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The Solvent-Solute Interaction in Supercritical Solution at Equilibrium: Modeling and Related Industrial Applications

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Abstract

Supercritical solutions are studied from the thermodynamic point of view by giving a comprehensive review of phase equilibrium of binary systems. The numerical modeling of the phase behavior is an approach used by several authors to describe and analyze supercritical applications. The thermodynamic equilibrium models are employed to determine the interaction coefficient between the solvent and the solute. Depending on the nature of the compound and the operating conditions three different experimental methods are used. Understanding the phase equilibrium of supercritical solutions and deeper knowledge of the supercritical fluids are needed for industrial applications such as powder elaboration by rapid expansion of supercritical solution and essential oil extraction processes.

Keywords: Phase equilibrium, supercritical solution, interaction coefficient, solubility, supercritical extraction.

1. Introduction

A supercritical fluid state is a phase that is neither liquid nor gas; it is a state above the critical temperature and the critical pressure. The finishing of the vaporization curve at the critical point means that beyond the corresponding temperature and pressure it is impossible to distinguish clearly the gaseous state from the liquid one, see *Figure 1*. This phase shows unique properties that are different from those of either gases or liquids under standard conditions. A supercritical fluid has both the gaseous property of high compressibility and the liquid property of being able to dissolve materials into their components. In addition, its density changes to a great extent in a continuous manner. In this account, the use of carbon dioxide under supercritical state offers a substitute for organic solvents in the fields of food industry and medical supplies. The supercritical carbon dioxide is well used as a solvent in many applications. Its advantages are numerous; these can be summarized as follows: a convenient critical temperature (31.2°C), chemically inert, non-flammable, easily recycled, easily removed when the solute separation occurs.

Solubility data are essential for the assessment and development of new applications of supercritical fluids. One of the great advantages of supercritical fluids is that a solute's solubility may be adjusted through changing the operating conditions of pressure and temperature. The high-pressure level may be used to increase the solubility to extract, for example, a specified solute from vegetable matrices. Then, a drop in pressure may be used to recover the solute and regenerate the supercritical fluid for reuse. A large solubility database must be generated for each solute, as the solubility is a function of the temperature, the pressure and the presence of other constituents.

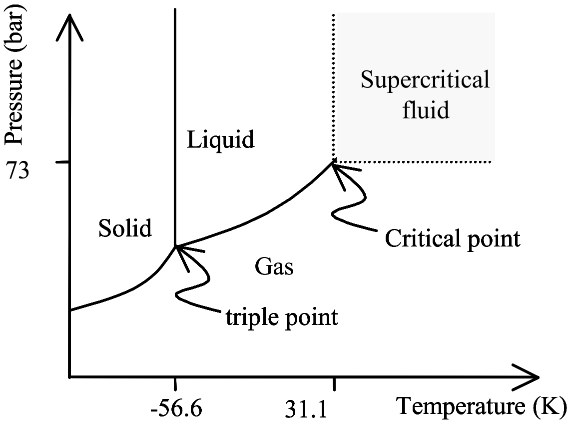

Figure 1. The supercritical phase domain of the carbon dioxide

This complexity is the motivation for the development of correlation and prediction techniques.

Cagniard de la Tour (1822) described the pure phase behavior at the beginning of the 19th century. He noticed that the gas-liquid phase boundary disappears when a certain temperature is exceeded. Andrews (1869) carried out further studies concerning dense carbon dioxide and the carbon dioxide/nitrogen system. Moreover, Hannay and Hogarth (1879) studied the solubility of solids (inorganic salts) in supercritical solvents (ethanol). By the early 1900s, Buchner (1906) discovered that the solubility of organic compounds such as naphthalene in supercritical carbon dioxide is a function of the pressure.

At equilibrium of phases in a multi component system (n components), intensive variables to describe the state are: the pressure P, the temperature T, and different mole fractions of each component (y_i = 1,...(n-1)). The phase equilibrium occurs when chemical potentials (μ_ι) of each component at different phases are equal:

$$\mu_i^\alpha = \mu_i^\beta = ... = \mu_i^\varsigma \qquad (1)$$

(α,β, …, ξ) denote the various phases which has total number ϕ and i indicates the component (i =1, 2 ….., n) .

Here, the Gibbs phase rule (1875), which determines the degree of freedom v, is written as:

$$v = c + 2 - \phi \qquad (2)$$

c = n - r stands for the number of the independent components of the system, r is the number of relations between the various mole fractions due to the equilibrium conditions for the existing chemical reactions.

ϕ is equal to 2 in the region closest to the critical point where liquid and vapor are unseparated. Moreover, the chemical potential equality is translated into a fugacity equality (*f*), which can be deduced directly by using a suitable equation of state:

$$f_i^L = f_i^{SC} \quad \text{or} \quad f_i^S = f_i^{SC} \qquad (3)$$

L, S, SC denotes liquid, solid, and supercritical phases respectively.

