

# Solubility of Solids in Supercritical Fluids: Consistency of Data and a New Model for Cosolvent Systems

Janette Mendez-Santiago<sup>†</sup> and Aryn S. Teja<sup>\*</sup>

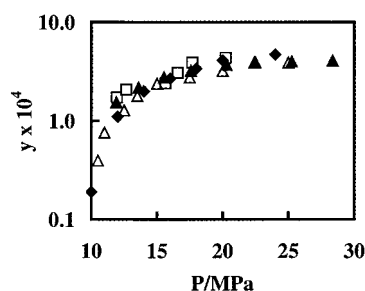
School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332

The ability to correlate and predict the solubility of solids in supercritical fluids is important in the design and evaluation of supercritical extraction processes. However, a review of the literature reveals that solid solubility data obtained by different investigators often do not agree within the reported uncertainties of the measurements. We have shown previously that a simple theory of dilute solutions can be used to check the consistency of supercritical CO<sub>2</sub>–solid solubility data and also that such data can be reduced to a single straight line over a significant range of solvent density and temperature. In the present work, we first show that our binary solution model is applicable to systems in which the solvent is not CO<sub>2</sub>. We then extend the approach to ternary cosolvent systems and show that data over a range of temperatures, pressures, and cosolvent concentrations can be correlated within experimental error using a single equation. The new model has three parameters that are independent of temperature, pressure, and cosolvent concentration. The approach may therefore be used to extrapolate limited data sets over a range of these variables.

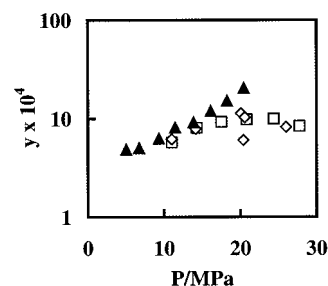
## Introduction

Knowledge of the solubility of solids in supercritical fluids is essential for evaluating the feasibility of supercritical separation processes and for establishing optimum conditions of operation. Solubility measurements have therefore received considerable attention in the literature, as evidenced by the fact that more than 4500 data have been published for CO<sub>2</sub>–solid solute systems.<sup>1</sup> The reliability of the data, however, is sometimes difficult to establish, and it is not uncommon to find measurements by different investigators that disagree by more than the reported experimental uncertainties. This is demonstrated in Figure 1 in the case of the solubility of *n*-octacosane in carbon dioxide.<sup>2–5</sup> Although the four sets of data shown in the diagram follow a common trend, some data points at the same conditions disagree by more than  $\pm 25\%$  when the reported uncertainties of the data are  $\pm 5\%$ . In some systems, published data even exhibit different trends with respect to temperature or pressure as shown for the solubility of *n*-tetracosane in carbon dioxide in Figure 2. These two examples clearly demonstrate the need to establish the reliability of solid solubility data.

Thermodynamic models that employ equations of state, lattice gas equations, or expanded liquid models have been proposed to describe the solubility behavior of solids in compressed gas solvents.<sup>1</sup> However, these models require several adjustable parameters to correlate data, and they can seldom be used for extrapolation. Often, the adjustable parameters in the models depend not only on the temperature but also on the particular set of data chosen for study. In many of these models, physical properties of the solute (such as vapor pressure, critical temperature, critical pressure, and



**Figure 1.** Solubility of *n*-octacosane in carbon dioxide at 308 K. Data of Smith et al.<sup>2</sup> (□), McHugh et al.<sup>3</sup> (△), Reverchon et al.<sup>4</sup> (▲), and Chandler et al.<sup>5</sup> (◆).



**Figure 2.** Solubility of *n*-tetracosane in carbon dioxide. Data of Smith et al.<sup>2</sup> at 310 K (□), Schmitt and Reid<sup>6</sup> at 310 K (◇), and Yau and Tsai at 308 K (▲).

sublimation pressure) must be estimated, because these properties are rarely available for the solute. As a result, these thermodynamic models are of limited utility in separation process design.

