

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

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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 [Chrastil, 1982; Gurdial and Foster, 1991]. Since the density and some other physical properties of SCF are close to those of liquid [Zhu, 2000; Bamberger 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 Scatchard 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 correlation 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 .

$$\mu_i^s = \mu_i^l \quad (1)$$

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.

$$\mu_i^s + d\mu_i^s = \mu_i^l + d\mu_i^l \quad (2)$$

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

$$d\mu_i^s = d\mu_i^l \quad (3)$$

$$\text{Therefore } \left(\frac{\partial \mu_i^s}{\partial T}\right)_P dT = \left(\frac{\partial \mu_i^l}{\partial T}\right)_{P, a_i} dT + \left(\frac{\partial \mu_i^l}{\partial a_i}\right)_{T, P} da_i \quad (4)$$

where a_i is the activity of the solute.

From thermodynamic theory, we have

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P, n_i, n_j} = -S_i \quad (5)$$

$$\mu_i^l = \mu_i^{ol} + RT \ln a_i \quad (6)$$

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

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

$$-S_i^s dT = -\bar{S}_i^l dT + RT d \ln a_i \quad (7)$$

$$\text{and } \bar{S}_i^l - S_i^s = \Delta \bar{H}_i / T \quad (8)$$

where $\Delta \bar{H}_i$ 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,

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$$d \ln a_1 \approx \frac{\Delta H_f}{RT^2} dT \quad (9)$$

and

$$\Delta H_j = \Delta H_{f,m} + \Delta c_p (T - T_m) \quad (10)$$

$$\Delta c_{p1} = c_{p1}^L - c_{p1}^S \quad (11)$$

$$a_1 = x_1 \gamma_1 \quad (12)$$

where ΔH_j and $\Delta H_{f,m}$ are the melting enthalpy at the solution temperature T and melting point T_m , respectively. c_{p1}^L and c_{p1}^S are the heat capacity of solute in liquid and solid phases respectively, and γ_1 is the activity coefficient of the solute.

Integrating Eq. (9) from melting point T_m to the solution (with activity a_1) temperature T , we have

$$\ln(x_1 \gamma_1) = -\frac{\Delta H_{f,m}}{RT} \left(1 - \frac{T}{T_m}\right) + \frac{\Delta c_{p1}(T_m - T)}{RT} - \frac{\Delta c_{p1}}{R} \ln \frac{T_m}{T} \quad (13)$$

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:

$$\ln(x_1 \gamma_1) \approx -\frac{\Delta H_{f,m}}{RT} \left(1 - \frac{T}{T_m}\right) \quad (14)$$

Eq. (14) can be used to calculate the solubility, x_1 , while γ_1 can be calculated by using a solution theory.

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

$$\begin{aligned} RT \ln \gamma_1 &= V_1^L \varphi_2^2 (C_{11} + C_{22} - 2C_{12}) \\ \varphi_2 &= x_2 V_2^L / (x_1 V_1^L + x_2 V_2^L) \\ C_{ii} &= (\Delta H_{vi} - RT) / V_i^L \\ C_{12} &= \sqrt{C_{11} C_{22}} (1 - l_{12}) \end{aligned} \quad (15)$$

where

ΔH_{vi} : evaporation enthalpy of the component i ;
 l_{12} : interaction parameters between molecules of solid and solvent;

While for ternary systems,

$$RT \ln \gamma_1 = V_1^L \sum_{i=1}^3 \sum_{j=1}^3 (A_{i1} - A_{ij}/2) \varphi_i \varphi_j$$

$$\begin{aligned} A_{ij} &= (\delta_i - \delta_j) + 2l_{ij} \delta_i \delta_j \\ \delta_i &= \sqrt{C_{ii}}, \\ \varphi_i &= V_i^L x_i / \sum_{i=1}^3 (V_i^L x_i) \end{aligned} \quad (16)$$

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, $\Delta H_{i2} = 0$, $C_{22} = -RT/V_2^L = -RT\rho$

(b) V_1^L is related to V_1^S by D. H. Diger et al. [Hu, 1982] and it was recommended that: $V_1^L = 1.02V_1^S$

(c) For SCF we can approximately replace H_{v1} by the melting enthalpy, $\Delta H_{f,m}$. Thus $C_{11} = (\Delta H_{f,m} - RT) / V_1^L$