In literature, the phase equilibrium diagrams show the system (pure substances or multi-components) evolutions at a given temperature or pressure. In practice, two-dimensional diagrams are used to represent the phase equilibrium. Thus, isotherm network can be drawn for such system components in the P - y diagram. Van Konynenburg and Scott have classified the main types of fluid phase behavior diagrams for binary mixtures (1980), see *Figure 2.* In these diagrams, solid lines (ending in bullets) represent vapor pressure curves ending in critical points, other solid curves are the projections of three boundaries and dashed curves show the critical lines. For ternary systems at constant pressure and constant temperature, the Gibbs's triangular diagrams are well known to show the phase behavior at equilibrium. In *Figure 3*, the ternary diagram of water, ethane, and carbon dioxide is given. The solid curve represents the critical line that limits the miscibility domain. The equilibrium lines show constant ethanol fractions in the vapor phase. Carbon dioxide extracts ethanol selectively from ethanol-water solution.

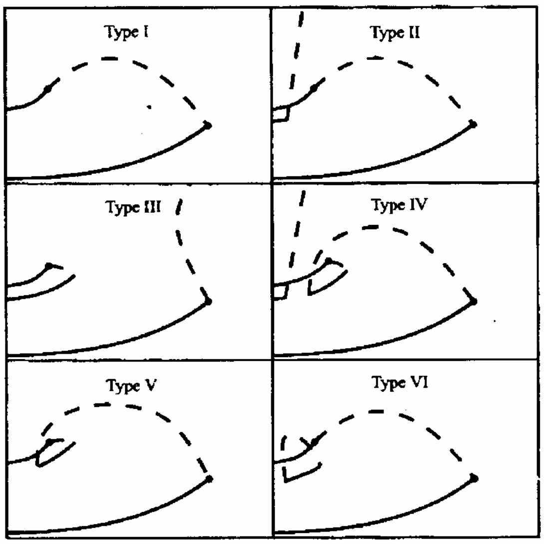

Figure 2. Main types of phase diagrams for the binary mixtures projected on P - T plane.

We note that the phase behavior depends strongly on the component nature. Indeed, the molecular composition, the polarity, the density, the dielectric properties of the solute, etc, have considerable effects on the phase equilibrium establishment.

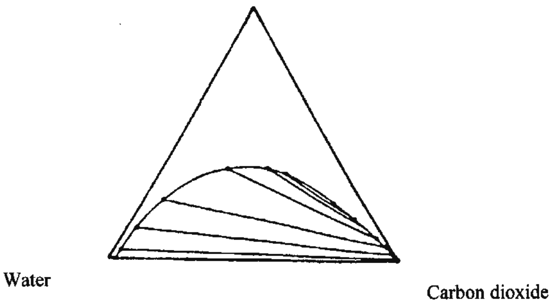

Figure 3. The Gibbs's triangular diagram of ternary mixture at equilibrium.

2. Phase Behavior Equations

As seen before, the chemical potential equality at equilibrium is taken into account by equating the fugacity of each component at each phase. So, for the mathematical description, an adequate equation of state (EOS) is needed. Usually established for pure component, the EOS could be extended to a solution at equilibrium of a multi-component system by using suitable mixing rules that define the homogenous supercritical mixture characteristics.

Numerous equations of state are proposed in the literature, their use is strongly related to the domains of the operating parameters and the nature of the chemical components. The best known EOS for pure compounds are the cubic equations of state, such as Redlich - Kwong - Soave (RKS) EOS (1972) and Peng - Robinson (PR) EOS (1976); these equations can be written respectively as:

$$P = \frac{RT}{(V-b)} - \frac{a}{V(V+b)} f\,(T_r) \qquad (4)$$

$$P = \frac{RT}{(V-b)} - \frac{a}{V(V+b)+b(V-b)} f\,(T_r) \qquad (5)$$

R is the perfect gas constant, a denotes the attractive term and *b* is the covolume. The corrective terms *a* and *b* are expressed as functions of the critical coordinates of the compound, and are written respectively as:

$$a = \Omega_a \frac{R^2\,T_c^2}{P_c} \;;\; b = \Omega_b \frac{R\,T_c}{P_c} \qquad (6)$$

Applying the critical constraints, the parameters Ω_a and Ω_b, are calculated differently for the above equations (4) and (5), giving for RKS EOS:

$\Omega_a = 0.42748$; $\Omega_b = 0.08664$.

For PR EOS:

$\Omega_a = 0.4524$; $\Omega_b = 0.0778$.