In 1990, Harvey<sup>8</sup> proposed a simple theory of dilute solutions, which demonstrated that solid solubility data (plotted in terms of an effective Henry's constant) could be reduced to a single straight line over a range of temperatures. The linear range was limited to low densities and to temperatures not far from the critical point of the solvent. More recently, we have demonstrated<sup>9</sup> that the solubility of solids in supercritical carbon dioxide can be plotted on a single straight line

<sup>\*</sup> To whom correspondence should be addressed. E-mail: amyn.teja@che.gatech.edu. Phone: 404-894-3098. Fax: 404-894-2866.

<sup>†</sup> Current address: Exxon Mobil Upstream Research Co., P.O. Box 2189, Houston, TX 77252-2189.

over a wide range of temperatures and densities. Deviations from this linear behavior occur only at densities greater than twice, or less than half, the critical density of the solvent. In this paper, we briefly outline the application of dilute solution theory to solvents other than carbon dioxide. We then derive an extended theory for ternary mixtures, where the third component is a cosolvent.

The presence of a third component has been shown to have a dramatic effect on the solubility of solids in supercritical fluids.<sup>10–12</sup> In most cases, the cosolvent or cosolute enhances the solubility of the solid in the supercritical solvent.<sup>10,11</sup> However, there are cases when there is a decrease in the solubility.<sup>12</sup> An extended theory that accounts for this behavior is therefore of great practical significance in the design of supercritical separation processes.

### Theory of Dilute Solutions

The theory of dilute solutions has been studied extensively by a number of investigators.<sup>13–16</sup> It is based on a Taylor expansion of the Helmholtz energy about the critical point of a solvent and leads to simple expressions for many thermodynamic properties of dilute near-critical binary mixtures. In particular, a simple linear expression is obtained for the effective Henry's constant of a solid in a supercritical solvent<sup>8</sup> as follows:

$$T \ln \left( \frac{H_{2,1}^{\text{eff}}}{f_1} \right) = A + B(\rho - \rho_c) \quad (1)$$

where  $f_1$  is the fugacity and  $\rho$  and  $\rho_c$  are the density and critical density of the solvent at a given temperature  $T$  and pressure  $P$ .  $H_{2,1}^{\text{eff}}$  is an effective Henry's constant of solute 2 in solvent 1 defined by

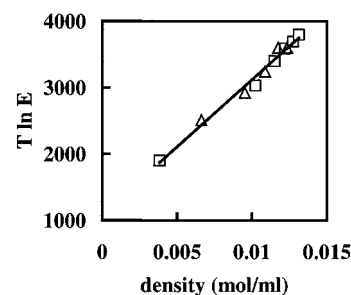
$$H_{2,1}^{\text{eff}} = \frac{P_2^s}{y_2} \exp \left[ \frac{v_2(P - P_2^s)}{RT} \right] \quad (2)$$

Here,  $y_2$  is the solubility of the solute,  $v_2$  is the solid molar volume, and  $P_2^s$  is the sublimation pressure of the (solid) solute. Harvey<sup>8</sup> applied these equations to systems consisting of naphthalene in carbon dioxide, naphthalene in ethylene, and hexachloroethane in ethylene and showed that the theory is valid for these systems over a limited range of conditions. For example, naphthalene in carbon dioxide data followed a linear trend from a solvent density of about 5 up to 14 mol/L (with  $\rho_c = 10.63$  mol/L). At higher densities, the relationship was no longer linear. As a result, the theory could not be used to extrapolate Henry's constants (and, therefore, solubilities) to high densities from low-density data. Harvey also obtained the following relationship by substituting eq 2 into eq 1:

$$\ln y_2 = -[A + B(\rho - \rho_c)]/T + \ln f_2 - \ln f_1 \quad (3)$$

Furthermore, he showed that when the enhancement factor is defined as  $E = y_2 P / P_2^s$ , eq 3 reduces to

$$T \ln E = -[A + B(\rho_1 - \rho_{c,1})] + v_2(P - P_2^s) - T \ln \phi_1 \quad (4)$$



**Figure 3.** Solubility of diamantane in ethane. Data of Smith and Teja<sup>18</sup> at 318 K ( $\square$ ) and 333 K ( $\triangle$ ).

Harvey suggested that the solubility plotted as  $T \ln E$  vs the density of the solvent would yield a single line if the last two terms in eq 4 could be neglected. However, he did not test this hypothesis, perhaps because of the limited range of applicability found for the Henry's constant expression.

