

Solubilities in supercritical fluids*

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Abstract: Solubilities in supercritical fluids are of great importance in a wide variety of applications. These applications include: production of controlled drug delivery systems, powder processing, pollution prevention and remediation, methods for spraying paints and coatings, precipitation/crystallization processes, bioseparations, and food processing. Examples of some of these applications will be given.

Supercritical fluid processes make use of the significant variation of solubility with pressure when the solvent is a supercritical fluid. This permits the accomplishment of many processes that would be otherwise very difficult to achieve. To fully understand the benefits of such processes, one must understand the phase behavior of such systems. The types of phase behavior that can be observed will be discussed, along with the ways that this behavior can be used to modify solubilities in such fluids.

There have been many methods proposed for the experimental determination of solubilities in supercritical fluids. These will be reviewed in general, and recommendations for preferred methods given.

Solubilities in supercritical fluids can be correlated and predicted by making use of thermodynamic calculations involving equations of state, as well as by other methods. The various methods will be reviewed, and recommendations given for various applications.

Keywords: supercritical fluids; solubility; review; experimental; applications; theoretical.

INTRODUCTION

In the 1980s, the use of supercritical fluids began to be touted as the solution to a wide variety of problems. Although some of these claims were not realistic, the attention to supercritical fluids in the scientific literature skyrocketed. As an example, prior to 1985, there were fewer than 5 articles per year in the literature discussing solubilities of substances in supercritical carbon dioxide; in the past 10 years, that number exceeded 65 per year. The number of applications and technologies involving supercritical fluids has also grown explosively. A simple search of the Web site <www.bn.com> recently showed 92 books about supercritical fluids alone. A search conducted using SciFinder Scholar returned 11 907 items dealing with supercritical fluids, 4255 dealing with supercritical fluid extraction (SFE) processes, and 1252 articles in the same time span dealing with supercritical solubilities, all in just the past 10 years alone. (There is doubtless some overlap between these.)

Clearly, there are many references that can be given to readers interested in further information. Some books that give summaries of applications using supercritical fluids are those by McHugh and Krukonis [1], Taylor [2], Gopalan et al. [3], Kiran et al. [4], Abraham and Sunol [5], and Johnston and

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Penninger [6], among others. Many texts in physical chemistry and thermodynamics address the physical basis and description of supercritical fluids. The classic references include Rowlinson [7] and the original article by Van Konynenburg and Scott [8], although one of the most lucid descriptions is provided by Clifford [9]. Methods for the experimental determination of solubilities in supercritical fluids are reviewed by Aim and Fermeglia [10]. Methods for the calculation/estimation of solubilities are addressed by Prausnitz et al. [11]. Of course, this short list necessarily omits many other works, some of which are also excellent references.

This paper will consist of four principal parts. The first part will survey the many varied applications, both historical and current, of supercritical fluids. The second part will discuss the physical nature of supercritical fluids and fluid mixtures. The third part will review the various experimental techniques available for determination of solubilities in supercritical fluids. The fourth part will examine the correlations and numerical techniques available for computing solubilities. The paper will conclude with some general observations about the future of this intriguing field.

APPLICATIONS INVOLVING THE USE OF SUPERCRITICAL FLUIDS

Applications that make use of the unique properties of fluids in the critical region have existed for at least 80 years. Most of the applications have been in the area of SFE. Although earlier, well-known processes existed, it was probably the commercialization of coffee decaffeination by SFE in the 1970s in Germany [12] that led to the explosion of interest in the 1980s. Other SFE processes related to the food industry include hops resin extraction [13], tea decaffeination [12], and the SFE of a wide variety of aromas and colors as well as fats and oils [14].

The earliest documented application making use of the unique properties of a solvent in its critical region involved oil deasphalting with propane in the 1930s [15]. By varying the temperature and pressure, including near-critical conditions, this single solvent was able to separate a feedstock stream into a wide range of product streams.

The 1940s saw the development of the Solexol process [16]. It also used propane as a selective solvent by varying its temperature and pressure in the near-critical and supercritical region. The best-known application of the process was to the purification and separation of vegetable and fish oils [17].

Perhaps the best known of the early processes making use of near-critical or supercritical fluids is the ROSE process. ROSE is an acronym for the residuum oil supercritical extraction process developed by Kerr McGee in the 1970s [18]. It typically used butane or pentane as the solvent and again exploited the variation in solvent power in the critical region of the solvent to separate its feed into an asphalt product and a deasphalted oil.

Since the 1980s, many more applications of SFE have appeared as well. SFE is used in the pharmaceutical and other industries to isolate a particular component or active ingredient; often this is a thermally labile compound for which SFE at ordinary temperatures is particularly attractive [19–23]. SFE has also been used for the remediation of contaminated soils [24–29], the extraction of fragrances [30–33], and other applications.

The recent literature reflects the wide variety of current applications involving supercritical fluids. There are many other applications besides SFE that make use of the variation of solubility with temperature and/or pressure. Applications that involve materials processing include painting (e.g., the UNICARB process [34]), various polymer processes [35–37], particle formation [38–42], and tablet coating in the pharmaceutical industry [43,44].