The corrective function, depending on the temperature, is defined for EOS (4) and (5) as:

$$f\,(T_r) = \left(1 + \kappa\,\left(1 - \sqrt{T_r}\right)\right)^2 \qquad (7)$$

where T_r is the reduced temperature $\left(T_r = T/T_c\right)$ and κ is expressed for both equations (4) and (5) respectively:

$$\kappa_{RKS} = 0.048508 + 1.55171\omega - 0.15613\omega^2$$

$$\kappa_{PR} = 0.037464 + 1.54226\omega - 0.026992\omega^2$$

ω is an empirical constant termed the acentric factor. It is given By Reid et al. (1987) for different compounds.

These two PVT relationships can accurately describe the supercritical phase of the carbon dioxide. Valderrama (2003) has summarized the use of cubic equations of state, especially RKS EOS for supercritical fluid and mixtures. For the critical region, few contributions dealing with a suitable mathematical representation of the state based on the experimental data fitting are given in the literature. In this field, the EOS for both pure substances and mixtures are reviewed by Sengers et al. (2000) where different techniques such as the cubic equation formulation, the perturbation theory and the corresponding states are well commented. Recently, Iglesias Silva and Hall (1998) have established a more general equation for a pure substance near its critical point. Moreover, Lue and Prausnitz (1998) have developed a theory for formulating an EOS for a simple fluid mixture valid both near to and far from the critical point. They have explained that the base EOS obtained from the integral equation theory was used to compute the contribution of the short wavelength fluctuations to the free energy of the fluid mixture near its critical region. The cubic crossover EOS also yielded a satisfactory representation of the mixture properties for liquid-vapor equilibrium and beyond the critical region as noticed by Kiselev and Rainwater (1997).

Other methods based on group contributions are used to determine phase equilibrium conditions such as UNIFAC developed by Fredenslund et al. (1977), the modified UNIFAC given by Weidlich et al. (1987), and the analytical solutions of groups ASOG introduced by Tochigi et al. (1998). These methods are utilized for predicting vapor-liquid equilibrium for many systems containing polar as well as non-polar compounds. For particular substances such as polymers, a specific analytical description of state, depending on the swelling parameters, is given by Sung et al. (1998).

When equilibrium is established between the two phases, an integration of the fugacity parameter can be obtained by using the appropriate EOS. In liquid-supercritical phase equilibrium of the solute, the liquid phase fugacity is implemented directly by using a suitable saturation pressure (P^{sat}) model and an accurate approximation of the solute molar volume V^{solute}. For the solid-supercritical phase equilibrium, the solid-state solute is related to a fictitious liquid state with the intention of deducing the solid fugacity, as developed by Prausnitz et al. (1986).

$$\ln\left(\frac{f^S}{f^L}\right)=\frac{\Delta_f h_i^{\oplus}}{RT}\left(1-\frac{T_{f,i}^{\oplus}}{T}\right) \qquad (8)$$

$\Delta_f h_i^{\oplus}$ and $T_{f_i}^{\oplus}$ are the heat of fusion and the melting point temperature, respectively.

The molar volume of the solid solute is determined experimentally by weighting or from the extension of the Fedors (1974) group contributions to the crystalline state when there are no available data in the literature.

The phase equilibrium calculation for a given mixture involves both suitable EOS and mixing rules which define the EOS corrective terms (a, b) of the solution. Orbey (1994) has reviewed the mixing rules for the estimation of vapor liquid equilibrium. The most used are those of Van der Waals (VDW), where k_{ij} is the binary interaction parameter :

$$\begin{cases} b = \Sigma\, x_i b_i \\ a = \Sigma\, \Sigma\, x_i x_j a_{ij} \end{cases} \qquad (9)$$

and

$$a_{i \neq j} = \sqrt{a_i a_j}\,(1-k_{ij}) \qquad (10)$$

x_i and x_j denote mole fractions of both solvent and solute at equilibrium.

Recently, Schwartzentruber and Renon (1991) have given an additional interaction parameter l_{ij} for the Van der Waals mixing rules. The attractive term of the formed mixture is written as:

$$a = \Sigma x_i\ \Sigma x_j\ \sqrt{(a_i a_j)}\left[1-k_{ij}-l_{ij}(x_i-x_j)\right] \qquad (11)$$

Using the Gibbs excess free energy (G^{ex}) models, Huron and Vidal (1979) have developed a new class of mixing rules. In this field, Wong and Sandler (1992) have carried out a fundamental change in mixing rules by using the excess free energy concept. Recently Lee et al. (2000) carried out a comparative study on different mixing rules. They have showed a good agreement between several mixing rules when binary equilibrium measurements and calculations were compared. For a solid-supercritical fluid mixture Gonzalo et al. (2001) have successfully used the G^{ex} approach to describe the phase behavior of mixtures that involve both polar and associating fluid.

