Screening of Cosolvents for a Supercritical Fluid: A Fully Predictive Approach

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Solubility of solids was modeled in modified supercritical carbon dioxide as a predictive method. The Peng-Robinson equation of state was used to characterize the ternary systems using the one-fluid van der Waals rules. Ternary mixture parameters k_{12}, k_{23}, and k_{13} were obtained from the binary mixtures using Wong-Sandler mixing rules or the linear combination of Vidal-Michelsen mixing rules together with UNIFAC as required as a fully predictive tool for the liquid activity coefficients. When this method was applied to predict the solubility of β-naphthol in CO_2 modified with 6% and 10% toluene, values for the predicted solubility were very similar to the measured ones, with deviations of 9.6 and 26.3%, respectively. However, when the method was applied to the data of Simon et al. who examined six common cosolvents, the results were not as good in absolute terms, but the solvents were sorted in about the same order as found experimentally. The method provides quite an approximate guide to judge the most effective cosolvent from several candidates using a fully predictive methodology.

Introduction

Knowledge of solubility is essential for the design of separation processes such as extraction or leaching with a supercritical solvent. Solubility data are also required in the design of the extract recovery and purification operations. The solubilities of solids and liquids in supercritical fluids can be calculated by the use of cubic equations of state for mixtures with empirically-fitted binary interaction coefficients appearing in the mixing rules for the energy parameters *a* and *b*. Correlation of the binary interaction parameter has been attempted, for example, by Hederer et al. (1976) with the Soave-Redlich-Kwong EoS (Soave, 1972; Brunner, 1994). In the last 20 years, emphasis has been placed (Vidal, 1978) on the use of the excess Gibbs energy models in the attractive term parameter of the cubic equations-of-state, or the so-called g^E/EoS models. In this direction, significant advances were made by Michelsen (1990b), Wong and Sandler (1992), Tassios and co-workers (Boukouvalas et al., 1994), among others (Yakoumis et al., 1996). The interesting point in this approach is that it allows a group-contribution method such as UNIFAC (Fredenslund et al., 1975) to be used in the calculation of the activity coefficients, and the excess Gibbs energy of the high density phase as a function of composition. This is very important since the EoS/g^E model, together with UNIFAC, has become fully predictive (Orbey and Sandler, 1998).

In the extraction with SC solvents, carbon dioxide is the fluid of choice for a number of engineering, safety, and economic reasons. However, the low polarity of carbon dioxide limits its use whenever a solute with very different polarity is treated. In that case very high operating pressures would be required. A so-called entrainer, or modifier, is used in such cases. A practical advantage of a modifier is that in some cases the operating pressure can be reduced (as reported in one case examined by Abaroudi et al. (1999) and Eychenne et al. (2001). In other cases, a remarkable solubility enhancement can be achieved for small cosolvent concentrations (5%). Several authors have attempted to correlate the solubility of a solute in modified carbon dioxide using either empirical methods (Sunol et al., 1985; Anitescu and Tavlarides, 1999; Sovová et al., 1999), or generalized equations of state such as the Soave-Redlich-Kwong (SRK) (Soave, 1972), and others (Peng and Robinson, 1976; Simon et al., 1993; Dobbs et al., 1987). See Brennecke and Eckert (1989) for a review. The hard sphere-van der Waals (Dobbs et al., 1987; Trabelsi et al., 1999), and the Sánchez-Lacombe lattice theory (West et al., 1998) are among the methods to characterize such solubility, as well as the Scatchard-Hildebrand regular solution and the Flory-Huggins theories considering a supercritical phase like the liquid phase (Gurdial et al., 1993).

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Very few authors have attempted prediction of solubility of a solid in a modified supercritical fluid as a ternary system (Sunol et al., 1985). Using the PR-EoS with the one-fluid mixing rules, Macnaughton et al. (1994) have taken two of the three binary interaction coefficients from the literature, and the third coefficient was calculated from Henry's constant of the solvent in the solute as determined from chromatography. This is extremely important because it would reduce the prediction of solubility to the indirect measurement of using only a Henry constant by low-pressure gas-liquid chromatography. To our knowledge, only Jaubert and Coniglio (1999a, b) used the group-contribution theory alone for the estimation of phase diagrams for binary, ternary, and quaternary systems in which SC carbon dioxide was one of the components in dew-point and bubble-point calculations. Their results are most encouraging.

In this work, we attempt to predict the solubility of a solid in carbon dioxide modified with toluene, making use of the three separate binary data, that is, from the CO_2-liquid system, the CO_2-solid system, and the solid-liquid system, each characterized with the predictive EoS method. The results of the calculations are applied to sorting the best entrainer from a list of candidates for dissolving Naproxen as reported by Simon et al. (1993), as a check of our theory with their data.

Phase Equilibrium Considerations

In this work, the following components were considered: The fluid solvent (carbon dioxide in our case) = component 1; the cosolvent = component 2 (usually a liquid at ambient conditions); and the solute = component 3 (usually a solid at ambient conditions). These components are assumed to be in the SC phase, in equilibrium with the solid. Further, it is assumed that neither the fluid solvent nor the cosolvent dissolves in the solid. In other words, the solid phase is pure component 3 in equilibrium with a supercritical phase.

Imposing the equifugacity condition to this problem, the solubility y_3 in the SCF phase is obtained as (Prausnitz et al., 1999)

$$y_3 = \frac{P_3^{\text{sat}} \exp \int_{P_3^{\text{sat}}}^{P} \frac{V_3^s}{RT} dP}{P\phi_3} \tag{1}$$

in which the nonidealities of the fluid phase, due to high pressure, are included. The fugacity factor appearing in the denominator can be calculated from an equation of state for the mixture. Since the value of ϕ_3 can change from 10^{-3} to 10^{-6}, this is an important factor in the solubility enhancement. Other factors affecting solubility in a supercritical fluid are seen in Eq. 1. Using the PR-EoS with the classical mixing rules, there are enough equations to determine ϕ_3 as a function of y_3, and solve for y_3. The necessary equations for the Peng-Robinson case are as follows

$$P = \frac{RT}{v - b_{\text{mix}}} - \frac{a_{\text{mix}}(T)}{v(v + b_{\text{mix}}) + b_{\text{mix}}(v - b_{\text{mix}})} \tag{2a}$$

where a_{mix} and b_{mix} are, respectively, the energy parameter and the size parameter for the mixture. These are calculated from pure fluid data using the one-fluid van der Waals hypothesis with the following mixing rules as (McHugh and Krukonis, 1994)

$$a_{\text{mix}} = \sum_{i=1}^{3} \sum_{j=1}^{3} y_i y_j a_{ij} \tag{2b}$$

$$a_{ij} = (1 - k_{ij}) \sqrt{a_i a_j} \tag{2c}$$

where the pure component values are those specified by the PR-EOS equations as (Reid, 1981; McHugh and Krukonis, 1994)

$$b_i = 0.0778 \left(\frac{RT_{ci}}{P_{ci}} \right) \tag{3a}$$

$$a_i(T) = a(T_{ci}) \alpha(T_{Ri}, \omega_i) \tag{3b}$$

$$a(T_{ci}) = 0.45724 \frac{R^2 T_{ci}^2}{P_{ci}} \tag{3c}$$

$$\alpha(T_{Ri}, \omega_i) = \left[1 + m_i \left(1 - \sqrt{T_{Ri}} \right) \right]^2 \tag{3d}$$

$$m_i = 0.37464 + 1.54226 \omega_i - 0.26992 \omega_i^2 \tag{3e}$$

Equation 2c involves a binary interaction parameter k_{ij} that is usually calculated either by fitting experimental phase-equilibrum data, or with data generated with a completely predictive method. The latter approach is used here.