### Solubility Model for Binary Systems

We have shown in our previous work<sup>9</sup> that eq 4 can be approximated by

$$T \ln E = C + D\rho_1 \quad (5)$$

and have successfully modeled the solubility of numerous solids in supercritical carbon dioxide using this expression. We have also shown that solubility data for binary systems over an extended temperature and density range can be reduced to a single straight line when plotted in terms of  $T \ln E$  vs the density of the solvent. The lower density limit of this linear behavior is about half the critical density of the solvent. Furthermore, there is apparently no upper density limit, although the maximum density of the data used to test the expression was about twice the critical density of the solvent. It was also shown that the model can be used to determine the self-consistency of solubility data. Moreover, a thermodynamic consistency test was developed by noting that the slope  $D$  in eq 5 is related to the limiting slope of the critical locus in the binary system and the limiting slope of the vapor pressure curve of the solvent as follows:

$$DR\rho_c^2 = -\left(\frac{\partial P}{\partial x_2}\right)_{v,T}^{\infty} = -\left(\frac{dP_c}{dx_2}\right)^{\infty} + \left(\frac{dT_c}{dx_2}\right)^{\infty} \left(\frac{dP}{dT}\right)_c \quad (6)$$

Unfortunately, critical loci for systems of interest in supercritical fluid technology are seldom available. We have, therefore, developed a consistency test based on critical loci of homologous series of solutes, as discussed elsewhere.<sup>17</sup>

Equation 5 was also tested with other solvents such as methane and ethane and found to be valid for these systems. Figure 3 shows a plot of the solubility of diamantane in ethane and confirms that linear behavior is not limited to carbon dioxide systems.

### New Model for Cosolvent Systems

We have extended the binary solubility model to incorporate cosolvent concentration effects as described below. In this derivation, subscript 1 refers to the solvent, subscript 2 refers to the solute, and subscript 3 refers to the cosolvent. For component 2 in a mixture,

Henry's law constant is given by

$$H_{2,m} = \lim_{x_2 \rightarrow 0} \left( \frac{f_2}{x_2} \right) = \lim_{x_2 \rightarrow 0} \left( \frac{x_2 \hat{\phi}_2 P}{x_2} \right) = \lim_{x_2 \rightarrow 0} (\hat{\phi}_2 P) = \hat{\phi}_2^\infty P \quad (7)$$

where the fugacity coefficient is given by the thermodynamic expression

$$\ln \hat{\phi}_2 = \int_0^P \left( \frac{\bar{v}_2}{RT} - \frac{1}{P} \right) dP \quad (8)$$

At a given  $T$  and  $P$ , the molar volume of a mixture can be written in terms of the partial molar volume  $\bar{v}_2$  as follows:

$$v = x_1 \bar{v}_1 + x_2 \bar{v}_2 + x_3 \bar{v}_3 \quad (9)$$

which may be differentiated to give

$$\left( \frac{\partial v}{\partial x_2} \right)_{T,P} = x_1 \left( \frac{\partial \bar{v}_1}{\partial x_2} \right)_{T,P} + x_2 \left( \frac{\partial \bar{v}_2}{\partial x_2} \right)_{T,P} + x_3 \left( \frac{\partial \bar{v}_3}{\partial x_2} \right)_{T,P} + \bar{v}_1 \left( \frac{\partial x_1}{\partial x_2} \right)_{T,P} + \bar{v}_2 \left( \frac{\partial x_2}{\partial x_2} \right)_{T,P} + \bar{v}_3 \left( \frac{\partial x_3}{\partial x_2} \right)_{T,P} \quad (10)$$

The first three terms in eq 10 sum to zero according to the Gibbs–Duhem equation. Also, for a ternary mixture

$$x_1 + x_2 + x_3 = 1 \quad (11)$$

which may be differentiated with respect to  $x_2$  to give

$$\left( \frac{\partial x_1}{\partial x_2} \right)_{T,P} + 1 + \left( \frac{\partial x_3}{\partial x_2} \right)_{T,P} = 0 \quad (12)$$