Other processes also take advantage of the high diffusivities possible with supercritical fluids. Several applications, for instance, involve impregnation. Examples include the manufacture of drug patches in the pharmaceutical industry [45–47], dyeing of textiles [48–57], infusing wood with preservatives [58–61], and aromas to food [62–64]. Still other processes take advantage of both higher diffusivities and solubilities to perform cleaning operations. Examples include the use of supercritical fluids as a dry cleaning fluid [65–68] or as a solvent in metal degreasing [69,70] or cleaning [66,71–74].

Other applications involving supercritical fluids include supercritical fluid fractionation [75,76], supercritical fluid chromatography [77–82], use as a solvent replacement for green chemistry [83–86], and antisolvent applications [87–93]. Last, but not least, are the applications where supercritical fluids are used as a reaction medium [94–99]. Supercritical water oxidation applications [100–103], for instance, are capable of very efficiently achieving complete oxidation of many substances, including otherwise hard-to-destroy contaminants.

Review articles that address applications include those by Perrut [104], Erkey [105], Teja and Eckert [106], Sihvonen et al. [107], McAvoy et al. [108], and Palmer and Ting [14], among others. A number of additional review articles have appeared in recent years. Hauthal [109] published a review of the recent advances with supercritical fluids that included approximately 200 references. Meireles [110] reviewed recent developments in supercritical extraction from solid substrates. Dehghani and Foster [111] reviewed antisolvent processes for pharmaceutical formulation. Senorans et al. [112] reviewed the newest trends in food processing and prominently featured the use of supercritical fluid technology. Zougagh et al. [113] reviewed the use of SFE as an analytical tool. Several authors have reviewed particle design and formation using various supercritical fluid processes [114–117]. Weidner et al. [118] reviewed high-pressure spray processes to produce powders and composites. Reverchon et al. [119] reviewed the production of microcomposites, foams and membranes. Shah et al. [120] reviewed nanomaterial synthesis in supercritical fluids. This sampling of recent review articles demonstrates the great interest that exists in applications of supercritical fluids. As may be judged from the earlier citation of the number of articles in the literature, many more could have been cited as well.

PHASE BEHAVIOR OF SUPERCRITICAL FLUIDS AND FLUID MIXTURES

To understand the phenomenon of solubility in supercritical fluids, it is first necessary to understand the unique characteristics of supercritical fluids. The typical PT phase diagram of a pure substance is shown in Fig. 1.

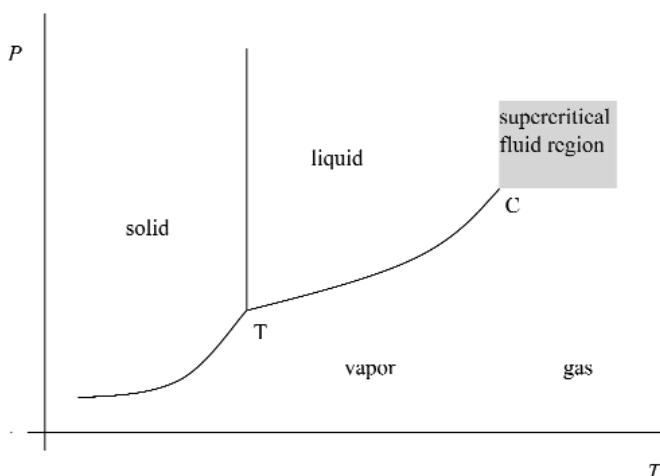


Fig. 1 Pressure–temperature diagram for a typical pure substance.

The diagram shows which state of matter (solid, liquid, vapor) exists for the pure substance at all possible combinations of temperature and pressure. There is only a single combination of temperature and pressure at which all three phases can coexist; that point is the triple point. Thus, it is also the point at which the three-phase equilibrium (sublimation, fusion, and vaporization) curves coincide. The vaporization curve begins at the triple point, T , and ends at the critical point, C . Along this curve, both temperature and pressure continuously increase, but are of course equal for the two phases in equilib-

rium. Other thermodynamic properties not shown on the diagram, such as volume, enthalpy, entropy, and internal energy, also vary along the curve but are generally not equal for the two phases in equilibrium. However, as the critical point is approached, all of the thermodynamic properties of the two phases gradually become equal. At the critical point, all of the properties of the two phases are equal and the two phases become a single continuous phase. This is commonly demonstrated by a pressure–volume (PV) diagram, as in Fig. 2.