3. Solubility Optimization

The calculation of the solubility of a compound in the supercritical fluid has included both correlative and predictive approaches. Three models are well used in the literature to establish correlations for binary systems' solubility data. These models are: Chrastil (1982), Redlich Kwong and Soave (1972), and a modified Peng - Robinson introduced by Schmitt and Reid (1986).

3.1 Solubility calculation using the Chrastil approximation

For quantitative determination of the solute mole fraction in supercritical solution at equilibrium, the Chrastil method is the most widely used technique for correlating solubilities. This model is based on the postulate that, at equilibrium a solute molecule is associated with a fixed number of solvent molecules to form a solvato-complex. This model, although simple, relies much on the knowledge of the thermodynamic behavior of the supercritical solvent rather than of the solute and it is mostly capable of correlating, rather than predicting, the solubility. Other groups of researchers correlate the solubility by using equations of state. It relies on the common characteristic that a log-log plot of the solubility versus supercritical fluid density is often a straight line at a given temperature.

The Chrastil empirical relation is as follows:

$$y_2 = \rho_1^k \exp\left(\frac{a}{T}+b\right) \qquad (12)$$

where y_2 is the solute solubility (mol/mol), ρ_1 is the supercritical fluid density and *a, b* and *k* are empirical fitting parameters. Calculating the solubility using Chrastil relation involves the determination of the supercritical fluid density for the temperature and pressure of interest and then solving equation (12). It may be applied to all cases because it does not require any physical-chemical property data for the solute; whereas the fitting of three parameters *a*, *b* and *k* at each solution is one of the disadvantages of this technique.

3.2 Solubility calculation using a cubic EOS and mixing rules

The fitting aspect bases on the molecular interaction coefficient as the adjustable solute parameter. The solute properties necessary to effectively correlate solubilities based on the modified Peng - Robinson approach of RKS EOS include the molar volume and the saturated vapor pressure (as a function of temperature).

The prediction of solubility using the chosen EOS model assumes that the solute phase remains pure. This assumption is thought to be quite reasonable for solid solutes. However, in the case of liquid solutes, it is likely that carbon dioxide will dissolve into the liquid solute at the same time as the liquid is dissolving in the supercritical carbon dioxide. Indeed, McHugh and Krukonis (1994) provide the necessary equations to handle these phase equilibrium of the liquid solute within the supercritical fluid.

The solubility can be expressed by equating fugacity terms of the solute (2) at each state. Using equation (3), the solute solubility is written as:

$$\psi_2 = \frac{\Pi_2^{\sigma\alpha\tau}\varphi_2^{\sigma\alpha\tau}}{\varphi_2^{\Sigma\Phi}\Pi}\varepsilon\xi\pi\left(\frac{\varsigma_2^{\sigma}\left(\Pi-\Pi_2^{\sigma\alpha\tau}\right)}{\mathrm{PT}}\right) \quad (13)$$

where φ_2^{sat} and φ_2^{SF} are the fugacity coefficients of the saturated pure vapor and the supercritical state of the solute, respectively. The coefficient φ_2^{sat} is equal to 1, and the second one is calculated using the chosen EOS.

3.2.1 Vapor pressure model

The knowledge of the vapor pressure of the solute P_2^{sat} is also an essential step in the calculation of solubility. If the P_2^{sat} model is not available as a function of temperature, it is still possible to attempt to fit the solubility data, but the quality of fitting is likely to be poor.

Indeed, several works yield accurate vapor pressure from the triple point up to the critical point. Rogalski et al. (1990) give adequate representations of both the saturated vapor pressure expression and the molar volume estimation for different ranges of operating conditions. Using mathematical relationships of vapor tension given in the literature depends highly on the state of the solute state at ambient conditions. Generally, these equations are based on the Clausuis - Clapeyron model where vapor pressure, $P^{\mathrm{sat},}$ is given as a logarithmic function of the temperature:

$$\mathrm{Log}_{10}\left(\mathrm{P}^{\mathrm{sat}}\right) = \mathrm{A} - \mathrm{B/T} \quad (14)$$

A and B are two constants depending on the molecular structure of the solute.

In a few cases careful extensions of the vapor liquid curve can be applied to describe sublimation phenomena. In this case, we can assume that the slope of the sublimation curve is very close to that of the vaporization one.

3.2.2 k_{ij} optimization

As can be seen, the EOS corrective coefficients (a, b) require the interaction parameters for phase behavior description. Many papers, such as Gourguillon and da Ponte (1999) and Bartle et al. (1992), have given averaged values of this binary interaction. They have used numerous couples of supercritical solvent and solute presented in the literature, and then by linear fitting, Bartle et al. have obtained an empirical correlation for the binary interaction factor *(Figure 4)*:

$$k_{ij} = 0.51\,\mathrm{B} \quad (15)$$

where *B* is a function of different physical properties of the solution such as critical coordinates, molecular polarity, weight… Nevertheless, *Figure 4* shows several points far from the drawn linear correlation (15). We notice that this assumption is valid just for a few kinds of solutes and cannot be extended for large application domains.