(d) For the interaction parameter C_{12} , we assume $C_{12} = \sqrt{C_{11} \cdot C_{22}} (1 - l_{12})$, and $l_{12} = k_1/\rho + k_2$, 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 $x_1 < x_3 < x_2$, $\varphi_1 \approx 0$, so one approximately obtains

$$RT \ln \gamma_1 = V_1^L (C_{11} + C_{22} \varphi_2^2 + C_{33} \varphi_3^2 - 2C_{12} \varphi_2 - 2C_{13} \varphi_3 + 2C_{23} \varphi_2 \varphi_3) \quad (17)$$

$$\begin{aligned} \text{where } C_{22} &= -RT\rho(1 - x_3) \\ C_{33} &= [\Delta H_{v3} - c_{p3}^L(T_b - T) - RT] / V_3^L \\ l_{12} &= k_1 / [\rho(1 - x_3)] + k_2 \\ l_{22} &= 0, C_{23} = \sqrt{C_{22} \cdot C_{33}} \\ C_{13} &= \sqrt{C_{11} C_{33}} (1 - l_{13}), l_{13} = k_3 / (\rho x_3) + k_4 \end{aligned}$$

and

c_{p3}^L : the heat capacity of cosolvent;
 ΔH_{vi} : evaporation enthalpy of the component i ;
 l_{13} : interaction parameters of solid and cosolvent molecules;
 T_b : the boiling temperature of cosolvent;

and k_3, k_4 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 HSDW1 and HSDW2

Solute	Cosolvent	T (K)	P (MPa)	Mole fraction of cosolvent	No. of data points	AAD %*			Data source
						this work	HSDW1	HSDW2	
Benzoic acid	acetone	308	10.0-33.0	3.5	7	2.4	5.0	7	15
Benzoic acid	methanol	308	9.0-35.0	3.5	10	4.8	5.0	32	15
Benzoic acid	octane	308	10.0-30.0	3.5	5	3.0	12	51	15
2-Aminobenzoic acid	acetone	308	9.0-30.0	3.5	6	4.3	2.5		15
2-Aminobenzoic acid	methanol	308	9.0-30.0	3.5	6	1.2	5.5		15
Phenanthrene	n-pentane	308	12.0-35.0	3.5	6	2.4	21.0	12.1	16
Phenanthrene	octane	308	12.0-35.1	3.5-7.0	18	8.2	8.9	8.5	16
Phenanthrene	n-undecane	308	12.0-35.2	3.5	4	3.3	5.3	18.8	16
Average						4.5	7.9	18.5	

$$* \text{AAD} = \frac{1}{N} \sum_{i=1}^N \left| \frac{y^{cal} - y^{exp}}{y^{exp}} \right| \times 100\%$$

Table 2. Comparison of the experimental and calculated solubility of 2-naphthol in pure SC CO₂ using the proposed model

T (K)	P (MPa)	ρ (mol/l)	X_1^{exp} ($\times 10^4$)	X_1^{cal} ($\times 10^4$)	AAD%
		$k_1=-3192.1$	$k_2=0.974$		
308.1	10.05	14.584	2.485	2.634	6.00
308.1	14.0	17.183	4.332	3.908	-9.80
308.1	18.0	18.648	5.086	4.923	-5.17
308.1	22.05	19.709	5.469	5.595	2.30
308.1	26.0	20.536	6.096	6.268	2.82
308.1	30.0	21.212	6.541	6.870	5.04
		$k_1=4283.1$	$k_2=1.121$		
318.1	10.05	10.34	1.481	1.538	3.85
318.1	14.0	15.065	4.701	4.239	-9.83
318.1	18.0	17.053	6.485	6.103	-5.89
318.1	22.05	18.377	7.721	7.682	-0.51
318.1	26.0	19.354	8.466	9.056	6.97
318.1	30.0	20.156	9.642	10.336	7.20
		$k_1=5627.6$	$k_2=1.045$		
328.1	10.05	7.337	1.158	1.166	0.72
328.1	14.0	12.739	4.408	4.281	-2.88
328.1	18.0	15.363	6.921	6.960	0.57
328.1	22.05	16.991	9.250	9.191	-0.64
328.1	26.0	18.147	11.38	11.11	-2.41
328.1	30.0	19.075	12.25	12.87	5.11
average					4.32

Table 4. Comparison of the experimental and calculated solubility of 2-naphthol in SC CO₂ with 3.6 mol% cosolvent of acetone using the proposed model