The co-volume for the mixture b_{mix} is calculated with the parameter η_{ij}.

$$b_{\text{mix}} = \sum_{i=1}^{3} \sum_{j=1}^{3} y_i y_j b_{ij} \tag{4a}$$

$$b_{ij} = \frac{(b_i + b_j)}{2} (1 - \eta_{ij}) \tag{4b}$$

This is usually set to zero, $\eta_{ij} = 0$ (Vidal, 1978; McHugh and Krukonis, 1994), as k_{ij} is sufficiently sensitive.

The expression for the fugacity coefficient in terms of the composition of the fluid phase is as follows

$$\ln \phi_3 = \frac{b_3^*}{b_{\text{mix}}} (z_g - 1) - \ln(z_g - B) - \frac{A}{2.828B} \left(\frac{2 \sum_{j=1}^{3} y_j a_{3j}}{a_{\text{mix}}} - \frac{b_3^*}{b_{\text{mix}}} \right) \ln \left(\frac{z_g - 2.414B}{z_g - 0.414B} \right) \tag{5a}$$

where A, B and b^* can be calculated from the following equations

$$A = \frac{a_{\text{mix}} P}{R^2 T^2} \tag{5b}$$

$$B = \frac{b_{\text{mix}} P}{RT} \tag{5c}$$

$$b_3^* = 2 \sum_{j=1}^{3} y_j b_{3j} - b_{\text{mix}} \tag{5d}$$

To predict the solubility of a solid in a modified supercritical fluid, it is necessary to predict the mixture parameters. In what follows we describe how these can be calculated from the three binary pair systems and the type of models used to do that.

Solid solute-compressed gas equilibrium

We first predict the solubility of the solid in pure, compressed gaseous CO_2 using the equation of state of Peng-Robinson with two mixing rules: the linear combination of Vidal and Michelsen rules (LCVM) and that of Wong and Sandler (WS), together with the UNIFAC method to calculate the activity coefficients of a dense (liquid) phase. Once information on the liquid phase is available, estimation of the fluid phase fugacity coefficients (Smith et al., 1996), is possible. Secondly, the binary interaction parameter (k_{13}) is found by fitting the solubility data predicted from UNIFAC with the Peng-Robinson equation with the classical mixing rules. The LCVM and the Wong-Sandler mixing rules are as follows:

The LCVM Mixing Rules. In the development of these rules, the energy parameter of the equation of state a_{mix} is written in terms of the excess free energy. In this method there is linear combination of the Vidal and the Michelsen rules through proper weights λ and $1-\lambda$. Thus

$$\alpha = \lambda\alpha_V + (1-\lambda)\alpha_M \tag{6a}$$

$$\alpha_V = \frac{1}{A_V}\frac{g^E}{RT} + \sum_i y_i\alpha_i \tag{6b}$$

$$\alpha_M = \frac{1}{A_M}\left[\frac{g^E}{RT} + \sum_i y_i \ln\frac{b_{\text{mix}}}{b_i}\right] + \sum_i y_i\alpha_i \tag{6c}$$

in which α_V and α_M are the original expressions proposed by Boukouvalas et al. (1994). The resulting expression for α is

$$\alpha = \left(\frac{\lambda}{A_V} + \frac{1-\lambda}{A_M}\right)\frac{g^E}{RT} + \frac{1-\lambda}{A_M}\left(y_1\ln\left(\frac{b_{\text{mix}}}{b_1}\right) + y_3\ln\left(\frac{b_{\text{mix}}}{b_3}\right)\right) + \sum_{i=1}^{n} y_i\alpha_i \tag{6d}$$

where

$$\alpha_i = \frac{a_i}{b_i RT} \tag{6e}$$

The other equations are

$$b_{\text{mix}} = \Sigma y_i b_i \tag{6d}$$

$$a_{\text{mix}} = \alpha b_{\text{mix}} RT \tag{6e}$$

When the Peng-Robinson equation of state is used as the EoS, then $\lambda = 0.36$, $A_V = -0.623$ (Vidal, 1978), and $A_M = -0.53$ (Michelsen, 1990b). Then, the analytical expression for the fugacity coefficient in the fluid phase is obtained after integration as

$$\ln\phi_3 = \frac{b_3}{b_{\text{mix}}}\left(z_g - 1\right) - \ln\frac{P(v - b_{\text{mix}})}{RT} - \frac{\bar{\alpha}_3}{2\sqrt{2}}\ln\left[\frac{v + \left(1+\sqrt{2}\right)b_{\text{mix}}}{v + \left(1-\sqrt{2}\right)b_{\text{mix}}}\right] \tag{7a}$$

$$\bar{\alpha}_3 = \left(\frac{\lambda}{A_V} + \frac{1-\lambda}{A_M}\right)\ln\gamma_3 + \frac{1-\lambda}{A_M}\left(\ln\frac{b_{\text{mix}}}{b_3} + \frac{b_3}{b_{\text{mix}}} - 1\right) + \alpha_3 \tag{7b}$$

where γ_3 is estimated from UNIFAC group-contribution method (Fredenslund et al., 1975) and α_3 defined by Eq. 6c for $i = 3$.

The Wong-Sandler Mixing Rules. In this case, the energy parameter (Eq. 8a) and the co-volume (Eq. 8b) for the mixture are written in terms of the excess Gibbs free energy. One mixing rule stems from the limiting behavior at low pressure where the difference *b-a/RT* should be directly related to the second virial coefficient. The other mixing rule refers to the limit of the Helmholtz energy function at high density (or infinite pressure). The resulting equations are (Sandler, 1999)

$$b_{\text{mix}} = \frac{Q}{(1-D)} \tag{8a}$$

$$\frac{a_{\text{mix}}}{RT} = Q\frac{D}{(1-D)} \tag{8b}$$

$$Q = b_{\text{mix}} - \frac{a_{\text{mix}}}{RT} = \sum_{i=1}^{3}\sum_{j=1}^{3} y_i y_j\left(b_i - \frac{a_i}{RT}\right) \tag{8c}$$

$$\left(b - \frac{a}{RT}\right)_{13} = \frac{1}{2}(b_1 + b_3) - \frac{\sqrt{a_1 a_3}}{RT}(1 - s_{13}) \tag{8d}$$

$$D = \frac{a}{bRT} = \frac{a_\infty^E}{CRT} + \frac{y_1 a_1}{b_1 RT} + \frac{y_3 a_3}{b_3 RT} \tag{8e}$$

$$C = \frac{1}{\sqrt{2}}\ln\left(\sqrt{2} - 1\right) \tag{8f}$$

In view of the second hypothesis

$$g^E(T,x,P\to 0) = a^E(T,x,P\to 0) = a^E(T,x,P\to\infty) \tag{9}$$

where,

$$g^E = RT(y_1\ln\gamma_1 + y_3\ln\gamma_3) \tag{10}$$

and

$$\frac{a_\infty^E}{RT} = y_1\ln\gamma_1 + y_3\ln\gamma_3 \tag{11}$$

The corresponding expression for the fugacity coefficient is

$$\ln\phi_3 = -\ln\left[\frac{P(v-b_{\text{mix}})}{RT}\right] + \frac{1}{b}\left(\frac{\partial nb_{\text{mix}}}{\partial n_3}\right)(z_g - 1) + \frac{1}{2\sqrt{2}}\left(\frac{a_{\text{mix}}}{b_{\text{mix}}RT}\right)\left[\frac{1}{a_{\text{mix}}}\left(\frac{1}{n}\frac{\partial n^2 a_{\text{mix}}}{\partial n_3}\right) - \frac{1}{b_{\text{mix}}}\left(\frac{\partial nb_{\text{mix}}}{\partial n_3}\right)\right]\ln\left[\frac{v + b_{\text{mix}}(1-\sqrt{2})}{v + b_{\text{mix}}(1+\sqrt{2})}\right] \quad (12)$$