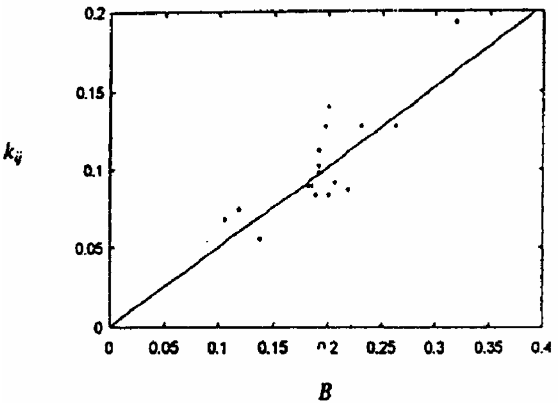

Figure 4. The Bartle et al. correlation of the binary interaction parameter

Moreover, binary interaction correlations are introduced considering the effects of both the compound nature and the operating parameters. Anlkeev et al. (1998) have estimated the binary interaction for the vapor liquid equilibrium mixture by using the Redlich Kwong Soave equation of state . Both temperature and pressure effects on the binary interaction factor are shown. For supercritical solution at equilibrium, this parameter is fitted numerically from experimental solubility data by Ksibi (1999).

The numerical calculation of this parameter is based on the modified Peng - Robinson EOS and the Van der Waals (VDW) mixing rules. The “golden section search” optimization technique is suitable to determine the interaction parameter k_{ij} by a number of iterations. Indeed, it is shown as a function of characteristic parameters of the mixture and the temperature. This empirical relation is written as:

$$k_{ij} = c_1 e^{-T/T_c} + c_2 \quad (16)$$

where c_1 and c_2 are two additive constants depending on solute and solvent characteristics, and T_c is the critical temperature of the carbon dioxide.

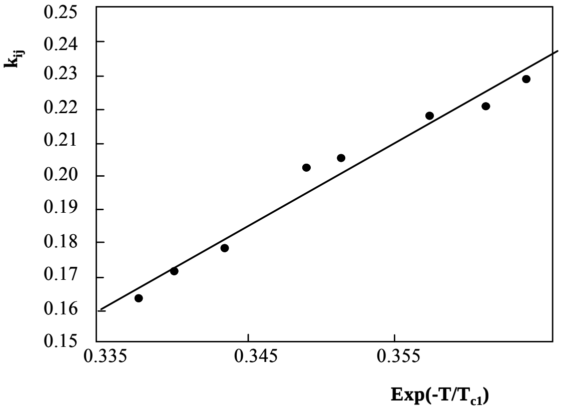

Figure 5. k_{ij} as a function of the temperature for the salicylic acid/carbon dioxide system (• experimental data; ___ fitting line).

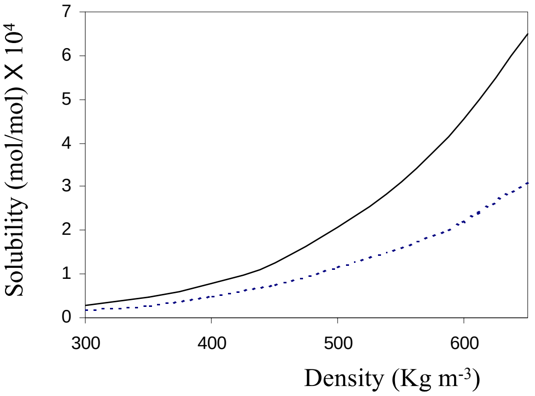

Figure 6. The calculated caffeine solubility in supercritical carbon dioxide as a function of density at 350 K.[_____k_{ij} = 0.205 , --------- k_{ij} from relation (16)].

The supercritical solution of salicylic acid and carbon dioxide at equilibrium is studied numerically by using the RKS EOS coupled with VDW mixing rules. The obtained k_{ij} values from experimental data are shown in *Figure (5).* The solid line depicts the empirical relation (16). Therefore, a good agreement with solubility measurements can be noticed and averaged relative deviation of experimental points is less than 10%.

To show the importance of an accurate representation of the binary interaction, we have calculated the solubility of caffeine in supercritical CO_2 at equilibrium with two k_{ij} assumptions for the same isotherm (340K). First, solubility values are obtained by using the k_{ij} empirical correlation (16), and secondly, they are estimated with an averaged value of the binary interaction parameter (k_{ij}=0.205). These calculations are performed by using the modified Peng - Robinson EOS and the conventional mixing rules. *Figure 6* shows a significant difference between the two model graphs where caffeine solubility is drawn as a function of the carbon dioxide density. Here we note that at high density, the estimated solubility value is strongly altered by the k_{ij} model and error increases enormously.