T (K)	P (MPa)	ρ (mol/l)	X_1^{exp} ($\times 10^4$)	X_1^{cal} ($\times 10^4$)	AAD%
		$k_3=-4413.7$	$k_4=-6.987$		
308.1	10.05	16.247	4.827	4.712	-2.38
308.1	14.0	17.849	5.854	5.815	0.67
308.1	18.0	18.929	6.354	6.678	5.10
308.1	22.05	19.762	7.055	7.420	5.17
308.1	26.0	20.423	8.156	8.059	-1.19
308.1	30.0	20.991	9.158	8.648	-5.57
		$k_3=-1969.7$	$k_4=-13.912$		
318.1	10.05	13.621	4.781	4.783	0.05
318.1	14.0	16.165	7.664	7.587	-1.00
318.1	18.0	17.587	9.772	9.651	-1.24
318.1	22.05	18.613	10.98	11.41	3.94
318.1	26.0	19.401	12.59	12.94	2.80
318.1	30.0	20.063	15.01	14.36	-4.33
		$k_3=7512$	$k_4=-40.923$		
328.1	10.05	9.931	3.788	3.747	-1.06
328.1	14.0	14.255	10.74	10.70	-0.41
328.1	18.0	16.143	15.10	15.53	2.87
328.1	22.05	17.406	18.70	19.59	4.77
328.1	26.0	18.339	22.25	23.09	3.78
328.1	30.0	19.105	29.01	26.33	-9.26
average					3.09

Table 3. Comparison of the experimental and calculated solubility of 2-naphthol in SC CO₂ with 3.6 mol% cosolvent of hexamethylene using the proposed model

T (K)	P (MPa)	ρ (mol/l)	X_1^{exp} ($\times 10^4$)	X_1^{cal} ($\times 10^4$)	AAD%
		$k_3=-14995.9$	$k_4=-17.038$		
308.1	10.05	16.167	7.333	7.359	0.36
308.1	14.0	17.649	8.839	8.715	-1.40
308.1	18.0	18.667	9.744	9.784	0.41
308.1	22.05	19.459	10.59	10.70	1.06
308.1	26.0	20.092	11.36	11.49	1.19
308.1	30.0	20.636	12.42	12.22	-1.59
		$k_3=4676.1$	$k_4=-22.696$		
318.1	10.05	13.808	5.800	5.789	-0.19
318.1	14.0	16.078	8.510	8.632	1.43
318.1	18.0	17.404	10.69	10.76	0.63
318.1	22.05	18.374	13.29	12.57	-5.39
318.1	26.0	19.124	13.77	14.15	2.77
318.1	30.0	19.755	15.46	15.61	0.96
		$k_3=4676.1$	$k_4=-22.696$		
328.1	10.05	10.539	3.125	3.232	3.46
328.1	14.0	14.307	8.927	8.307	-6.95
328.1	18.0	16.048	12.21	11.92	-2.31
328.1	22.05	17.234	14.60	14.677	0.53
328.1	26.0	18.118	17.75	17.64	-0.62
328.1	30.0	18.847	18.87	20.10	6.51
average					2.10

Table 5. Comparison of the experimental and calculated solubility of 2-naphthol in SC CO₂ with 3.6 mol% cosolvent of ethanol using the proposed model

T (K)	P (MPa)	ρ (mol/l)	X_1^{exp} ($\times 10^4$)	X_1^{cal} ($\times 10^4$)	AAD%
		$k_3=-17288.2$	$k_4=-19.708$		
308.1	10.05	17.011	18.21	18.56	1.96
308.1	14.0	18.54	21.73	21.22	-2.33
308.1	18.0	19.593	23.59	23.34	-1.05
308.1	22.05	20.413	25.27	25.17	-0.39
308.1	26.0	21.068	26.77	26.76	-0.05
308.1	30.0	21.633	27.68	28.21	1.94
		$k_3=-7293.8$	$k_4=-24.094$		
318.1	10.05	14.35	11.45	12.41	8.36
318.1	14.0	16.796	20.58	18.10	-12.07
318.1	18.0	18.196	23.57	22.27	-5.50
318.1	22.05	19.215	25.73	25.83	0.39
318.1	26.0	20	27.51	28.91	5.08
318.1	30.0	20.661	30.16	31.75	5.27
		$k_3=3109.2$	$k_4=-33.272$		
328.1	10.05	10.401	5.526	5.619	1.69
328.1	14.0	14.795	14.86	14.48	-2.59
328.1	18.0	16.682	21.59	20.38	-5.63
328.1	22.05	17.948	24.29	25.28	4.09
328.1	26.0	18.885	29.33	29.50	0.57
328.1	30.0	19.656	32.67	33.38	2.19
average					3.40