Where the partial derivatives are known (Sandler, 1999), as

$$\frac{\partial nb_{\text{mix}}}{\partial n_3} = \frac{1}{(1-D)}\left(\frac{1}{n}\frac{\partial n^2 Q}{\partial n_3}\right) - \frac{Q}{(1-D)^2}\left(1 - \frac{\partial nD}{\partial n_3}\right) \quad (13a)$$

$$\frac{1}{RT}\left(\frac{1}{n}\frac{\partial n^2 a_{\text{mix}}}{\partial n_3}\right) = D\frac{\partial nb_{\text{mix}}}{\partial n_3} + b_{\text{mix}}\frac{\partial nD}{\partial n_3} \quad (13b)$$

$$\frac{1}{n}\frac{\partial n^2 Q}{\partial n_3} = 2\left(y_1\left(b_{\text{mix}} - \frac{a_{\text{mix}}}{RT}\right)_{13} + y_3\left(b_3 - \frac{a_3}{RT}\right)\right) \quad (13c)$$

$$\frac{\partial D}{\partial n_3} = \frac{a_3}{b_3 RT} + \frac{\ln\gamma_3^{\infty}}{C} \quad (13d)$$

In these equations, γ_1 and γ_3 are calculated from the UNIFAC group-contribution method. In order to have a predictive method, the binary interaction parameter for the Wong-Sandler mixing rules, s_{13}, is set to zero as suggested by Orbey and Sandler (1998). Alternatively, this can be estimated by the methodology proposed by Smith et al. (1996).

Liquid solvent-compressed gas equilibrium

A treatment of the equilibrium similar to the pure solid/compressed gas case is carried out (except that in the presence of a liquid phase, there is a large fraction of dissolved fluid in the liquid). The solubility of carbon dioxide in the liquid depends on the molar partial volume of CO_2 in the liquid phase, the Henry constant for CO_2 dissolving in the liquid, the fugacity coefficient of CO_2 in the vapor phase, and the mol fraction of CO_2 in the vapor phase. The equilibrium mol fractions (Prausnitz et al., 1999) in the SCF and in the liquid, are

$$y_2 = \frac{(1-x_1)P_2^{\text{sat}}\phi_2^{\text{sat}}\exp\left(\int_{P_2^{\text{sat}}}^{P}\frac{v_2^L dP}{RT}\right)}{\phi_2 P} \quad (14a)$$

$$x_1 = \frac{(1-y_2)\phi_1 P}{H_{1,2}\exp\left(\int_{P_2^{\text{sat}}}^{P}\frac{\bar{v}_1^{\infty} dP}{RT}\right)} \quad (14b)$$

ϕ_2^{sat} is assumed to be unity.

The fugacity coefficient ϕ_1 in the last equation is estimated letting $x_2 = 0$ and $x_1 = 1$, as

$$\ln\phi_1 = (z_g - 1) - \ln(z_g - B) - \frac{A}{2B\sqrt{2}}\ln\left(\frac{z_g + (1+\sqrt{2})B}{z_g - (1-\sqrt{2})B}\right) \quad (15)$$

where z_g is solved from the polynomial

$$(z_g)^3 + (B-1)(z_g)^2 + (A - 3B^2 - 2B)z_g - (AB - B^2 - B^3) = 0 \quad (16a)$$

$$A = \frac{a_1 P}{R^2 T^2} \quad (16b)$$

$$B = \frac{b_1 P}{RT} \quad (16c)$$

The partial molar volume of CO_2 in the liquid phase (Eq. 15a) is obtained from the PR-EOS (Recasens et al., 1993)

$$\bar{v}_1^{\infty} = \left|\frac{-\left(\frac{\partial P}{\partial n_1}\right)_{v,T,n_i\neq 1}}{\left(\frac{\partial P}{\partial v}\right)_{T,n_i}}\right|_{n_1\approx 0} \quad (17a)$$

$$\left(\frac{\partial P}{\partial n_1}\right)_{v,T,n_i\neq 1,n_1=0} = \frac{RT}{(v_2^L - b_2)} + \frac{b_1 RT}{(v_2^L - b_2)^2} - \frac{a_0}{\left[(v_2^L)^2 + 2b_2 v_2^L - (b_2)\right]^2} + \frac{2a_2 b_1(v_2 - b_2)}{\left[(v_2^L)^2 + 2b_2 v_2^L - (b_2)^2\right]} \quad (17b)$$

$$\left(\frac{\partial P}{\partial V}\right)_{T,n_i} = \frac{-RT}{(v_2^L - b_2)^2} + \frac{2a_2(v_2^L + b_2)}{\left[v_2^L + 2b_2 v_2^L - (b_2)^2\right]^2} \quad (17c)$$

The Henry constant for CO_2 dissolving in the liquid is found as follows. First, the fugacity of CO_2 as a liquid at temperature T and 1 atm is calculated from the Prausnitz and Shair correlation (Prausnitz and Shair, 1961), with the parameters of the fitting equation given by Antunes and Tassios (1983). Then, the fugacity is updated from pressure $P = 1$ atm to the actual pressure P, using the Poynting correction factor. The required equations are

$$f_1^L(P = 1\text{ atm}) = (P_{c_1})\exp\left[A_0 + A_1\left(\frac{T}{T_{c_1}}\right) + A_2\left(\frac{T}{T_{c_1}}\right) + A_3\left(\frac{T}{T_{c_1}}\right)^2 + A_4\left(\frac{T}{T_{c_1}}\right)^3\right] \quad (18a)$$

$$f_1^L(P,T) = f_1^L(P = 1.013\,\text{bar}, T)\exp\left[\frac{v_1^L(P - 1.013)}{RT}\right] \quad (18b)$$

Finally, the Henry constant for CO_2 is calculated using the equation relating the activity coefficient with the Henry's law coefficient, in the following way

$$H_{1,2}(T,P) = f_1^L(T,P)\gamma_1(T,P) \tag{19}$$

where the activity coefficient corresponds to infinite dilution. This is readily calculated using again the group-contribution method (UNIFAC) (Fredenslund et al., 1975).

Solid-liquid equilibrium

There are several ways to estimate the solubility of a nonelectrolyte solid in a pure liquid. Using the theory of the real liquid (Prausnitz et al., 1999),

$$\ln \gamma_3 x_3 = \frac{-\Delta h_f}{RT}\left(1 - \frac{T}{T_f}\right) \tag{20}$$

As shown, three parameters are required to predict the solubility value x_3. These are: the melting enthalpy for the pure solid, the melting temperature, and the activity coefficient of the solute in the solution. In a particular case, the first quantity is obtained from tabulated data (Yaws, 1996). The melting enthalpy of pure solute is obtained from Yaws (1996), or using the Bondi (1967) correlation. In the Bondi method, the melting enthalpy is predicted from the molecular structure of the substance. In order to obtain the activity coefficient of the solute Eq. 20, the regular solution theory or the UNIFAC method can be used. In our case, the latter was used.