By using the binary interaction coefficient relationship (16), the solubility of salicylic acid in supercritical carbon dioxide is calculated as a function of the pressure. The thermodynamic description is based on the Peng - Robinson EOS and the Van der Waals mixing rules. *Figure 7* shows the mole fraction for the isotherm (330K) at different pressures. The numerical fitting used the experimental data given by Reverchon and Donsi (1993). A good agreement of the calculated solubility is noticed when it is compared with the experimental value at the same pressure and temperature.

Similarly, the solubility calculation of tri-ethylene glycol in supercritical carbon dioxide is performed with the k_{ij} parameter optimization, Ksibi (1999b). Here the RKS equation of state and the conventional mixing rules are used to calculate the mole fraction. An accurate fitting of the tri-ethylene glycol solubility data for the isotherm 333K is obtained, *Figure 8.*

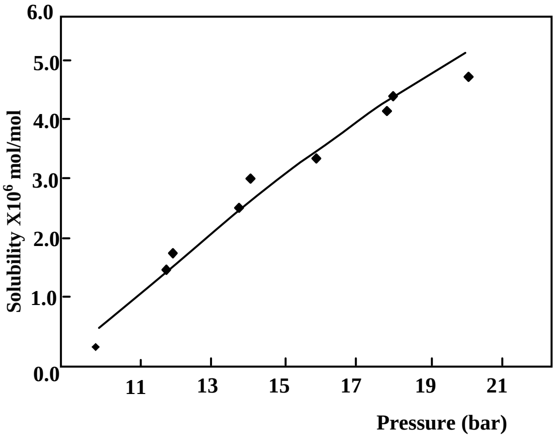

Figure 7. Solubility of salicyclic acid in supercritical carbon dioxide at 330K; Comparison between the experimental points and the curve calculated with adjusted parameters

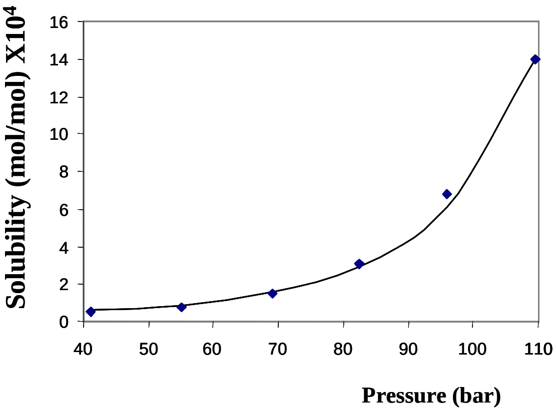

Figure 8. Solubility of Tri-ethylene glycol in supercritical CO2 at 333 K. Comparison between experimental values (squares) and calculated values (the continuous curve)

Sometimes for a complex solute molecule both critical and binary interaction parameters are unknown. Nevertheless, we find in the literature a few measurable data such as the burning temperature, density. The critical coordinates and k_{ij} are computed by optimization techniques and comparison at each iteration with the experimental solubility values. When critical pressure of the solute is obtained, both the Lee Kesler and the Joback group contribution methods (Reid et al. 1987) are used to determine the critical temperature, the critical volume and the acentric factor. This calculation is implemented for the β-carotene - supercritical carbon dioxide system by Subra et al. (1997), see *Figure 9*. The solubility is drawn as a function of carbon dioxide density for four isotherms. The obtained results show a good agreement of calculated and experimental solubilities at different ranges of temperature and pressure.

In some papers, extrapolations were done towards elevated temperatures and modeling and optimized parameters from experiments. Indeed, Ksibi et al. (1995) have used caffeine solubility extrapolation for the rapid expansion of supercritical solution (RESS) process modeling. In *Figure 10*, the caffeine solubility is shown as a function of the supercritical density for a wide range of temperatures. The solubility curves are obtained from numerical computations.

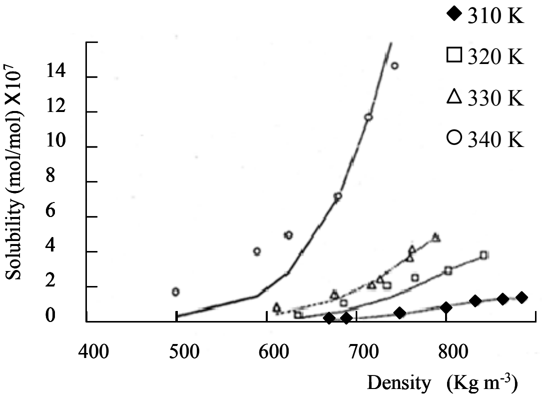

Figure 9. Isothermal network of β-carotene solubility in carbon dioxide. Comparison between the experimental and the calculated values.