RESULTS AND DISCUSSION

In order to test the above model, experimental data were collected from the literature and compared with the results of the literature models, hard sphere Van der Waals 1 (HSVDW1) and hard sphere Van der Waals 2 (HSVDW2) [Dobbs et al., 1987; Dobbs et al., 1986]; the results are shown in Table 1. The density in Table 1 was calculated with the Petal-Teja (PT) EOS [Patal and Teja, 1982], which has been proven to be an excellent EOS for the calculation of density. From Table 1, it is clear that the proposed model shows much better accuracy than the other two models, with the average absolute deviation (AAD) of 4.5% against 7.9% and 18.5% for HSVDW1 and HSVDW2 models, respectively.

In our previous work, the solubility of 2-naphthol in CO₂ with and without cosolvent was measured. The experimental data and the correlated results with the proposed model are shown in Tables 2-5. Obviously, the new model works quite well, with the overall AAD of 3.23%.

Fig. 1 gives the experimental and the calculated solubility of 2-naphthol in CO₂ with and without cosolvent at 308.1 K. It is evident that the cosolvent can enhance the solubility of 2-naphthol. Ethanol shows the largest enhancement, which may be evidence that the interactions between the molecules of ethanol and 2-naphthol are the strongest ones among them.

CONCLUSION

A new model for the correlation of the solid solubility in SCF with and without cosolvent was proposed based on the regular solu-

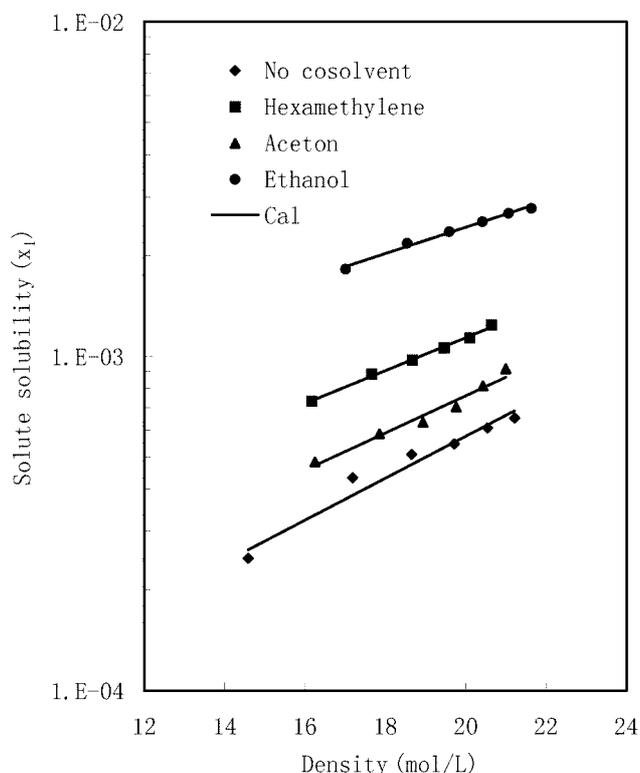


Fig. 1. Solubility of 2-naphthol in CO₂ with 3.6% mol cosolvent or without cosolvent at 308.1 K.

November, 2004

tion theory in this work. The new model simply introduces some approximations suitable to the features of solid +SCF systems. The results show that the new model gives good correlative accuracy for both binary and ternary systems, which may be useful for the reproduction of the solubility of solids in SCF with and without cosolvent.

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NOMENCLATURE

a	: activity
C	: energy density [J/m ³]
c _p	: heat capacity [J/(mol·K)]
k _i	: (i=1~4) Model parameters
ΔH	: melting enthalpy [J/mol]
l	: binary interaction parameter
M	: molecular weight [kg/kmol]
n	: number of moles
P	: system pressure [Pa]
R	: gas constant [J/(mol·K)]
S	: entropy [J/(mol·K)]
T	: system temperature [K]
V	: molar volume [m ³ /mol]
x	: molar fraction of liquid phase
y	: molar fraction of supercritical phase

Greek Letters

γ	: fugacity coefficient
δ	: solubility parameters [MPa ^{1/2}]
μ	: chemical potential [J/mol]
ρ	: density [mol/m ³]
φ	: volume fraction

Subscripts

b, m	: boiling point and melting point, respectively
i, j	: component i and j
1, 2, 3	: solute, SCF, cosolvent component, respectively

Superscripts

cal	: calculated value
exp	: experimental value
L, S	: liquid and solid phase, respectively
-	: mixture property

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