Once the solubility of the solid in the liquid has been calculated, the parameter k_{23} is obtained from fitting the predicted values with that given by the PR-EOS (with the classical mixing rules).

Finally, it must be pointed out that we have used extensively a group-contribution method (UNIFAC) for all binary systems, so that no empirical data correlation was necessary.

Results and Discussion

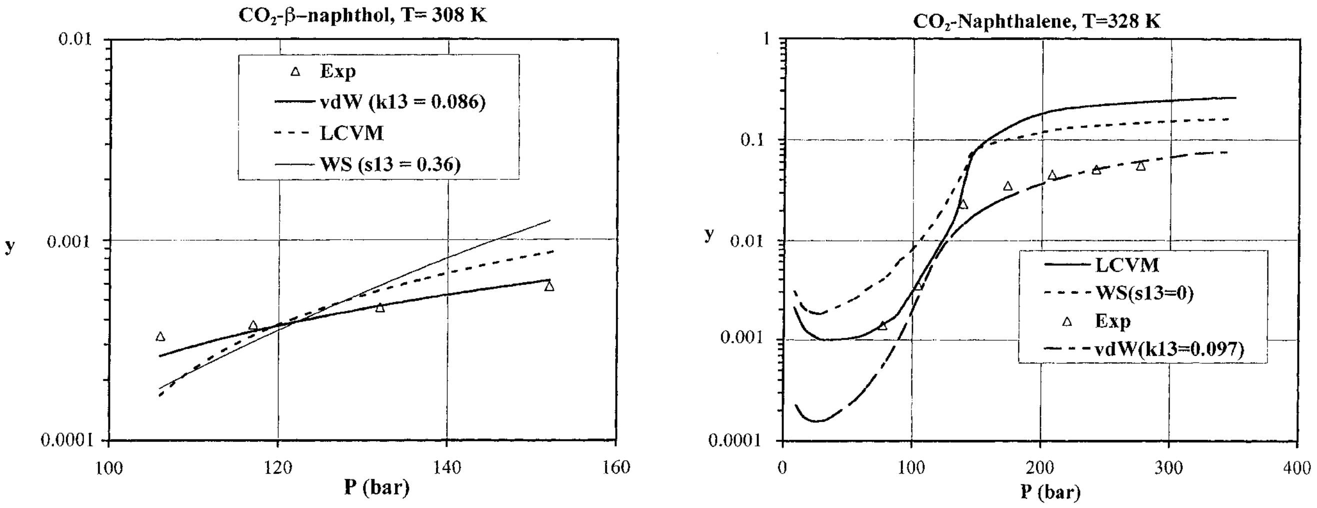
In order to test the theory, we examined the system of β-naphthol dissolving in carbon dioxide, neat and modified with either 6% or 10% toluene. The system was chosen because data on the system was available (Abaroudi et al., 1999). We also examined the data of Simon et al. (1993) about the extraction of Naproxen^{TM} using CO_2 modified with one of 6 possible cosolvents (acetone, methanol, ethyl acetate, ethanol, 1-propanol and 2-propanol). Table 1 lists a summary of the references used to perform this study.

In Figure 1a the experimental solubilities of naphthol in neat CO_2 at 308 K are presented. Data were fitted using the PR-EoS with the standard one-fluid mixing rules. Predicted solubilities (shown as lines over the graph) were generated with the PR-EoS with either the LCVM or the Wong-Sandler (WS) mixing rules. The triangles are measured data points. The behavior with the LCVM is very satisfactory (AARD = 28.4%), while the WS mixing rules give a satisfactory approximation over the central pressures (AARD = 49.7%). The error can, of course, be minimized to ARRD = 9.4% fitting the data points to get the interaction parameter ($k_{13} = 0.086$, the continuous line in Figure 1a). For other temperatures (318 K, 328 K, 342 K, 358 K, and 368 K), similar results are obtained. In general, it is observed that both the LCVM mixing rules and the WS mixing rules can be used to predict with some error the solubility of solid naphthol in SC CO_2, perhaps 40% or so on average.

Table 1. Conditions for Binary and Ternary Solubility Data

System	T (K)	P (bar)	Source
CO_2-ethanol	333	5-106	Suzuki et al. (1990)
CO_2-1-propanol	333	7-108	Suzuki et al. (1990)
CO_2-2-propanol	334	14-93	Radosz (1986)
CO_2-toluene	308	8-70	Fink and Hershey (1990)
	323	6-88	Fink and Hershey (1990)
	353	3-123	Fink and Hershey (1990); Morris and Donohue (1985); Ng and Robinson (1978)
CO_2-β-naphthol	308	90-160	Tan and Weng (1987); Abaroudi et al. (2000)
	318	100-150	Tan and Weng (1987); Abaroudi et al. (2000)
	328	100-170	Tan and Weng (1987); Abaroudi et al. (2000)
	343	105-146	Schmitt and Reid (1986)
	358	150-220	Abaroudi et al. (1999)
	368	150-220	Abaroudi et al. (1999)
CO_2-Naproxen	333	124-193	Simon et al. (1993)
CO_2-naphthalene	328	77-277	McHugh and Poulaitis (1980)
	338	150-271	McHugh and Poulaitis (1980)
CO_2-toluene-β-naphthol	358	150-220	Abaroudi et al. (1999)
CO_2-toluene-β-naphthol	368	150-220	Abaroudi et al. (1999)
CO_2-methanol-Naproxen	333	124-179	Simon et al. (1993)
CO_2-ethanol-Naproxen	333	124-179	Simon et al. (1993)
CO_2-acetone-Naproxen	333	124-193	Simon et al. (1993)
CO_2-1-propanol-Naproxen	333	124-179	Simon et al. (1993)
CO_2-2-propanol-Naproxen	333	124-179	Simon et al. (1993)
CO_2-ethylacetate-Naproxen	333	124-179	Simon et al. (1993)

Physical properties of pure substances can be found in Tan and Weng (1987) (α- and β-naphthol), Simon et al. (1993), McHugh and Paulaitis (1980) (Naproxen, naphthalene, cosolvents), and in Reid et al. (1987).