Careful extrapolations, especially at constant temperature can be used for quantitative purposes, but mostly extrapolations yield qualitative results and sometimes incorrect values.

Shyu et al. (1997) gave a new procedure to obtain an interaction parameter by relating it to experimental Cross-second Virial Coefficients with the Wong Sandler mixing rules for water supercritical carbon dioxide equilibrium, Huron and Vidal (1979). For a multicomponent system, Jaubert and Coniglio (1999) used the Abdoul's group contribution method to predict the binary interaction for the excess Gibbs energy model. Nevertheless, the interaction parameter correlation can be canceled by using the Monte Carlo phase equilibrium simulation techniques as explained by Errington et al. (1998).

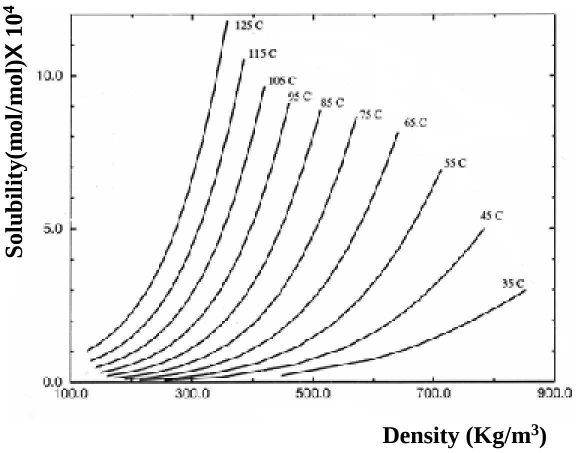

Figure 10. Solubility of caffeine in super-critical carbon dioxide. Extrapolation at elevated temperature domain

3.3 Solubility error control

Due to the fact that the optimization technique relies on the solubility parameters generated from experimental data, the quality control has focused on the binary experimental solubilities. The quality control areas of concern fall into one of three categories: solubility data entry errors; errors generated by the EOS model; and quality of fit.

To ensure that the experimental data used to generate the solubility parameters are of high quality, the chosen isotherm is systematically compared with the others given in the literature. Once these data have been verified, the solubility code first determines the density of carbon dioxide at the given temperature and pressure. This density is then used to correlate and predict various solubilities.

The performance of the correlations is quantified by an absolute average relative deviation (AARD). The AARD approach is the most widely used assessment for evaluating the success of the numerical model. An AARD is calculated according to equation (17):

$$\text{AARD}\ (\%) = \frac{1}{N}\left|\Sigma\ \frac{y_e - y_c}{y_e}\right| 100 \qquad (17)$$

where y_c and y_e denote the calculated and the experimental solubilities, respectively.

In many papers dealing with the solubility estimation, the squared absolute average relative deviation (SAARD) is also used as a criterion of fitting convergence and minimizing generated error technique. It is expressed as follows:

$$\mathrm{SAARD}(\%) \;=\; \frac{1}{N}\sum\left|\frac{y_e - y_c}{y_e}\right|^2 100 \quad (18)$$

The performance of the binary predictions is quantified by another way of evaluating errors called the absolute average factor out (AAFO). An AAFO is calculated as written:

$$\mathrm{AAFO} = \frac{1}{N}\left(\sum_{ye<yc}\frac{y_c}{y_e} + \sum_{ye<yc}\frac{y_e}{y_c}\right) \quad (19)$$

The AAFO approach assesses overestimation and underestimation equally.

4. Solubility Measurements and Apparatus

Phase equilibrium measurements are performed by determining intensive variables: the temperature, the pressure and the composition of all phases under thermodynamic equilibrium conditions. Depending on the substance nature (complex and heavy molecule, low volatile…), results of phase equilibrium experiments are required. Therefore an accurate experimental method for solubility measuring should be chosen. There are in the literature a few methods used at elevated pressure by several authors, e.g. Christov and Dohrn (2002).

Static methods comprise all experimental techniques where the analyzed mixture is placed within a closed volume (autoclave) and equilibrium is established by waiting until equilibrium conditions are reached. The apparatus for phase equilibrium measurements by the static analytical method is described by several authors such as Takenouchi et al.(1964), and Maier et al. (1984). The apparatus consists essentially of pressure resistant cell installations for temperature control and equipment for removing and analyzing samples of the phases.