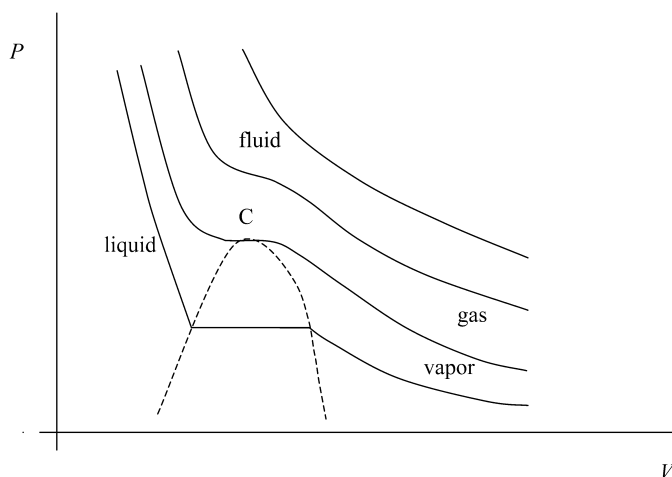


Fig. 2 Pressure–volume diagram for a typical pure substance.

The curves in Fig. 2 represent isotherms. Isotherms at temperatures above the critical temperature are continuous and monotonic with negative values of $(\partial P/\partial V)_T$. At temperatures below the critical temperature, the equilibrium isotherm is no longer of the same character. The slope is discontinuous at the boundary of the two-phase region. The length of the horizontal section of a subcritical isotherm reflects the difference between the molar volumes of the liquid and vapor phases in equilibrium. As the temperature is raised toward the critical temperature, the properties of the two phases in equilibrium approach each other, finally becoming identical at the critical point. The isotherm at the critical temperature is characterized by a horizontal inflection point at the critical point. Thus, at the critical pressure the isothermal compressibility becomes infinite. This leads to the phenomenon of critical opalescence, which reflects the sudden onset of longer-range order throughout the macroscopic system.

The region corresponding to temperatures above the critical temperature and to pressures above the critical pressure is referred to as the supercritical fluid, or fluid, region. The properties of a supercritical fluid are intermediate to those of normal liquids and gases. The density, while less than that of the liquid, is significantly higher than that of a gas. The diffusivity, while lower than that of a gas, is significantly higher than that for a liquid. The combination of these two properties makes supercritical fluids much better solvents than would normally be expected. This is particularly true when the temperature and pressure are not too far above the critical temperature and pressure. Table 1 lists the critical temperature, critical pressure, and acentric factor for several substances commonly considered for use as supercritical solvents [121,122].

Table 1 Critical temperature and pressure and acentric factor for common SCF solvents.

Solvent	T_c/K	P_c/bar	ω
Carbon dioxide	304	73.7	0.225
Water	647	221	0.344
Ethane	305	48.7	0.099
Ethene	282	50.4	0.087
Propane	370	42.5	0.152
Ammonia	405	114	0.257
Nitrous oxide	310	72.5	0.141
Trifluoromethane	299	48.4	0.267

Processes that make use of supercritical fluid solvents are necessarily at elevated pressures. Dependent upon the solvent, they may also be at elevated temperatures. Solvents are frequently chosen on the basis of the suitability of the temperatures and pressures corresponding to the supercritical region for the substance. However, other factors are important as well. These include toxicity and other hazards, cost, availability, and environmental friendliness (or lack thereof) of the solvent. On these bases, carbon dioxide is the most preferred solvent. However, it is not always a good solvent for the solute of interest. Thus, a common approach is to include a small amount of a cosolvent to increase the solubility of the solute. The cosolvent will be a substance that has a greater affinity for the solute than does carbon dioxide. Table 2 lists the critical temperature, critical pressure, and acentric factor of several substances commonly used as cosolvents for carbon dioxide [121,122].

Table 2 Critical temperature and pressure and acentric factor for common cosolvents for carbon dioxide.

Solvent	T_c/K	P_c/bar	ω
Methanol	513	81.0	0.565
Ethanol	514	61.5	0.649
1-Propanol	537	51.8	0.629
2-Propanol	508	47.6	0.665
2-Butanol	536	41.8	0.574
Acetone	508	47.0	0.307
Acetonitrile	546	48.3	0.338
Acetic acid	593	57.9	0.445
Diethyl ether	467	36.4	0.281
Dichloromethane	510	60.8	0.199
Chloroform	536	54.7	0.222
Hexane	508	30.3	0.300
Benzene	562	49.0	0.210
Toluene	592	41.1	0.264

Understanding solubilities in supercritical fluids necessarily requires the understanding of mixture behavior in the critical region. Van Koynenburg and Scott [8] described several types of observable behavior, but for the purposes of this paper only two of them are relevant. Figure 3 portrays the two relevant types of behavior. Type I behavior would be typical of two components with not-too-dissimilar critical points and would describe many solvent/cosolvent mixtures. Type III behavior, on the other hand, occurs when the two components have greatly dissimilar critical points and would be typical for solvent/solute mixtures. The diagrams represent the projections onto a single pressure–temperature