At infinite dilution of component 2,  $x_1 + x_3$  approaches 1 and  $x_2$  approaches zero. We may also assume that the ratio of the mole fraction of component 1 to that of component 3 remains constant as  $x_2$  approaches zero. Thus

$$\frac{x_1}{x_3} = \text{constant} \Rightarrow \left[ \frac{\partial (x_1/x_3)}{\partial x_2} \right]_{T,P} = 0 \quad (13)$$

and

$$\frac{-x_1}{x_3^2} \left( \frac{\partial x_3}{\partial x_2} \right)_{T,P} + \frac{1}{x_3} \left( \frac{\partial x_1}{\partial x_2} \right)_{T,P} = 0 \quad (14)$$

Combining eq 14 with eq 12 gives

$$\left( \frac{\partial x_1}{\partial x_2} \right)_{T,P} = \frac{-x_1}{x_1 + x_3} \quad \text{and} \quad \left( \frac{\partial x_3}{\partial x_2} \right)_{T,P} = \frac{-x_3}{x_1 + x_3} \quad (15)$$

Substituting eq 10 into eq 8, we get

$$\ln \hat{\phi}_2 = \int_0^P \left[ \frac{1}{RT} \left( \frac{\partial v}{\partial x_2} \right)_{T,P} - \frac{1}{RT} \left( \frac{\partial x_1}{\partial x_2} \right)_{T,P} \bar{v}_1 - \frac{1}{RT} \left( \frac{\partial x_3}{\partial x_2} \right)_{T,P} \bar{v}_3 - \frac{1}{P} \right] dP \quad (16)$$

which may be combined with eq 15 and the identity

$$\left( \frac{\partial v}{\partial x_2} \right)_{T,P} = - \left( \frac{\partial P}{\partial x_2} \right)_{v,T} \left( \frac{\partial v}{\partial P} \right)_{T,x_2} \quad (17)$$

to obtain the following expression for the fugacity coefficient:

$$\ln \hat{\phi}_2 = \int_\infty^v - \frac{1}{RT} \left( \frac{\partial P}{\partial x_2} \right)_{v,T} dV + \int_0^P \left[ \left( \frac{x_1}{x_1 + x_3} \right) \frac{\bar{v}_1}{RT} + \left( \frac{x_3}{x_1 + x_3} \right) \frac{\bar{v}_3}{RT} - \frac{1}{P} \right] dP \quad (18)$$

At infinite dilution of component 2

$$\lim_{x_2 \rightarrow 0} \left[ \left( \frac{x_1}{x_1 + x_3} \right) \frac{\bar{v}_1}{RT} + \left( \frac{x_3}{x_1 + x_3} \right) \frac{\bar{v}_3}{RT} \right] = \frac{x_1 \bar{v}_1 + x_3 \bar{v}_3}{RT} = \frac{v}{RT} \quad (19)$$

Equation 18 then becomes

$$\ln \hat{\phi}_2^\infty = \int_\infty^v - \frac{1}{RT} \left( \frac{\partial P}{\partial x_2} \right)_{v,T}^\infty dV + \int_0^P \left[ \frac{v}{RT} - \frac{1}{P} \right] dP \quad (20)$$

The second integral of eq 20 corresponds to the fugacity coefficient of the mixed solvent and therefore

$$\ln \hat{\phi}_2^\infty = \frac{1}{RT} \left( \frac{\partial A}{\partial x} \right)_{v,T}^{r,\infty} + \ln \phi_s \quad (21)$$

where  $\phi_s$  is the fugacity of the mixed solvent.

If we perform a Taylor expansion on the Helmholtz energy derivative about the binary system ( $x_3 = 0$ ), we obtain

$$\left( \frac{\partial A}{\partial x_2} \right)_{v,T}^{r,\infty} = \left( \frac{\partial A}{\partial x_2} \right)_{v,T}^{r,\infty} \Big|_{x_3=0} + (x_3 - 0) \left[ \frac{\partial}{\partial x_3} \left( \frac{\partial A}{\partial x_2} \right) \right]_{v,T}^{r,\infty} \Big|_{x_3=0} \quad (22)$$