The synthetic method is very convenient for determining binary phase equilibrium and phase boundary envelopes in a multi component system. Several authors have described in more detail their apparatus, such as Lentz (1969), Schroder and Arndt (1976), and Crampon et al.(1999). Simply, the apparatus consists of a thermostatic cell with windows for viewing the inner cell. A stirrer mixes its content, and its volume can be very small, typically in the range of few ccs, since no samples are removed. For determining measurements, the pressure is varied at constant temperature (or temperature at constant pressure), until the appearance or disappearance of the phase. The phase transition can be detected by viewing the inner part or by monitoring physical properties of the mixture that change markedly when a phase appears or disappears.

The dynamic method has been used by several researchers, such as Van Leer et al. (1980) and Kurnik et al. (1982). The condensed phase remains in the equilibrium cell, while the gaseous phase flows through it. During residence time of the gaseous phase in the autoclave, the equilibrium concentration is established in the gas as well as in the condensed phase. The equilibrated gaseous phase is withdrawn from the cell and analyzed. A certain version of this method was given by Brunner (1994). He explained that dynamic methods are best applicable to the binary systems, since in a multi component system, due to the different equilibrium solubility in supercritical fluid, the composition of the condensed phase can change. Brunner added that the static analytical method, carried out with an equilibrium cell of around 1000 cc, is a method covering most of the needs of acquiring basic data. However, this method has serious limitations when the critical region is reached and when we have small concentrations without chromatographic analyzing techniques. The synthetic method, uses a relatively simple set up, and phase equilibrium can be detected easily in more than two phase's studies. Recently, Schneider (1998) reviewed experimental high-pressure investigations on fluid-fluid, solid-fluid, near critical region, and liquid-liquid phase equilibrium obtained from different experimental methods. Other special methods are given in the literature, where authors have deduced phase equilibrium by measuring other physical properties of compounds as dielectric constants, Hourri et al. (1998). Accuracy of solubility measurements depends strongly on the method used and the concentration level of different components at equilibrium. For analyzing in most cases, chromatographic methods are applied and accuracy is at best 2%, Brunner (1994).

5. Supercritical Industrial Applications

Industrial applications of supercritical solvents have been known since the beginning of the 20th century. In 1936, Wilson et al. (1936) devised a process for phase equilibrium separation. It became the basis for the propane de-asphalting process still in use today for refining lubrication oils. Many years ago, Dickinson and Meyers (1952) used propane as a selective solvent for purification and separation of vegetable and fish oils. In the last fifty years, many supercritical phase equilibrium applications have been developed essentially in food and pharmaceutical industrial fields. For several powder formation processes the phase equilibrium knowledge allows an adequate choice of operating conditions, i.e. pressure, temperature and the compound concentrations. Indeed, the rapid expansion of supercritical solution (RESS) (Matson et al. (1987), Ksibi et al. (1995), and Liu and Nagahama (1997)), the supercritical anti-solvent (SAS) (Dixon et al.(1993); Berends et al. (1996)), and the particles from gas saturated solutions (PGSS) (Weidner et al. (1994)) are processes where fine particles formation depends strongly on the solute solubility in the supercritical solvent at equilibrium.

The supercritical extraction process of essential oils is one of the potential applications of phase equilibrium. Reverchon (1997) reviewed solubilities of several compounds belonging to essential oils and discussed processes for isolating and fractionating these substances from natural matrices. In the field of food industry, DelValle et al. (1999) described coffee decaffeination, extraction and fractionation of edible fats and oils, concentration of fermentation broth and other extracts with supercritical carbon dioxide.

Concerning the phase equilibrium of the polymer-supercritical carbon dioxide system, much research dealing with both experimental and modeling aspects has been published. As an example, the supercritical carbon dioxide has been used to fractionate polydimethylsiloxane (PDMS), polycarbosilane (PCS), and polystyrene (PS) polymers, Kim et al. (1998).

Some relevant applications have also been developed by using the phase equilibrium properties of binary, ternary and complex mixtures, such as the substitution of HFC (134a) by supercritical carbon dioxide by Abbott et al. (1999), and the heavy metal ions supercritical extraction obtained via binding the metal ions to an appropriate ligand as shown by Laintz et al. (1992).

6. Conclusions

Phase equilibrium in supercritical region is investigated from theoretical and experimental points of view. Phase equilibrium diagrams are briefly reviewed by giving different plots for binary mixtures. Concerning modeling, an accurate determination of the phase behavior at equilibrium needs a suitable choice of an EOS, mixing rules, an accurate correlation of the interaction coefficients, and a saturated vapor pressure model. Experimental methods of phase equilibrium are briefly explained by comparing different apparatuses where their use is strongly related to the operating pressure and temperature levels and the solute nature. Finally, direct applications of phase equilibrium are detailed. Indeed, industrial factors such as the rate of production, the upper pressure and the temperature of the installation are evaluated by apprehending phase equilibrium of supercritical solutions.

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