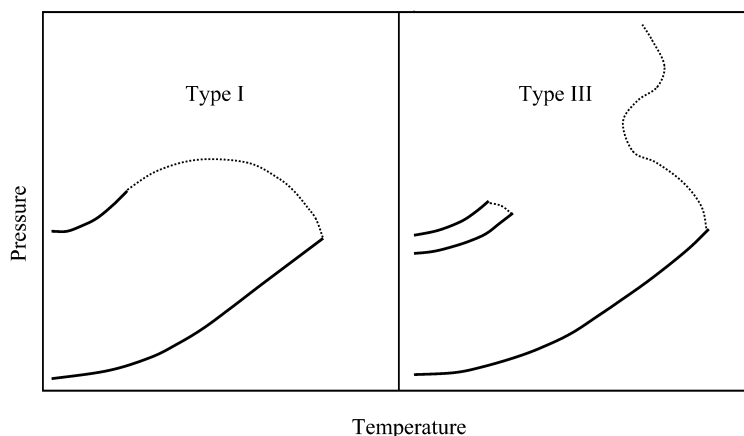


Fig. 3 Critical region phase behavior in the critical region projected onto pressure–temperature plane.

plane of the ends of the pure component vaporization curves (solid lines) and the locus of mixture critical points (dotted lines). In the case of Type III behavior, the projection of the three-phase liquid–liquid–vapor line is also present.

Systems which exhibit Type I behavior in the critical region would typically exhibit normal vapor–liquid equilibrium behavior at ordinary conditions (refer to Fig. 4). As the temperature is raised, eventually the critical temperature of the solvent (more volatile component) is passed. Above that temperature, the solvent can no longer undergo a phase transition as a pure component; thus the vapor–liquid equilibrium loop “detaches” from the right edge of the diagram.

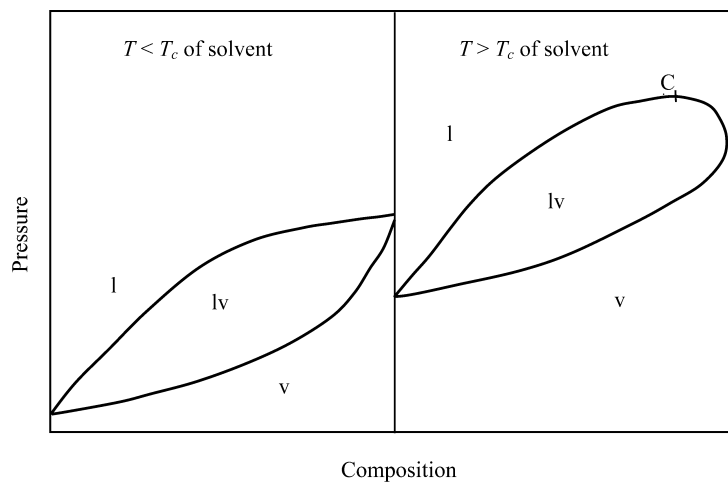


Fig. 4 Pressure vs. composition of liquid (l) and vapor (v) phases for Type I systems.

Since horizontal lines in this diagram connect two phases (one liquid and one vapor) at the same temperature and pressure, the maximum point on the loop represents a mixture critical point, where the liquid and vapor mixtures at that temperature and pressure become identical. At still higher temperatures, the loop becomes smaller and smaller, the composition of the mixture critical point shifts to lower and lower compositions of the solvent (and, of course, higher and higher compositions of the second component). Type I behavior is characterized by this process continuing until the critical point of the second component is reached. A plot of the various mixture critical points on a pressure vs. tempera-

ture diagram yields a continuous critical line that connects the critical points of the two pure substances, as shown in Fig. 3.

It should be noted that while the mixture critical point is always at an extremum of pressure on a plot of pressure vs. composition (and at an extremum of temperature on a plot of temperature vs. composition), the same cannot be said for pressure vs. temperature plots at constant composition. It is quite possible, even expected, that the mixture critical point for a given composition will be neither the extremum of pressure nor the extremum of temperature. This possibility is what gives rise to phenomena such as retrograde condensation [7,122].

The phenomenon can be readily visualized by considering the second part of Fig. 4. For some compositions to the right of the mixture critical point, it is possible to expand a vapor mixture at constant temperature and composition so that it crosses the dew-point curve twice. In between these points, the system will be partially liquid. Thus decreasing the pressure has caused the formation of a liquid phase—retrograde condensation. A similar process may also occur by variation of temperature at constant pressure.

In practice, the location of the mixture critical point for a solvent mixture consisting of a solvent and a cosolvent will thus depend on the composition of the solvent mixture. Care should be taken to ensure that a process designed to use such a mixture as a supercritical fluid solvent is indeed in a single-phase region as regards the solvent mixture.

Systems that exhibit Type III behavior generally have very dissimilar critical points, thus, Type III behavior is most commonly found with mixtures of supercritical solvents with solutes. Typically, at ambient conditions, the solute and solvent have only very limited miscibility. If the solute is a solid rather than a liquid, then the mutual solubilities are virtually negligible.

