Modeling of the Solubility of Solid Solutes in Supercritical CO₂ with and without Cosolvent using Solution Theory

Qunsheng Li, Chongli Zhong, Zeting Zhang and Qingrong Zhou

Dept. of Chem. Eng., Beijing University of Chemical Technology, Beijing 100029, China

(Received 15 January 2004 • accepted 9 July 2004)

Abstract—In this work, regular solution theory was applied to study the solubility of solids in a supercritical fluid (SCF) with and without cosolvent, and a new model for binary and ternary systems was proposed. The activity coefficient can be obtained from the model and the solubility can then be calculated easily. For a binary system there are two adjustable parameters and for a ternary system, four adjustable parameters; the parameters are related to the interactions between molecules in solution. The proposed model was compared with the HSVDW1 and HSVDW2 models. The calculated results show that the proposed model is more accurate, and the AAD for the three models is 4.5%, 7.9% and 18.5%, respectively. The model was further used to correlate the solubility data of 2-naphthol in SC CO₂ with and without cosolvent measured by us before, and the overall AAD is 3.23%.

Key words: Supercritical Fluid, Solubility, Cosolvent, Solution Theory, Modeling

INTRODUCTION

In equilibrium study, a supercritical fluid (SCF) is normally regarded as a dense gas. Researchers [Hwang et al., 1995; Noh et al., 1995; Bush and Echert, 1998; Mendez-Santiago and Teja, 1999; Soave, 2000; Ashour et al., 2000; Chen et al., 1995; Valderrama and Silva, 2003; Li et al., 2003a, b; Baek et al., 2004], therefore, always use some related equations of state (EOS) or correlate the experimental data to establish empirical models [Chrustil, 1982; Gur-dial and Foster, 1991]. Since the density and some other physical properties of SCF are close to those of liquid [Zhu, 2000; Bam-berger et al., 1988], it can also be treated as liquid and be applied to the solution theory. Many solution theories have been proposed, such as the regular solution theory given by Hildebrand and Scat-chard in 1962 [Reid et al., 1987], which is used to calculate the activity of mixtures. Many researchers [Johnston and Eckert, 1989] have applied this theory and made great developments in this field.

Although it has been argued by several authors [Hu, 1982] that the use of regular solution theory to predict solute solubility is only qualitative, valuable insights into the equilibrium behavior of SCF mixtures can be obtained. There are many advantages of using the introduction suggested by Ziger and Eckert [1983]. For example, the introduction of the enhancement factor accounts for the effect of vapor pressure and provides qualitative information about the solute-solvent interaction. The introduction of the Hildebrand solubility parameter for the solute and solvent not only takes the size and nature of the molecules into consideration but also accounts for the strength of solute-solute and solvent-solvent intermolecular forces [Barton, 1983]. In this work the regular solution theory was used to establish a semi-empirical correlation, which shows good agreement with the experimental data.

THEORY

If an SCF is treated as a pseudo-liquid, solubility of solute in SCF can be studied by the solid-liquid equilibrium.

When the solid and liquid phases reach phase equilibrium, the chemical potential of solute in solid phase μ_i^s is equal to that in the liquid phase μ_i^l:

μ_i^l = μ_i^s

(1)

When the temperature changes from T to T+dT at constant pressure, the chemical potentials of the solute in the liquid and the solid phases are still equal.

μ_i^l + dμ_i^l = μ_i^s + dμ_i^s

(2)

Combining Eqs. (1) and (2), one obtains:

dμ_i^l = dμ_i^s

(3)

Therefore, the activity of the solute:

where a_i is the activity of the solute.

From thermodynamic theory, we have

(4)

Therefore

where n_i and n_j are the number of moles of component i and j, and μ_i^e is the chemical potentials of the solute in the liquid phase at the standard state.

Combining Eq. (4)-(6), one obtains

and

where ΔH is the heat that one mole pure solid solute melts and enters the solution with activity a_i. For dilute solution it approximately equals the melting enthalpy; therefore,

Key words: Supercritical Fluid, Solubility, Cosolvent, Solution Theory, Modeling

INTRODUCTION

In equilibrium study, a supercritical fluid (SCF) is normally regarded as a dense gas. Researchers [Hwang et al., 1995; Noh et al., 1995; Bush and Echert, 1998; Mendez-Santiago and Teja, 1999; Soave, 2000; Ashour et al., 2000; Chen et al., 1995; Valderrama and Silva, 2003; Li et al., 2003a, b; Baek et al., 2004], therefore, always use some related equations of state (EOS) or correlate the experimental data to establish empirical models [Chrustil, 1982; Gur-dial and Foster, 1991]. Since the density and some other physical properties of SCF are close to those of liquid [Zhu, 2000; Bam-berger et al., 1988], it can also be treated as liquid and be applied to the solution theory. Many solution theories have been proposed, such as the regular solution theory given by Hildebrand and Scat-chard in 1962 [Reid et al., 1987], which is used to calculate the activity of mixtures. Many researchers [Johnston and Eckert, 1989] have applied this theory and made great developments in this field.

