48	1.82
373	210	5.88	3.52	3.55	7.72	7.63	373	60	0.77	1.56	1.57	2.34	1.67
373	205	5.71	3.48	3.51	7.55	7.46	373	55	0.67	1.48	1.49	2.21	1.51
373	200	5.52	3.43	3.47	7.37	7.29	373	50	0.59	1.40	1.42	2.08	1.36
373	195	5.34	3.39	3.42	7.19	7.11	373	45	0.51	1.32	1.34	1.95	1.21
373	190	5.14	3.34	3.37	7.00	6.93	373	40	0.43	1.24	1.25	1.82	1.07
373	185	4.95	3.29	3.32	6.81	6.74	373	35	0.36	1.15	1.16	1.67	0.93
373	180	4.74	3.23	3.26	6.60	6.35	373	30	0.29	1.06	1.07	1.54	0.79

Appendix D: Equation of State References:

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