Figure 5 gives an example of Type III behavior. Such systems have two phases across most of the composition range at all temperatures and pressures of interest. Below the critical temperature of the solvent, there are two liquid phases, one rich in the solvent and the other rich in the solute. (The sizes of these regions have been portrayed somewhat larger than they are in most cases for ease of understanding.) At lower pressures, a vapor phase appears, and thus a three-phase equilibrium line exists at a particular pressure. This projection of these points (the pressure corresponding to the three-phase line for each temperature) gives the third solid line in Fig. 3 for Type III behavior. As the temperature is raised beyond the critical temperature of the solvent, the vapor–liquid equilibrium loop again detaches from the right edge of the diagram, much as it does for Type I systems. However, in this case, as the temperature is further raised and the loop shrinks in size, it eventually disappears not at the left edge of

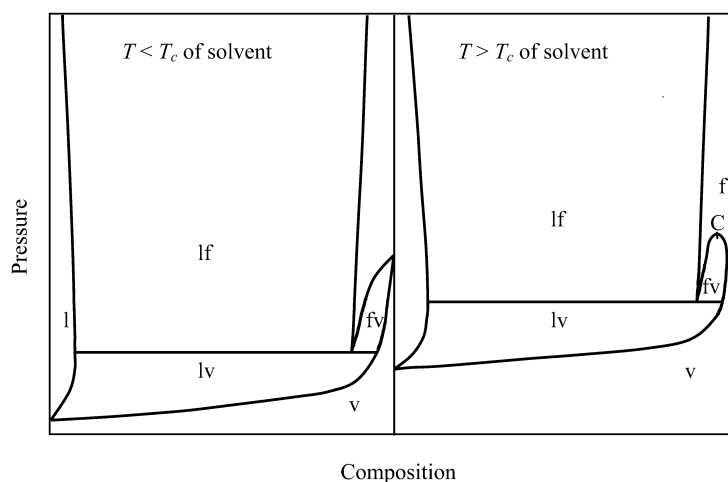


Fig. 5 Pressure vs. composition for liquid (l), vapor (v), and fluid (f) phases for Type III systems.

the diagram (as was the case for Type I behavior where the critical line ended at the second component's critical point) but at the liquid–liquid phase envelope. Thus, the critical line originating at the critical point of the solvent ends at the critical end point, which also marks the end of the three-phase line. For a temperature above the critical end point, the phase diagram appears as in Fig. 6.

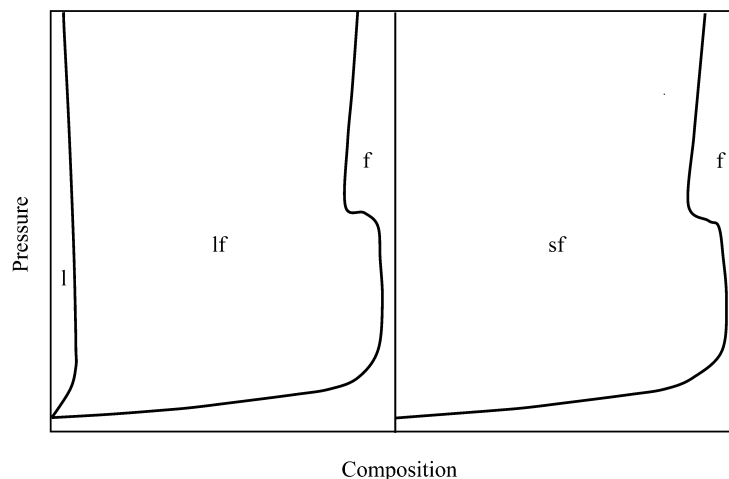


Fig. 6 Mutual solubilities for a supercritical solvent and a liquid solute (left) or a solid solute (right).

Once the critical end point is passed, the diagram simplifies dramatically. The three-phase line is gone, and the only remnant is the shift to the left for the right-hand curve. This shift is the basis for almost all of the applications of supercritical fluids as solvents. The right-hand curve represents the solubility of the solute in the supercritical fluid, and the shift to the left represents the often dramatic jump in solubility above the critical pressure of the solvent. The left-hand curve represents the solubility of the solvent in the liquid solute at these conditions.

Solid solutes exhibit similar behavior to liquid solutes, with two main differences. First, and most obvious in the above diagrams, the solubility of the solvent in the solid solute is usually negligible at all conditions. Thus, the left-hand curves in Figs. 5 and 6, if they exist at all, are essentially superimposed on the left edge of the diagram. This is shown in the second part of Fig. 6. Second, for most substances the solid–liquid equilibrium curve, as presented in Fig. 1, rises almost vertically from the triple point, usually with a slight tilt to the right (water being a notable exception). Even for such substances, though, the presence of the supercritical fluid phase may permit the formation of a liquid phase at temperatures below, but still near to, the triple-point temperature.

Most applications will want to avoid these various three-phase regions. Thus, they need to be designed to operate at temperatures above the temperature corresponding to the critical end point, which is normally somewhat above the critical temperature of the solvent. In the case of a solid solute, they need to operate at a temperature sufficiently below the triple-point temperature of the solute.