(a) **(b)**

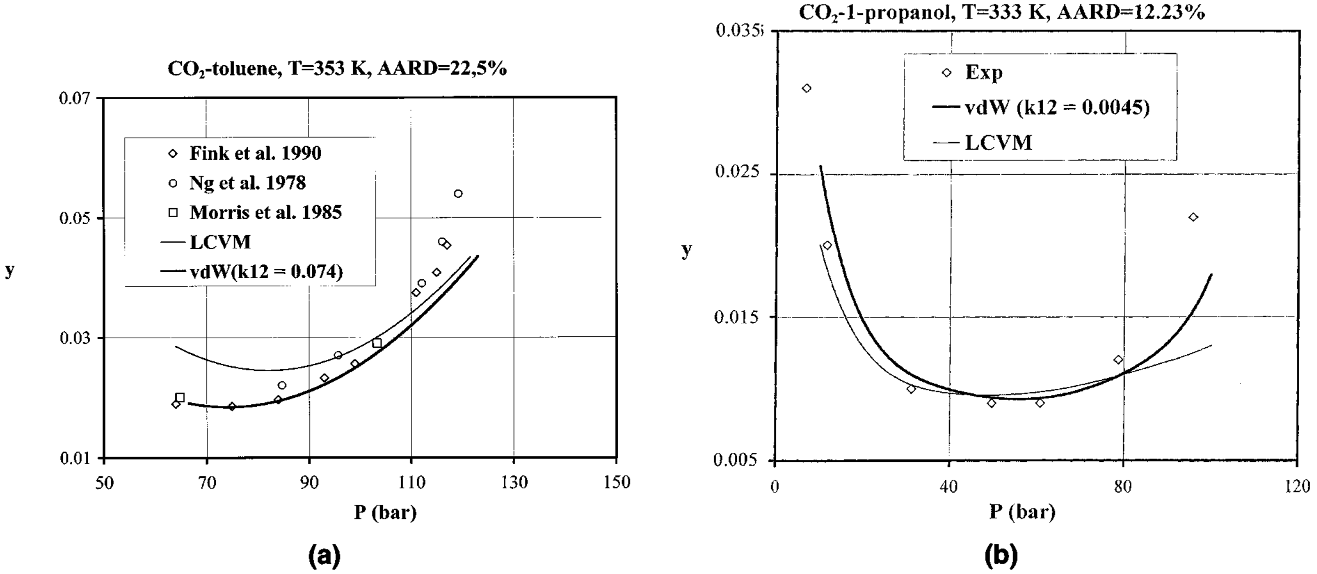
Figure 1. Experimental solubilities of solids (a) β-naphthol, (b) naphthalene in pure CO_2 (binary system) vs. pressure compared with predicted values (WS and LCVM).

The vdW line corresponds to a binary parameter obtained by fitting the values given by the PR-EoS with vdW mixing rules.

For engineering purposes, this error may be acceptable under certain noncritical circumstances. However, if a more precise estimate is required, a minimum amount of experiments will be necessary to determine solubility. This should allow obtaining the mixture parameter k_{13}, and use this value for predicting the solubility at other pressures. This procedure is shown in Figure 1b where the solubility in CO_2 of naphthalene at 328 K is given.

Figure 2a shows the experimental data for the toluene-CO_2 binary system at 353 K. Data were fitted using the standard PR-EoS. Predictive data were generated with the same PR-EOS with LCVM mixing rules. In this case, the LCVM rules predict the solubility of toluene rather well (AARD = 22.5%), particularly at pressures above the critical pressure of CO_2.

These results show that the different mixing rules work well for predicting the LV equilibrium (Orbey and Sandler, 1998). For predicting the solubility of a solid in a supercritical fluid, more error (maybe double in terms of % AARD) is involved. This is shown in Figure 2b where the equilibrium of 1-propanol in CO_2 are well fitted (AARD = 12.23%). In many ex-



(a) **(b)**

Figure 2. Experimental solubilities of liquid (a) toluene, (b) 1-propanol in pure CO_2 (binary systems) vs. pressure as predicted by the PR-LCVM, and fitted by the PR-vdW mixing rules (vdW line).

Table 2. Solubilities Calculated from Regular Solution Theory and P-$R(vdW)$ with Interaction Parameter Fitting the Scatchard-Hildebrand Model*

	(a) Acetone, Naproxen			(b) Ethyl Acetate, Naproxen		
P (bar)	$X \times 10^3$ (Est.)	$X \times 10^3$ ($k_{23} = -0.256$)	ARD (%)	$X \times 10^2$ (Est.)	$X \times 10^2$ ($k_{23} = -0.309$)	ARD (%)
10	9.07	9.91	9.26	2.04	2.29	12.25
30	9.07	9.74	7.39	2.04	2.23	9.31
50	9.07	9.57	5.51	2.04	2.18	6.86
70	9.07	9.41	3.75	2.04	2.13	4.41
90	9.07	9.24	1.87	2.04	2.08	1.96
120	9.07	8.99	0.88	2.04	2.01	1.47
150	9.07	8.74	3.64	2.04	1.94	4.90
180	8.07	8.50	6.28	2.04	1.86	8.82
200	9.07	8.34	8.05	2.04	1.82	10.78
220	9.07	8.17	9.92	2.04	1.77	13.24
			5.66*			7.40*

		(c) Toluene, β-naphthol					(d) Toluene, β-naphthol		
T (K)	P (bar)	$X \times 10^2$ (Est.)	$X \times 10^2$ ($k_{23} = -0.27$)	ARD (%)	T (K)	P (bar)	$X \times 10^2$ (Est.)	$X \times 10^2$ ($k_{23} = -0.262$)	ARD (%)
358	10	3.91	3.98	1.67	368	10	5.01	5.05	0.74
	30	3.91	3.97	1.42		30	5.01	5.04	0.52
	50	3.91	3.96	1.18		50	5.01	5.03	0.31
	70	3.91	3.95	0.93		70	5.01	5.02	0.09
	90	3.91	3.94	0.69		90	5.01	5.01	0.12
	120	3.91	3.92	0.32		120	5.01	4.99	0.44
	150	3.91	3.91	0.04		150	5.01	4.97	0.76
	180	3.91	3.90	0.41		180	5.01	4.96	1.08
	200	3.91	3.89	0.65		200	5.01	4.95	1.30
	220	3.91	3.88	0.89		220	5.01	4.94	1.51
				0.82*					0.69*

*AARD (average absolute relative deviation).

(a) Acetone-Naproxen at 333 K, (b) Ethyl acetate-Naproxen at 333 K, (c) Toluene-β-naphthol at 358 K, (d) Toluene-β-naphthol at 368 K.

amples studied involving CO_2 as one of the components (2-propanol, ethanol, methanol, acetone, and ethyl acetate), it has been observed that errors were well below ARRD = 30%. On the other hand, if the WS rules are used in the PR EOS, with $s_{ij} = 0$, the errors are higher than with the predictive method. Using the predictive g^E/EoS with the WS mixing rules, the errors are similar to those reported for the LCVM rules (that is, below 30% in AARD).

In Table 2 the predicted data for the solubility of solid-in-liquid are shown using the theory of the real liquid (Prausnitz et al., 1999), and the PR-EoS with the standard mixing rules. It can be seen in the table that the data are very well fitted, so the value of k_{23} can be obtained with good precision. Eight systems have been studied: β-naphthol-toluene at 358 K and 368 K, Naproxen-ethanol, Naproxen-methanol, Naproxen-1-propanol, Naproxen-2-propanol, Naproxen-ethyl acetate, Naproxen-acetone, and Naproxen-ethanol. The solvent-solute-cosolvent systems studied together with the binary interaction parameters found from the modeling as described in the theory to be used in describing the ternary system are summarized in Table 3. As will be noted, a negative k_{23} value is found in all cases. The same feature was found by Simon et al. (1993). This can be explained on a molecular basis by a large solvation effect of the solute by the entrainer.

Once the binary parameter values have been obtained, the solubility in the modified carbon dioxide can be predicted and tested. Figure 3 shows the comparison between the measured and the predicted solubilities of β-naphthol in 6% and 10% toluene, and at two temperatures (358 K and 368 K). It is seen that the proposed methodology gives a rather good approximation to the solubilities at a 6% and 10% modifier, and their change is with pressure and temperature. Thus, at 368 K, the errors are between 8.6% and 26.3%. On the other hand, if the data of Simon et al. (1993) on Naproxen and six cosolvents are modeled, the absolute errors increase, ranging from 44.1% to sometimes 77% (see Table 4). This scattering can be explained on a molecular basis. Naproxen is a polar molecule, whereas naphthol is much less polar so it interacts better with toluene. In this case probably a chemical approach for Naproxen would be more appropriate.