We have shown previously<sup>9</sup> that the first term on the right-hand side of the above equation (the binary solution term) can be approximated by

$$D + E\rho_1$$

If we further assume that the second term on the right-hand side can be approximated by  $Fx_3$ , then eq 22 can also be written as follows:

$$RT \ln \hat{\phi}_2^\infty = D + E\rho_1 + Fx_3 + RT \ln \phi_s \quad (23)$$

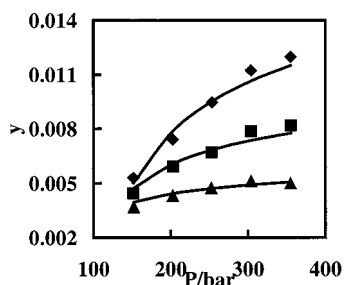
Substituting eq 23 into eq 7

$$RT \ln \left( \frac{H_{2,m}}{f_s} \right) = D + E\rho_1 + Fx_3 \quad (24)$$

where  $f_s = \phi_s P$  is the fugacity of the mixed solvent.

The use of eq 7 to obtain Henry's constant of a solid solute in a supercritical fluid is not straightforward, because the equilibrium fugacity ( $f_2$ ) is fixed at a nonzero value by the presence of the pure solid.<sup>8</sup> However, an effective Henry's constant can be defined by relaxing the infinite-dilution condition as

$$H_{2,m}^{\text{eff}} = f_2/y_2 \quad (25)$$



**Figure 4.** Solubility of benzoic acid in carbon dioxide + 5% hexane as a function of pressure. Data of Mendez-Santiago<sup>1</sup> at 308 K ( $\Delta$ ), 318 K ( $\blacksquare$ ), and 328 K ( $\blacklozenge$ ). The solid line represents calculations using eq 29.

where  $f_2$  is given by

$$f_2 = P_2^s \phi_2^s \exp \left[ \int_{P_2^s}^P \left( \frac{v_2}{RT} \right) dP \right] \approx P_2^s \exp \left[ \frac{v_2(P - P_2^s)}{RT} \right] \quad (26)$$

Combining eqs 24–26 leads to the following expression:

$$-RT \ln y_2 + RT \ln P_2^s + v_2(P - P_2^s) - RT \ln f_s = D + E\rho_1 + Fx_3 \quad (27)$$

Substituting  $E = y_2 P / P_2^s$ ,

$$RT \ln E = -D - E\rho_1 - Fx_3 + v_2(P - P_2^s) - RT \ln \left( \frac{f_s}{P} \right) \quad (28)$$

It can be assumed that the dominant terms in eq 28 are the density and the cosolvent concentration (see discussion below). The other three terms can, therefore, be combined into a single (constant) term to give

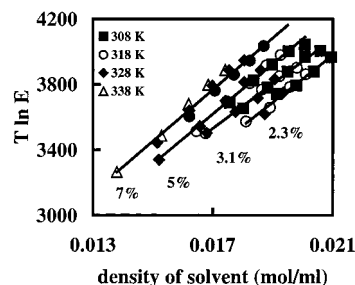
$$T \ln E = G + H\rho_1 + Jx_3 \quad (29)$$

where  $T$  is the temperature,  $E$  is the enhancement factor of solute 2,  $\rho_1$  is the pure solvent density (cosolvent and solute free), and  $x_3$  is the cosolvent mole fraction (solute free).

## Results

Equation 29 shows that, at a fixed cosolvent concentration, data over a range of temperatures can be reduced to a single line when plotted as  $T \ln E$  vs the density of the solvent. An example is illustrated in Figure 4 where the solubility of benzoic acid in  $\text{CO}_2$  + 5%  $n$ -hexane is plotted as a function of pressure. Note that all isotherms for a fixed cosolvent concentration can be represented within experimental error, so that the data are internally consistent.