EXPERIMENTAL DETERMINATION OF SOLUBILITIES

The experimental determination of solubilities in supercritical fluids has been well reviewed by Aim and Fermeglia [10] as well as in an article by Dohrn and Brunner [123]. Both references contain a very large number of references to various experimental techniques. They can be put into three categories: static methods, dynamic methods, and chromatographic methods. In this classification, static methods include bubble- and dew-point methods. Dynamic methods include recirculation methods, flow methods, and saturation methods. As may be judged from the previous section, there is a wide variety of phe-

nomena for which accommodation needs to be made by the experimentalist. Thus, for each of the different categories, there is a wide variety of specific techniques.

Static methods consist of a closed cell into which the components are then placed. There is no gross movement of either phase, although often there is a stirrer that may be turned on and off in order to promote achievement of equilibrium, especially for liquid solutes. Cells may be of variable volume and may have a view port. They are immersed in a temperature bath and are equipped with a pressure sensor. Determination of the phase compositions can be by either an analytic or a synthetic method.

If the phase compositions are determined analytically, then samples are taken of both phases. This is very difficult to do without disturbing the equilibrium in the cell. Furthermore, extreme care must be taken when handling the samples so as to prevent solute deposition prior to analysis.

If the phase compositions are determined synthetically, then very precise amounts of the compounds are injected into a previously evacuated cell. The phases are not sampled, but instead the compositions are determined by calculation. This requires knowledge of a highly accurate pressure–volume–temperature relation for the system. This approach can also be accomplished using a variable volume to locate phase transitions and/or a view cell that allows visual determination of bubble points, dew points, and critical points.

Some recent examples using static techniques include the following. Crampon et al. [124] describe a variable volume view cell that can be used in either an analytic or synthetic mode. Sherman et al. [125] describe a simple gravimetric method for measuring the solubility of a solid solute. Hourri et al. [126] describe a novel technique that uses measurements of dielectric constants to determine solubility in situ. Many others [127–135] have also recently published results using variations of the static approach.

Recirculation methods are similar to static cells. However, they add external recirculation loops that help to speed up the equilibration process. Some of them may also include a view cell, as with static cells. Some designs recirculate both phases, while others recirculate just one of the phases. The external loops may also facilitate sampling and/or analysis of the phases. However, the additional complexity frequently brings with it additional experimental difficulties. For instance, pressure drops in the recirculation loop may lead to precipitation of solute from the fluid phase.

Examples include the work by Daneshvar and Gulari [136], who used a dual recirculation system to measure the solubility of polyethylene glycol in carbon dioxide. Cheng et al. [137] also used a dual recirculation system to study the solubility of methyl oleate in carbon dioxide. Some others [138,139] have also published recent results using a recirculation method.

Flow methods feature continuous flow of all components into and out of the system. Phase formation and separation occur within the cell. Both phases are sampled and analyzed to determine the equilibrium compositions. The main disadvantages of these methods are that they consume more materials and that the pressure is subject to larger uncertainties. Of course, they are also subject to the problems mentioned earlier as well.

A recent example of a flow method is that of Ruivo et al. [140]. In their method, a static mixer is used to promote equilibrium between the phases. Both phases are collected and measured, and the solubility is determined by comparison of the amounts collected. Some others [141,142] have also published recent results using a flow method.

In saturation methods, an initial charge of the solute is placed into the cell. Then, a continuous flow of solvent is passed through the cell. By ensuring an adequate contact time, the exiting stream is assumed to be saturated with solute. The exiting solute is then captured in a trap, and the total flow of fluid measured. Comparison of these two quantities gives a measurement of the solubility. The primary new difficulty with this approach is how to ensure that the exiting stream truly is saturated.

Recent examples of saturation methods include the one described by Huang et al. [143], who used two extraction cells to ensure saturation when they studied the solubility of cholesterol in carbon dioxide. Ferri et al. [144] used a bypass to dilute solute concentration prior to depressurization to reduce

problems with solute deposition. Some others [145,146] have also recently described results obtained using a saturation method.

Chromatographic methods use the supercritical fluid as the mobile phase. The solute is injected just before the column. The method relies on having a relation between the retention time and the solubility in the fluid. This approach is not yet widely used in practice.

In summary, the saturation methods are the simplest and most widely used methods for measuring the solubility of solid solutes. For liquid solutes, static cell methods predominate. Any method involving sampling requires extra care in doing the sampling to prevent disturbing the equilibrium in the cell, and in sample handling to prevent deposition. Synthetic methods of determining composition require very precise methods of cell loading and monitoring.