Although it has been argued by several authors [Hu, 1982] that the use of regular solution theory to predict solute solubility is only qualitative, valuable insights into the equilibrium behavior of SCF mixtures can be obtained. There are many advantages of using the introduction suggested by Ziger and Eckert [1983]. For example, the introduction of the enhancement factor accounts for the effect of vapor pressure and provides qualitative information about the solute-solvent interaction. The introduction of the Hildebrand solubility parameter for the solute and solvent not only takes the size and nature of the molecules into consideration but also accounts for the strength of solute-solute and solvent-solvent intermolecular forces [Barton, 1983]. In this work the regular solution theory was used to establish a semi-empirical correlation, which shows good agreement with the experimental data.

THEORY

If an SCF is treated as a pseudo-liquid, solubility of solute in SCF can be studied by the solid-liquid equilibrium.

When the solid and liquid phases reach phase equilibrium, the chemical potential of solute in solid phase μ_i^s is equal to that in the liquid phase μ_i^l:

μ_i^l = μ_i^s

(1)

When the temperature changes from T to T+dT at constant pressure, the chemical potentials of the solute in the liquid and the solid phases are still equal.

μ_i^l + dμ_i^l = μ_i^s + dμ_i^s

(2)

Combining Eqs. (1) and (2), one obtains:

dμ_i^l = dμ_i^s

(3)

Therefore, the activity of the solute:

where a_i is the activity of the solute.

From thermodynamic theory, we have

(4)

Therefore

where n_i and n_j are the number of moles of component i and j, and μ_i^e is the chemical potentials of the solute in the liquid phase at the standard state.

Combining Eq. (4)-(6), one obtains

and

where ΔH is the heat that one mole pure solid solute melts and enters the solution with activity a_i. For dilute solution it approximately equals the melting enthalpy; therefore,
\[ d \ln a_i = \frac{\Delta H_i}{RT} dT \]  

and

\[ \Delta H_i = \Delta H_{i,n} + \Delta c_i (T - T_n) \]  

\[ \Delta c_i = c_i^L - c_i^S \]  

\[ a_i = c_i^L \gamma_i \]  

where \( \Delta H_i \) and \( \Delta H_{i,n} \) are the melting enthalpy at the solution temperature \( T \) and melting point \( T_n \), respectively. \( c_i^L \) and \( c_i^S \) are the heat capacity of solute in liquid and solid phases respectively, and \( \gamma_i \) is the activity coefficient of the solute.

Integrating Eq. (9) from melting point \( T_n \) to the solution (with activity \( a_i \)) temperature \( T \), we have

\[ \ln(x_i/y_i) = \frac{\Delta H_i}{RT (1 - T/T_n)} \int_{T_n}^{T} \frac{\Delta c_i (T_n - T)}{RT} dT + \Delta c_i \ln \frac{T}{T_n} \]  

Since the last two items of the right side of Eq. (13) are far smaller than the first one, it is reasonable to simplify Eq. (13) to:

\[ \ln(x_i/y_i) = -\frac{\Delta H_i}{RT (1 - T/T_n)} \int_{T_n}^{T} \frac{\Delta c_i (T_n - T)}{RT} dT \]  

Eq. (14) can be used to calculate the solubility, \( x_i \), while \( y_i \) can be calculated by using a solution theory.

By applying the regular solution theory, for a binary system one obtains:

\[ RT \ln y_i = V_i^L \phi_i^L (C_{1i} + C_{2i} - 2C_{12}) \]

\[ V_i^L = x_i V_i^L (x_i V_i^L + x_o V_o^L) \]

\[ C_{1i} = \Delta H_{i,n} - \Delta RT \ln \frac{RT}{T} \]

\[ C_{12} = \sqrt{C_{1i} C_{2i}} (1 - l_{12}) \]  

where

\( \Delta H_i \): evaporation enthalpy of the component \( i \);

\( l_{12} \): interaction parameters between molecules of solid and solvent;

While for ternary systems,

\[ RT \ln y_i = V_i^L \sum_{i=1}^{3} \sum_{j=1}^{3} (A_{ij} - A_{ij}/2) \phi_i \]