Equation 29 was also used to model the solubility of benzoic acid in carbon dioxide +  $n$ -hexane at several hexane concentrations using the data of Mendez-Santiago.<sup>1</sup> We were able to correlate all data in this system with an average absolute deviation of 6.22%, which compares well with experimental uncertainty. The data covered a temperature range of 308–338 K, a pressure range of 15–35 MPa (or a solvent reduced density range of  $\sim 1$ –2), and a cosolvent concentration range of 2.3–7 mol %. The regressed values of the parameters in eq 29 are  $G = 1500$ ,  $H = 108\,154$ , and  $J = 39.91$  (with  $\rho$  in mol/ml,  $P$  in bar, and  $T$  in K). Figure 5 illustrates the



**Figure 5.** Solubility of benzoic acid in carbon dioxide +  $n$ -hexane mixtures as a function of the carbon dioxide density. Data of Mendez-Santiago<sup>1</sup> at temperatures between 308 and 328 K. The solid lines represent calculations using eq 29. Mole fractions of the cosolvent ( $n$ -hexane) are indicated next to the lines.

results and shows the ability of the model to correlate data over a range of temperatures, solvent densities, and cosolvent concentrations. Because all three parameters in eq 29 were found to be independent of the conditions (at least over the range of temperatures, pressures, and cosolvent concentrations studied), the model can be used to predict data.

In the derivation of eq 29, it was assumed that the last two terms of eq 28 could be essentially neglected. To verify this assumption, estimates of these two terms were obtained. Because only 1 order of magnitude estimates are needed, the fugacity of the mixed solvent ( $f_s$ ) was assumed to be approximately equal to the fugacity of carbon dioxide (at the same temperature and pressure) and calculated using an equation of state for carbon dioxide.<sup>19</sup> Also, the molar volume of the benzoic acid ( $v_2$ ) was assumed to be 96.5 mL/mol.<sup>20</sup> For each data point, the variation of the sum of these two terms was compared to the contribution of the other terms in eq 28. It was determined that the contribution of these two terms was approximately 2.9% of the total contribution. Approximating eq 28 with eq 29 does not, therefore, introduce any significant errors into the model.

## Conclusions

A simple theory of dilute solutions was used to model the solubility of numerous solids in supercritical fluids. It was demonstrated that, for most systems, solubility isotherms collapse to a single straight line when plotted as  $T \ln E$  vs the density of the pure solvent. This behavior was observed from a density of about half the critical density of the solvent to about twice its critical density. Modeling solid–fluid equilibria with this very simple theory provides several advantages over more conventional models such as equations of state. Only two parameters, independent of temperature and pressure, are needed to model data over a wide range of conditions. This allows for prediction of the solubility at conditions where limited experimental data are available. Furthermore, the linear behavior allows for the self-consistency of the data to be evaluated.

The binary dilute solution model was also extended to cosolvent mixtures in this work. This allows the correlation and extrapolation of limited data sets using a single equation. The new model requires three parameters, which were shown to be independent of pressure, temperature, and cosolvent concentration.

## Acknowledgment

Financial support for this work was provided by the National Science Foundation Fellowship Program, the



Environmental Protection Agency's STAR Fellowship Program, and Eastman Chemical Co.

## Nomenclature

$a$  = Helmholtz energy  
 $A, B, C, D$  = constants  
 $D', E', F$  = constants  
 $E$  = enhancement factor,  $y_2 P/P_2^s$   
 $f_i$  = fugacity of pure component  $i$   
 $\hat{f}_i$  = fugacity of component  $i$  in a mixture  
 $f_s$  = solvent fugacity  
 $H_{2,m}$  = Henry's constant of component 2 in a mixture  
 $P$  = pressure  
 $P_i^s$  = sublimation pressure of component  $i$   
 $R$  = ideal gas constant  
 $T$  = temperature  
 $V$  = total volume  
 $v$  = molar volume  
 $\bar{v}_i$  = partial molar volume of component  $i$   
 $x_i$  = mole fraction of component  $i$   
 $y_i$  = mole fraction solubility of component  $i$   
 $\phi_i$  = fugacity coefficient of component  $i$  in a mixture  
 $\phi_i$  = fugacity coefficient of pure component  $i$   
 $\rho_i$  = density of compound  $i$

## Subscripts/Superscripts

1 = solvent  
 2 = solute  
 3 = cosolvent  
 c = critical value  
 eff = effective value  
 s = solid phase  
 v = vapor phase  
 $\infty$  = infinite dilution

## Literature Cited

- (1) Mendez-Santiago, J. Extensions of the Theory of Dilute Solutions. Ph.D. Thesis, Georgia Institute of Technology, Atlanta, GA, 1999.
- (2) Smith, V. S.; Campbell, P. O.; Teja, A. S. Solubilities of Long-Chain Hydrocarbons in Carbon Dioxide. *Int. J. Thermophys.* **1996**, 17 (1), 23.
- (3) McHugh, M. A.; Seckner, A. J.; Yogan, T. J. High-Pressure Phase Behavior of Binary Mixtures of Octacosane and Carbon Dioxide. *Ind. Eng. Chem. Res.* **1984**, 23, 493.