EMPIRICAL AND THEORETICAL DESCRIPTIONS OF SOLUBILITIES

If one were to make two plots, one of reduced density of a supercritical solvent vs. reduced pressure of the solvent, and the other solubility of a chosen solute in the solvent vs. reduced pressure of the solvent, at a temperature just above the critical temperature of the solvent, one would observe that the shapes of the two plots are very similar. This type of observation leads to the most widely used correlating equation for solubilities in supercritical fluids, the Chrastil [147] equation:

$$\ln S = k \ln \rho + a/T + b \quad (1)$$

In this expression, S is the solubility, ρ is the density of the supercritical fluid, T is the temperature, and the remaining constants are specific to the particular solvent/solute pair, as well as to the chosen units for the physical quantities. In the original work, these had a physical interpretation, however, in practice they are generally fit to solubility data. As a result, the expression should be considered an empirical correlating expression. Many authors, e.g., [132–135], have used the Chrastil equation for correlating solubility data.

A more exact approach is to treat the calculation of solubility in a supercritical fluid just as any other phase equilibrium calculation. Thermodynamic equilibrium is assumed to exist between the two phases, thus, they are assumed to be at the same temperature and pressure. Further, the chemical potential (or equivalently, the fugacity) of each component must be equal in each phase.

$$T^\alpha = T^\beta \quad (2)$$

$$P^\alpha = P^\beta \quad (3)$$

$$\mu_i^\alpha = \mu_i^\beta \quad \text{or} \quad \hat{f}_i^\alpha = \hat{f}_i^\beta \quad (4)$$

Solubilities of liquids

With liquid solutes, there is the potential for significant solubility of the solvent in the liquid solute. Thus, the equilibrium calculation will involve not only determining the composition of the solute in the solvent, but also determining the composition of the solvent in the solute. The component fugacity is normally computed in terms of the component fugacity coefficient:

$$\hat{\phi}_i = \hat{f}_i / x_i P \quad (5)$$

Combination with the isofugacity criterion yields, on solving for the solubility:

$$y_i = x_i \left(\hat{\phi}_i^{\text{liquid}} / \hat{\phi}_i^{\text{fluid}} \right) \quad (6)$$

In this expression, x_i is the mole fraction of the solute in the liquid phase, and y_i is the solubility of the solute in the fluid phase, expressed as a mole fraction. An identical equation is also valid for the solvent, except that the interpretations are reversed; in that case, y_i is the mole fraction of the solvent in the fluid phase, and x_i is the solubility of the solvent in the liquid phase. In addition to these two equations, there is also the requirement that the mole fractions in each phase sum to unity.

Unfortunately, the above equations are not as straightforward as they appear, as the fugacity coefficients for each component must be determined from an appropriate equation of state and are non-linear functions of temperature, pressure, and composition. Thus, for the simplest case of a single solute component and a single fluid component at a specified temperature and pressure, the calculation requires simultaneous solution of four equations—two of which are highly nonlinear—for four unknown compositions. The computation can be even more difficult, as there is the possibility of multiple solutions. From Fig. 5, for instance, it is clear that for some combinations of temperature and pressure below the mixture critical point, there is one solution representing an equilibrium between a liquid solute phase and a liquid solvent phase, and another solution representing an equilibrium between a liquid phase and a vapor phase.

The computation of the location of mixture critical points and of critical end points raises further complications. These types of calculations are the subject of current research [148,149] and will not be discussed here.

Solubilities of solids

In this case, it is usually safe to neglect the solubility of the solvent in the solid solute phase. Furthermore, since most equations of state in common use for fluid mixtures are not also applicable to solid phases, a different approach for evaluating the fugacity of the solid phase is required. Instead, the fugacity of the solid is determined by using its vapor pressure at the temperature of interest. At a pressure equal to its vapor pressure, the fugacity of the solid is equal to the fugacity of the vapor. This is then multiplied by a Poynting factor to obtain the solid fugacity at the temperature and pressure of interest.

$$\hat{f}_i = f_i = P_i^{\text{sat}} \phi_i^{\text{sat}} \exp\left(\int_{P_i^{\text{sat}}}^P V_i^{\text{solid}} dP / RT\right) \quad (7)$$

In this equation, f_i is the fugacity of the pure solid solute at the temperature and pressure of interest; P_i^{sat} is the vapor pressure of the pure solid solute at the temperature of interest; ϕ_i^{sat} is the fugacity of the equilibrium vapor phase at the vapor pressure (usually very near unity since the vapor pressure is usually quite low); and the exponential is the Poynting factor, which involves the molar volume of the pure solid solute [11,122].

The fluid phase is treated just as it was for liquid solutes, and thus requires an equation of state applicable to the supercritical fluid region. The solubility of the solid solute in the fluid phase is then calculated as:

$$y_i = E_i \left(P_i^{\text{sat}} / P \right) \quad (8)$$

where the enhancement factor, E_i , is defined as:

$$E_i = \left(\phi_i^{\text{sat}} / \hat{\phi}_i \right) \exp\left(\int_{P_i^{\text{sat}}}^P V_i^{\text{solid}} dP / RT\right) \quad (9)$$

As was true for liquids, the fugacity coefficient in the fluid phase is a function of composition. Thus, the equation for the solubility is again not as straightforward as it looks. Rather, it is a highly non-linear equation that must be solved by an iterative technique.