In Table 5, the measured and predicted efficiencies of the cosolvents in improving the Naproxen solubility are presented (Simon et al., 1993). As shown, except in the case of one solvent, our method sorts the solvents in the correct order as found experimentally by Simon et al. The error shown

Table 3. Binary Interaction Parameters for the PR-EoS, vdW Mixing Rules for Calculating Parameter $a(T)$ Based on Predicted Binary Solubility Data

Solvent	Cosolvent	Solute	T (K)	k_{12}	k_{13}	k_{23}
CO_2	Toluene	β-Naphthol	358	0.064	0.088	−0.2700
CO_2	Toluene	β-Naphthol	368	0.055	0.095	−0.2620
CO_2	Ethyl Acetate	Naproxen	333	0.0017	0.013	−0.3090
CO_2	Acetone	Naproxen	333	0.0021	0.013	−0.2560
CO_2	Methanol	Naproxen	333	0.0015	0.013	−0.2442
CO_2	Ethanol	Naproxen	333	0.0033	0.013	−0.2270
CO_2	1-Propanol	Naproxen	333	0.0045	0.013	−0.2536
CO_2	2-Propanol	Naproxen	333	0.0049	0.013	−0.2622

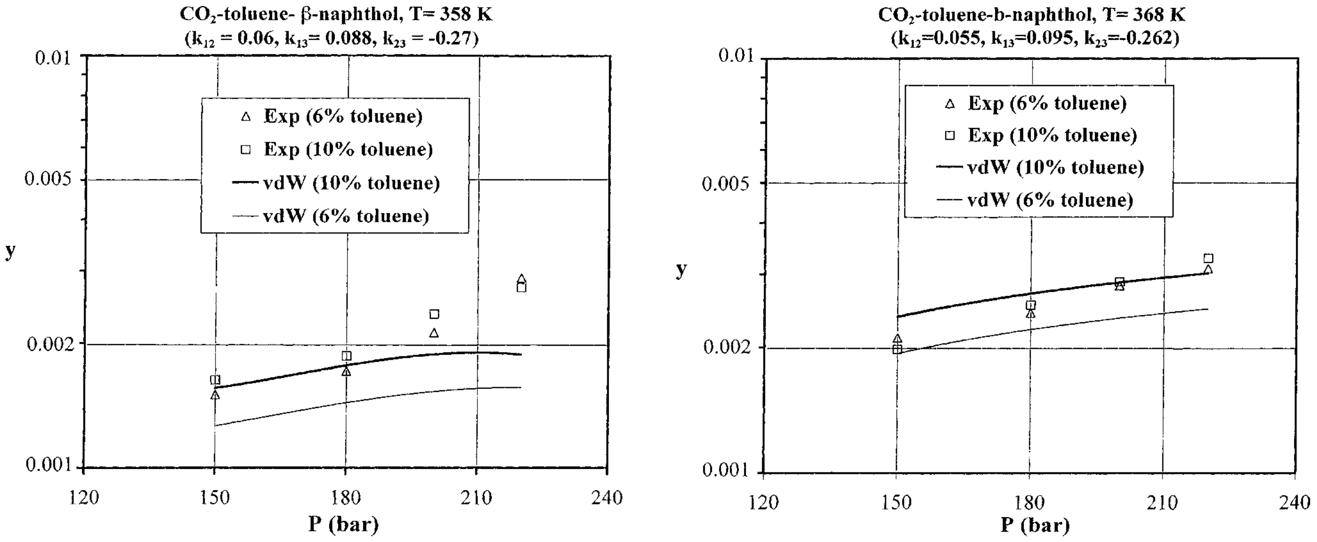


Figure 3. Solubility of β-naphthol in toluene modified (as a ternary system) vs. pressure.

Continuous lines were calculated with the PR-Eos with one-fluid vdW mixing rules using fully predicted, binary interaction parameters, (a) T = 358 K; (b) T = 368 K.

in one case is certainly due to the inaccuracies of the present method. Nevertheless, the proposed theory is useful because it would allow selecting a cosolvent from a list of selected candidates, based on an estimate of the solubilities.

Because of the many estimated properties and parameters involved in the method presented, future research on the effect of the individual effectiveness of fitting parameters would prove useful and eventually improve the accuracy of the method. In this regard, Macnaughton et al. (1994), using a semiempirical approach for describing the extraction of lindane with modified carbon dioxide, showed that certain parameters are irrelevant for the ternary system lindane-CO_2-cosolvent, while the other two interaction parameters proved to be very important. Thus, the solid solute-CO_2 binary system data were fitted experimentally and the solid-cosolvent binary system was estimated, while the CO_2-cosolvent system

Table 4. Experimental vs. Predicted Solubilities of Naproxen in Modified CO_2 as Ternary System

P (bar)	$Y \times 10^6$ (Exp.)	$Y \times 10^6$ (calc.)	ARD (%)	$Y \times 10^6$ (exp.)	$Y \times 10^6$ (Calc.)	ARD (%)
		CO_2, Acetone, Naproxen			*CO_2, Ethyl Acetate, Naproxen*	
124	14.90	7.4800	49.80	13.20	7.8347	40.64
138	26.70	11.0280	58.70	23.60	11.6050	50.82
152	39.10	15.9540	59.20	32.60	16.8828	48.21
165	50.50	22.1162	56.20	41.50	23.4963	43.38
179	60.90	30.7540	49.50	52.60	32.7921	37.66
193	57.50	41.4498	27.83		44.3727	
			50.20*			44.14*
		CO_3, Methanol, Naproxen			*CO_2, Ethanol, Naproxen*	
124	19.50	7.5533	61.26	26.90	7.6321	71.63
138	35.30	11.0850	68.60	44.20	11.2260	74.60
152	56.40	15.9988	71.63	62.60	16.3325	73.91
165	77.60	22.1190	71.50	80.90	24.2980	69.96
179	93.50	30.8476	67.01	95.50	31.0909	67.44
193		41.6164			41.7791	
			68.00*			71.51*
		CO_2, 1-Propanol, Naproxen			*CO_2, 2-Propanol, Naproxen*	
124	38.60	7.9090	79.51	32.00	7.8213	75.56
138	58.80	11.6572	80.18	53.20	11.5474	78.29
152	73.50	16.8924	77.02	72.20	16.7437	76.81
165		23.4161		89.10	23.2293	73.93
179	112.00	32.5203	70.96	108.40	32.3032	70.20
193		43.7431			43.7734	
			76.92*			74.95*

*AARD average absolute relative deviation.

Table 5. Sorting Best Entrainers for Naproxen as Solubility Enhancers for SC CO_2

Pred. Order	Exp. Observation
1. Acetone	1. Ethyl acetate
2. Methanol	2. Acetone
3. Ethanol	3. Methanol
4. 2-Propanol	4. Ethanol
5. 1-Propanol	5. 2-Propanol
6. Ethyl acetate	6. 1-Propanol

could well be set to zero as the binary interaction parameter had a minor influence in this case.