- (4) Reverchon, E.; Russo, P.; Stassi, A. Solubilities of Solid Octacosane and Triacotane in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **1993**, 38, 458.
- (5) Chandler, K.; Pouillot, F. L. L.; Eckert, C. A. Phase Equilibria in Natural Gas Systems. 3. Alkanes in Carbon Dioxide. *J. Chem. Eng. Data* **1995**, 40, 6.
- (6) Schmitt, W. J.; Reid, R. C. The Solubility of Paraffinic Hydrocarbons and Their Derivatives in Supercritical Carbon Dioxide. *Chem. Eng. Commun.* **1988**, 64, 155.
- (7) Yau, J.-S.; Tsai, F.-N. *J. Chem. Eng. Data* **1993**, 38, 458.
- (8) Harvey, A. H. Supercritical Solubility of Solids from Near-Critical Dilute-Mixture Theory. *J. Phys. Chem.* **1990**, 94, 8403.
- (9) Mendez-Santiago, J.; Teja, A. S. The Solubility of Solids in Supercritical Fluids. *Fluid Phase Equilib.* **1999**, 158–160, 501.
- (10) Dobbs, J. M.; Johnston, K. P. Selectivities in Pure and Mixed Supercritical Fluid Solvents. *Ind. Eng. Chem. Res.* **1987**, 26, 1476.
- (11) Kurnik, R. T.; Reid, R. C. Solubility of Solid Mixtures in Supercritical Fluids. *Fluid Phase Equilib.* **1982**, 8, 93.
- (12) Schaeffer, S. T.; Zalkow, L. H.; Teja, A. S. Extraction of monocrotaline from *Crotalaria spectabilis* using supercritical carbon dioxide and carbon dioxide-ethanol mixtures. *Biotechnol. Bioeng.* **1989**, 34 (11), 1357.
- (13) Levelt Sengers, J. M. H. Dilute Mixtures and Solutions Near Critical Points. *Fluid Phase Equilib.* **1986**, 30, 31.
- (14) Levelt Sengers, J. M. H. Solubility Near the Solvent's Critical Point. *J. Supercrit. Fluids* **1991**, 4, 215.
- (15) Harvey, A. H. Semiempirical Correlation for Henry's Constant over Large Temperature Ranges. *AIChE J.* **1996**, 42 (5), 1491.
- (16) Harvey, A. H. Applications of Near-Critical Dilute Solution Thermodynamics. *Ind. Eng. Chem. Res.* **1998**, 37, 3080.
- (17) Furuya, T.; Teja, A. S. Krichevskii Parameters and the Solubility of Heavy  $n$ -alkanes in Supercritical Carbon Dioxide. *Ind. Eng. Chem. Res.* **2000**, submitted for publication.
- (18) Smith, V. S.; Teja, A. S. Solubilities of Diamondoids in Supercritical Solvents. *J. Chem. Eng. Data* **1996**, 41, 923.
- (19) Ely, J. F.; Haynes, W. M.; Bain, B. C. Isochoric ( $p, V_m, T$ ) measurements on  $\text{CO}_2$  and on  $(0.982\text{CO}_2 + 0.018\text{N}_2)$  from 250 to 330 K at pressures to 35 MPa. *J. Chem. Thermodyn.* **1989**, 21, 879.
- (20) Schmitt, W. J.; Reid, R. C. Solubility of Monofunctional Organic Solids in Chemically Diverse Supercritical Fluids. *J. Chem. Eng. Data* **1986**, 31, 204.

Received for review March 17, 2000

Accepted September 27, 2000

IE000339U