Q. Li et al.

\[ A_{ij} = (\delta_{ij} - \delta_i + 2 \delta_i \delta_j) \]

\[ \delta_i = \sqrt{C_{ii}} \]

\[ \phi_i = V_i^L x_i \sum_{j=1}^{3} (V_j^L x_j) \]

Since the solubility of solid solute in SCF is small, a solute +SCF system can be treated as dilute solution. Therefore, for a binary system of solute-SCF, we can assume:

(a) There is no phase change when SCF is transferred into ideal gas, therefore, \( \Delta H_i = 0 \), \( C_{1i} = -RT \ln \phi_i^L - \Delta RT \)

(b) \( V_i^L \) is related to \( V_i \) by D. H. Diger et al. [Hu, 1982] and it was recommended that: \( V_i^L = 1.02V_i \)

(c) For SCF we can approximately replace \( H_i \) by the melting enthalpy, \( H_{i,n} \). Thus \( C_{1i} = \Delta H_{i,n} - \Delta RT/V_i^L \)

(d) For the interaction parameter \( C_{12} \), we assume \( C_{12} = \sqrt{C_{1i} C_{2i}} (1 - l_{12}) \), and \( l_{12} = k_1/k_2 \), where \( k_1 \) and \( k_2 \) are adjustable parameters, which can be regressed by fitting the experimental data and they are related to the interactions between molecules in the solution.

For a ternary system of solute-SCF-cosolvent, the solubility of solid solute in SCF is also small, and \( x_i < x_o \), \( \phi_i = 0 \), so one approximately obtains

\[ RT \ln y_i = V_i^L (C_{1i} + C_{2i} \phi_i^L - 2C_{1i} \phi_i - 2C_{12} \phi_i + 2C_{2i} \phi_i + 3C_{12} \phi_i) \]

where

\( C_{12} = -RT (1 - l_{12}) \)

\( C_{i} = \sqrt{C_{ii} C_{j} (1 - l_{ij}(1 - l_{ij}))} \)

and

\( \delta_i^L \): the heat capacity of cosolvent;

\( \Delta H_{i,n} \): evaporation enthalpy of the component \( i \);

\( l_{ij} \): interaction parameters of solid and cosolvent molecules;

\( T_b \): the boiling temperature of cosolvent;

and \( k_1 \), \( k_2 \) are the parameters of the model, which are also related to the interactions between molecules in solution theoretically and can be regressed by fitting the solubility data with cosolvent.

Eq. (14) together with Eqs. (16) and (17) is the model proposed in this work.

### Table 1. Comparison of the models of this work with HSVDW1 and HSVDW2

<table>
<thead>
<tr>
<th>Solute</th>
<th>Cosolvent</th>
<th>T (K)</th>
<th>P (MPa)</th>
<th>Mole fraction of cosolvent</th>
<th>No. of data points</th>
<th>AAD %*</th>
<th>Data source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzoic acid</td>
<td>acetone</td>
<td>308</td>
<td>10.0-33.0</td>
<td>3.5</td>
<td>7</td>
<td>2.4</td>
<td>5.0</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>methanol</td>
<td>308</td>
<td>9.0-35.0</td>
<td>3.5</td>
<td>10</td>
<td>4.8</td>
<td>5.0</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>octane</td>
<td>308</td>
<td>10.0-30.0</td>
<td>3.5</td>
<td>5</td>
<td>3.0</td>
<td>12</td>
</tr>
<tr>
<td>2-Aminobenzoic acid</td>
<td>acetone</td>
<td>308</td>
<td>9.0-30.0</td>
<td>3.5</td>
<td>6</td>
<td>4.3</td>
<td>2.5</td>
</tr>
<tr>
<td>2-Aminobenzoic acid</td>
<td>methanol</td>
<td>308</td>
<td>9.0-30.0</td>
<td>3.5</td>
<td>6</td>
<td>1.2</td>
<td>5.5</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>n-pentane</td>
<td>308</td>
<td>12.0-35.0</td>
<td>3.5</td>
<td>6</td>
<td>2.4</td>
<td>21.0</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>octane</td>
<td>308</td>
<td>12.0-35.1</td>
<td>3.5-7.0</td>
<td>18</td>
<td>8.2</td>
<td>8.9</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>n-undecane</td>
<td>308</td>
<td>12.0-35.2</td>
<td>3.5</td>
<td>4</td>
<td>3.3</td>
<td>5.3</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.5</td>
<td>7.9</td>
<td>18.5</td>
</tr>
</tbody>
</table>

\[ * \text{AAD} = \frac{1}{N} \sqrt{\frac{\sum_{i=1}^{N} (y_i - y_i^{'})^2}{\sum_{i=1}^{N} y_i^{'}}} \times 100\% \]  

November, 2004