Conclusions

We attempted to predict the solubilities of organic nonelectrolytes in a supercritical fluid modified with a cosolvent. The method proposed involves the use of three binary interaction parameters that describe the binary solutions with an equation of state. To calculate the binary parameters, use was made of a completely predictive excess Gibbs energy equation-of-state (Peng and Robinson) with the linear combination of the Vidal and the Michelsen mixing rules, or with the Wong and Sandler mixing rules. The test system was the solid β-naphthol dissolving in carbon dioxide modified with either 6% or 10% toluene. The results of the solubility estimates were 60% (on the average) accurate, in regard to the solubility in the modified carbon dioxide. The performance of the method was better when a list of cosolvents was examined for their potentially entraining power. In that examination, we followed the example of Simon et al. (1993) who used neat carbon dioxide for dissolving Naproxen with one of the following cosolvents: acetone, methanol, 1-propanol, 2-propanol, and ethyl acetate. The method proposed was moderately successful in matching the solubilities of Naproxen in modified carbon dioxide, but was able to sort the entrainers in an order similar to the order found experimentally.

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Notation

a = energy parameter in PR-EOS, a_{mix} for a mixture, $\text{Pa}\cdot\text{m}^6\cdot\text{mol}^{-2}$
a^E_∞ = the excess Helmholtz free energy at infinite pressure, J/mol
$a_i(T)$ = component coefficient, Eq. 3b, $\text{Pa}\cdot\text{m}^6\cdot\text{mol}^{-2}$
$a(Tci)$ = component coefficient, Eq. 3c, $\text{m}^6\cdot\text{Pa}\cdot\text{mol}^{-2}$
A = coefficient defined by Eq. 5b
Ai = coefficients in expression Eq. 18, $i = 0, 4$
A_V = mixing rule constant for the Vidal mixing rule, Eq. 7b = -0.623
A_M = mixing rule constant for the Michelsen mixing rule, Eq. 7b = 0.53
b = pure component volume parameter, b_{mix} for mixture, $\text{m}^3\cdot\text{mol}^{-1}$
b_i = pure component coefficient defined by Eq. 3a, $\text{m}^3\cdot\text{mol}^{-1}$
b_i^* = volume for component i defined by Eq. 5d for $i = 3$, $\text{m}^3\cdot\text{mol}^{-1}$
B = coefficient defined by Eq. 5c
C = real number defined by Eq. 8f
D = term used in Wong-Sandler mixing rule, Eq. 8e
f_i = fugacity of component i in a mixture, Pa
g^E = molar excess Gibbs-free-energy of mixture, J/mol
Δh_f = enthalpy of fusion of the solute at the melting temperature, J/mol
$H_{i,j}$ = Henry's constant for i in j, Pa per unit mol faction
k_{12} = mixture parameter (CO_2-liquid cosolvent)
k_{13} = mixture parameter (CO_2-solid solute)
k_{23} = mixture parameter (solid-liquid)
m_i = coefficient for component i, Eq. 3e
n = total number of mols, n_i = mols of component i
P = pressure, Pa
Pc = critical pressure, Pa
P_2^{sat} = saturation pressure of pure liquid, Pa
P_3^{sat} = saturation pressure of pure solid, Pa
Q = term used in Wong-Sandler's mixing rule, Eq. 8c, $\text{m}^3\cdot\text{mol}^{-1}$
R = ideal gas constant, 8.314 J, $\text{mol}\cdot\text{K}^{-1}$
s_{12} = second virial coefficient binary interaction parameter (CO_2-liquid)
s_{13} = second virial coefficient binary interaction parameter (CO_2-solid)
T = temperature, K
Tc = critical temperature, K
T_f = normal melting temperature of the solute, K
Tr = reduced temperature, T/Tc
v = molar volume of gas phase, m^3/mol
v_1^L = molar volume liquid of CO_2, m^3/mol
$\bar{v}_1^\infty$ = infinite dilution partial molar volume of CO_2 in liquid phase, m^3/mol
v_2^L = liquid molar volume, m^3/mol
v_3^S = solid molar volume, m^3/mol
x = liquid mol fraction
y = mol fraction in the vapor or supercritical phase
z_g = compressibility factor of fluid phase

Greek letters

α = EOS parameter, $\alpha = a/bRT$
α_M = EOS-dependent parameter, here *PR*, Eq. 6b
α_V = EOS-dependent parameter, here *PR*, Eq. 6d
γ = activity coefficient
λ = weighting factor of LCVM model, see Eq. 6a, = 0.36
ϕ_i = fugacity coefficient of component i in the fluid mixture
ϕ_i^{sat} = fugacity coefficient of pure component i at saturation
ω = Pitzer's acentric factor

Acronym

AARD = % Average absolute relative deviation = $(100/\text{N})\Sigma^N \,|(y_{\text{ex},\,i} - y_{\text{cal},\,i}/y_{\text{cal},i}|$

Literature Cited

Abaroudi, K., F. Trabelsi, B. Calloud-Gabriel, and F. Recasens, "Mass Transport Enhancement in Modified Supercritical Fluid," *Ind. & Eng. Chem. Res.*, **38**, 3505 (1999).

Abaroudi, K., F. Trabelsi, and F. Recasens, "Quasi-Static Measurement of Equilibrium Solubilities in SC Fluids: A Mass Transfer Criterion," *Fluid Phase Equilib.*, **169**, 177 (2000).

Anitescu, G., and L. L. Tavlarides, "Solubilities of Individual Polychlorinated Biphenyl (PCB) Congeners in Supercritical Fluids: CO_2, CO_2/MeOH and CO_2/n-C_4H_{10}," *J. Supercrit. Fluids*, **14**, 197 (1999).

Antunes, C., and D. Tassios, "Modified UNIFAC Model for the Prediction of Henry's Constants," *Ind. Eng. Chem. Res.*, **22**, 457 (1983).

Bondi, A., "A Correlation of the Entropy of Fusion of Molecular Crystals with Molecular Structure," *Chem. Rev.*, **67**, 565 (1967).

Brennecke, J. F., and C. A. Eckert, "Phase Equilibria for Supercritical Process Design," *AIChE J.*, **35**, 1409 (1989).

Brunner, G., *Gas Extraction*, Steinkopff Darmstadt and Springer Verlag, New York (1994).

Boukouvalas, C., N. Spiliotis, Ph. Coutsikos, N. Tzouvaras, and N. Tassios, "Prediction of Vapor-Liquid Equilibrium with the LCVM Model: A Linear Combination of the Vidal and Michelsen Mixing Rules Coupled with the Original UNIFAC and the t-mPR Equation of State," *Fluid Phase Equil.*, **92**, 75 (1994).

Dobbs, J. M., J. M. Wong, R. J. Lahiere, and K. P. Johnston, "Modification of Supercritical Fluid Phase Behavior Using Polar Cosolvents," *Ind. Eng. Chem. Res.*, **26**, 56 (1987).

Eychenne, V., S. Sáiz, F. Trabelsi, and F. Recasens, "Near-Critical Solvent Extraction of Raw Wool with Modified Carbon Dioxide—Experimental Results," *J. Supercrit. Fluids*, **21**, 23 (2001).

Fink, S. D., and H. C. Hershey, "Modelling the Vapor-Liquid Equilibria of 1-1-1-Tricloroetane + Carbon Dioxide and Toluene + Carbon Dioxide at 308; 328 and 358," *Ind. Eng. Chem. Res.*, **29**, 295 (1990).

Fredenslund, A., R. L. Jones, and J. M. Prausnitz, "Group-Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixture," *AIChE J.*, **21**, 1086 (1975).