Fugacity coefficient

For both cases above, it is necessary to calculate the component fugacity coefficients in the supercritical fluid region. This requires an equation of state to describe the mixture behavior in that region. Numerous equations of state have been proposed for fluids and fluid mixtures. Most equations of state are pressure-explicit. That is, they give pressure as a function of temperature and molar volume. In general, they also involve two or more equation-of-state parameters. For a pure substance, these parameters are typically determined by requiring the equation of state to reproduce the horizontal inflection point at the experimental critical temperature and pressure of the component [11]. Dependent upon the equation of state, it may or may not be possible or feasible to also reproduce the experimental value of the critical volume. When applied to mixtures, it is also necessary to specify mixing rules that give the composition dependence of the equation-of-state parameters.

Once an equation of state, and its mixing rules, have been specified, the expression for the fugacity coefficient follows the following thermodynamic relation [150]:

$$\ln \hat{\phi}_i = -\int_{\infty}^V \left\{ \left[\frac{\partial(nZ)}{\partial n_i} \right]_{T, V^t, n_j} - 1 \right\} \frac{dV}{V} - \ln Z \quad (10)$$

where Z the compressibility factor (equal to PV/RT), V^t is the extensive volume, and V is the molar volume.

The most widely used equations are still cubic equations of state, mainly due to ease of computation and to familiarity. The most well-known of the cubic equations of state are the Soave modification of the Redlich–Kwong (SRK) equation [151] and the Peng–Robinson (PR) equation [152]. The SRK equation can be written as:

$$Z = \frac{1}{1 - b/V} - \left(\frac{\theta}{bRT} \right) \frac{b/V}{1 + b/V} \quad (11)$$

for which the corresponding component fugacity coefficient is:

$$\ln \hat{\phi}_i = \frac{\hat{b}_i}{b} (Z - 1) - \ln [Z(1 - b/V)] + \frac{\theta}{bRT} \left(\frac{\hat{b}_i}{b} - \frac{\hat{\theta}_i}{\theta} - 1 \right) \ln(1 + b/V) \quad (12)$$

The expressions for the PR equation are similar:

$$Z = \frac{1}{1 - b/V} - \left(\frac{\theta}{bRT} \right) \frac{b/V}{1 + 2(b/V) - (b/V)^2} \quad (13)$$

$$\ln \hat{\phi}_i = \frac{\hat{b}_i}{b} (Z - 1) - \ln [Z(1 - b/V)] + \frac{\theta}{bRT} \left(\frac{\hat{b}_i}{b} - \frac{\hat{\theta}_i}{\theta} - 1 \right) \frac{1}{2\sqrt{2}} \ln \left[\frac{1 + (1 + \sqrt{2})b/V}{1 + (1 - \sqrt{2})b/V} \right] \quad (14)$$

In the above equations, the quantities θ and b represent the equation-of-state parameters for the SRK and the PR equations. They are, of course, functions of composition, these functions being given by the user-specified mixing rules. These mixing rules thus determine the following component-specific values:

$$\hat{\theta}_i = \left[\frac{\partial(n\theta)}{\partial n_i} \right]_{T, V^t, n_j} \quad (15)$$

$$\hat{b}_i = \left[\frac{\partial(nb)}{\partial n_i} \right]_{T, V^t, n_j} \quad (16)$$

The traditional mixing rules [11] have a quadratic dependence on composition for θ and a linear dependence on composition for b . They are simple to use, but do not well describe the composition dependence of dense phases. Other choices for mixing rules include those based on the approach of Huron and Vidal [153] or on that of Wong and Sandler [154,155], among others. Both of these approaches attempt to improve the composition dependence of mixing rules by incorporating expressions used to describe the composition dependence of the excess Gibbs energy of liquid mixtures.

The foregoing discussion notwithstanding, the rigorous calculation of solubilities in supercritical fluids is still problematic. The most commonly used equations of state, cubic equations of state, are well known to be inadequate to the proper description of the critical region. Indeed, no analytic equation will ever be adequate to describe this region [156,157]. The appropriate composition dependence of mixing rules is quite different for liquid regions and gaseous regions, and not well understood in fluid regions. There are also severe numerical complexities in the neighborhood of mixture critical points and critical end points. All of these are areas of active research [158–170].

CONCLUDING COMMENTS

The study of supercritical fluids is a fascinating subject with many aspects that are areas of active investigation around the world. New applications of supercritical fluids seem to appear every week and seem to be limited only by the ingenuity of the world's scientists and engineers. The phase behavior of mixtures in the critical region is so complex that new phenomena continue to be discovered. There is a vast literature reporting the results of solubility measurements in supercritical fluids, but many more combinations of solvent and solute remain to be investigated. New experimental approaches continue to be developed on a regular basis as well. Accurate theoretical descriptions rely on the accuracy of the available equations of state and their mixing rules, both of which continue to improve, but still need further improvement. Finally, the numerical solution of these equations is difficult, and methods for their solution also need improvement. It appears that the vast literature devoted to supercritical fluids will continue to grow over the coming years.

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