Gurdial, G. S., S. J. Macnaughton, D. L. Tomasko, and N. R. Foster, "Influence of Chemical Modifiers on the Solubility of o- and m-Hydroxybenzoic Acid in Supercritical CO_2," *Ind. Eng. Chem. Res.*, **32**, 1488 (1993).

Hederer, H., S. Peter, and H. Wenzel, "Calculation of Thermodynamic Properties from a Modified Redlich-Kwong Equation of State," *Chem. Eng. J.*, **11**, 183 (1976).

Jaubert, J. N., and L. Coniglio, L, "From the Correlation of Binary Systems Involving Supercritical CO_2 and Fatty Acid Esters to the Prediction of (CO_2-Fish Oils) Phase Behaviour," *Ind. Eng. Chem. Res.*, **38**, 3162 (1999a).

Jaubert, J. N., and L. Coniglio, "The Group Contribution Concept: A Useful Tool to Correlate Binary Systems and to Predict the Phase Behaviour of Multicomponent Systems Involving CO_2 and Fatty Acid," *Ind. Eng. Chem. Res.*, **38**, 5011 (1999*b*).

Macnaughton, S. J., P. Alessi, A. Cortesi, I. Kikic, and N. R. Foster, "Predictive and Experimental Methods for the Choise of Cosolvent in the Supercritical Fluid Extraction of Pesticides," K. W. Hutchenson and N. R. Foster, eds., *ACS Symposium Series 608,* American Chemical Society, Washington, DC, 126 (1994).

McHugh, M., and V. Krukonis, *Supercritical Fluid Extraction*, 2nd ed., Butterworth-Heinemann, Stoneham, MA (1994).

McHugh, M., and M. Paulaitis, "Solid Solubilities of Naphthalene and Biphenyl in Supercritical Carbon Dioxide," *J. Chem. Eng. Data*, **25**, 326 (1980).

Michelsen, M. L., "A Modified Huron-Vidal Mixing Rule for Cubic Equations of State," *Fluid Phase Equilibria*, **60**, 213 (1990b).

Morris, W. O., and M. D. Donohue, "Vapor-Liquid Equilibria in Mixtures Containing Carbon Dioxide; Toluene and 1-Methylnaphthalene," *J. Chem. Eng. Data*, **30**, 259 (1985).

Ng, H.-J., and D. B. Robinson, "Equilibrium Phase of the Toluene-Carbon Dioxide System," *J. Chem. Eng. Data*, **23**, 325 (1978).

Orbey, H., and S. I. Sandler, *Modeling Vapor-Liquid Equilibria*, Cambridge University Press, New York (1998).

Peng, D., and D. B. Robinson, "A New Two Constant Equation of State," *Ind. Eng. Chem. Fund.*, **15**, 59 (1976).

Prausnitz, J. M., R. N. Lichtenthaler, and E. Gomes de Acevedo, *Molecular Thermodynamics of Fluid Phase Equilibria*, 3rd ed., Prentice-Hall, Englewood Cliffs, NJ (1999).

Prausnitz, J. M., and F. H. Shair, "A Thermodynamic Correlation of Gas Solubilities," *AIChE J.*, **7**, 682 (1961).

Radosz, M., "Vapor-Liquid Equilibrium for 2-Propanol and Carbon Dioxide," *J. Chem. Eng. Data*, **31**, 43 (1986).

Recasens, F., E. Velo, M. A. Larrayoz, and J. Puiggené, "Endothermic Character of Toluene Adsorption from Supercritical Carbon Dioxide on Activated Carbon at Low Coverage," *Fluid Phase Equil.*, **90**, 265 (1993).

Reid, R. C., *Supercritical-Fluid Extraction—A Perspective*, Hougen Lecture Series, University of Wisconsin, Madison, WI (1981).

Reid, R. C., J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids*, 4th ed., McGraw-Hill, New York (1987).

Renon, H., and J. M. Prausnitz, "Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures," *AIChE J.*, **14**, 135 (1968).

Sandler, S. I., *Chemical and Engineering Thermodynamics*, 3rd ed., Wiley, New York (1999).

Schmitt, J. S., and J. C. Reid, "Solubility of Monofunctional Organoic Solids in Chemically Diverse Supercritical Fluids," *J. Chem. Eng. Data*, **31**, 204 (1986).

Simon, S. T. T., S. J. Macnaughton, D. C. Tomasko, and N. R. Foster, "Solubility of Naproxen in Supercritical Carbon Dioxide With and Without Cosolvents," *Ind. Eng. Chem. Res.*, **32**, 1471 (1993).

Smith, J. M., H. Van Ness, and M. M. Abbott, *Introduction to Chemical Engineering Thermodynamics*, 5th ed., McGraw-Hill, New York (1996).

Soave, G. S., "Equilibrium Constants from a Modified Redlich-Kwong Equation of State," *Chem. Eng. Sci.*, **33**, 225 (1972).

Sovová, H., V. Rat, M. Khachaturyan, and D. Vlcek, "Solubility of Squalane and Dinonyl Phthalate in CO_2 with Entrainers," *J. Supercrit. Fluids*, **14**, 145 (1999).

Sunol, A. K., B. Hagh, and S. Chen, "Entrainer Selection in Supercritical Extraction," J. M. L. Penninger, M. Radosz, M. A. McHugh, and V. J. Krukonis, eds., *Supercritical Fluid Technology*, Elsevier, Amsterdam (1985).

Suzuki, K., H. Sue, M. Itou, R. L. Smith, H. Inomata, K. Arai, and S. Saito, "Isothermal Vapor-Liquid Data for Binary Systems at High Pressure: Carbon Dioxide-Methanol, Carbon Dioxide-Ethanol, Carbon Dioxide-1-Propanol, Methane-Ethanol, Methane-1-Propanol, Ethane-Ethanol, and Ethane-1-Propanol Systems," *J. Chem. Eng. Data*, **35**, 63 (1990).

Tan, C.-S., and J.-Y. Weng, "Solubility Measurements of Naphthol Isomers in Supercritical CO_2 by a Recycle Technique," *Fluid Phase Equilib.*, **34**, 37 (1987).

Trabelsi, F., K. Abaroudi, and F. Recasens, "Predicting the Approximate Solubilities of Solids in Dense Carbon Dioxide," *J. Supercrit. Fluids*, **14**, 151 (1999).

Vidal, J., "Mixing Rules and Excess Properties in Cubic Equation of State," *Chem. Eng. Sci.*, **33**, 787 (1978).

West, B. L., D. Bush, N. H. Brantley, M. F. Vincent, S. G. Kazarian, and C. A. Eckert, "Modeling the Effects of Cosolvent-Modified Supercritical Fluids on Polymers with a Lattice Fluid Equation of State," *Ind. Eng. Chem. Res.*, **37**, 3305 (1998).

Wong, D. S. H., and S. I. Sandler, "A Theoretically Correct Mixing Rule for Cubic Equations of State," *AIChE J.*, **38**, 671 (1992).

Yakoumis, I. V., K. Viachos, G. M. Kontogeorgis, N. S. Kalospiros, and D. Tassios, "Application of the LCVM Model to Systems Containing Organic Compounds and Supercritical Carbon Dioxide," *J. Supercrit. Fluids*, **9**, 88 (1996).

Yaws, C. L., *Chemical Properties Handbook*, McGraw-Hill, NY (1996).

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