

A new model for predicting solute solubility in supercritical fluids based on the Wilson equation

Baohua Wang, Qunsheng Li[†], Zeting Zhang, Jinmiao Yang* and Yancheng Liu*

College of Chinese Pharmacy, Beijing University of Chinese Medicine and Pharmacy, Beijing, China, 100029

*College of Chemical Engineering, Beijing University of Chemical Technology, Beijing, China, 100029

(Received 20 June 2005 • accepted 20 September 2005)

Abstract—In this work, a new model based on the Wilson solution theory was proposed for predicting the solubility of solids in supercritical fluid (SCF) with and without cosolvent(s) of binary and ternary systems via computation of activity coefficients. For binary systems the model contains two adjustable parameters, while for ternary systems there are four adjustable parameters. The calculated results of the proposed model were compared with that of the literature models, and it is shown that the proposed model is a more accurate one.

Key words: Supercritical Fluid, Solubility, Cosolvent, Wilson Equation, Modeling

INTRODUCTION

In studies on the phase equilibrium of supercritical extraction, it is a meaningful work to build thermodynamics model of solid solute in supercritical fluid (SCF) exactly in order to evaluate the solubility of solid materials of interest. In the solubility study of supercritical fluid (SCF), the fluid is normally regarded as a dense gas. Researchers [Hwang et al., 1995; Noh et al., 1995; Yoo et al., 1997; Bush and Eckert, 1998; Mendez-Santiago and Teja, 1999; Soave, 2000; Ashour et al., 2000; Chen et al., 1995; Kim et al., 2002; 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], SCF can also be treated as liquid and be modeled according 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 achieved great developments in this field.

Although several authors [Hu, 1982] have argued that the use of regular solution theory to predict solute solubility is only qualitative, valuable insights into the equilibrium behaviors of SCF mixtures could be obtained. There are many advantages of using the correlation suggested by Ziger and Eckert [1983]. For example, the enhancement factor in the correlation 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. In our previous work [Li et al., 2003a, b, 2004], the regular solution theory was used to establish semi-empirical correlations, which yielded

good agreement with experimental data. In this work, we will use the Wilson Equation, which is appropriate to the normalized liquid, to predict solute solubilities in SCF; thereby, a new solubility model for SCF CO_2 is obtained. Compared with our experimental data and literature data, it is demonstrated that the model proposed has fewer adjustable parameters and is more accurate.

MODEL DEVELOPMENT

1. Derivation of Solubility Equation

In order to calculate the activity coefficient, γ of a solid solute in a liquid solvent, it is needed to first predict the solubility of solid solute in liquid by solid-liquid equilibrium theory. In what follows, it is denoted with (1) as the solvent, and (2) the solid component. It is assumed that the standard state corresponds to a pure liquid at the temperature and pressure of the system, and the solubility of solvent (1) in solid (2) is negligibly small. When the equilibrium of pure solid and liquid solution is reached, one has

$$f^s = \gamma_2 x_2 f^L \quad (1)$$

where f^s is the fugacity of pure solid; f^L is the fugacity of pure liquid at the temperature and pressure of the system; x_2 is the equilibrium concentration of solid solute in liquid solution, which is also the solubility in mole fraction; and γ_2 is activity coefficient of solid solute in liquid solution. Rearranging Eq. (1) one has

$$x_2 = f^s / \gamma_2 f^L \quad (2)$$

In the equation above, the ratio of fugacity, f^s/f^L , can be calculated by the following equation

$$\ln \frac{f^s}{f^L} = \frac{\Delta H_f}{R T_f} \left(\frac{T_f}{T} - 1 \right) - \frac{\Delta C_p}{R} \left(\frac{T_f}{T} - 1 \right) + \frac{\Delta C_p}{R} \ln \frac{T_f}{T} \quad (3)$$

where $\Delta C_p = C_p^L - C_p^s$; T_f is the temperature at the triple point; and ΔH_f is the melting heat at the triple point. Eq. (3) can be further simplified as follows. For most materials of interest, there are only little differences in their triple points and normal melting points, so T_f can be replaced with normal melting point T_f , and ΔH_f be replaced with melting heat ΔH_f at melting temperature. On the right side of

[†]To whom correspondence should be addressed.

E-mail: liqs@mail.buct.edu.cn

the equation, the first part is dominant, while the remaining two terms are canceled with each other. Thus Eq. (3) can be written as

$$\ln \frac{f^L}{f^s} = \frac{\Delta H_f}{RT_f} \left(\frac{T_f}{T} - 1 \right) \quad (4)$$

Substituting Eq. (4) into Eq. (2) one has

$$x_2 = \frac{1}{\gamma_2} \exp \left[- \frac{\Delta H_f}{RT} \left(\frac{T_f}{T} - 1 \right) \right] \quad (5)$$

Therefore,

$$\ln x_2 + \ln \gamma_2 = \frac{\Delta H_f}{RT_f} \left(1 - \frac{T_f}{T} \right) \quad (6)$$

Eq. (6) is used to calculate the solubility of solid solute in liquid. If the activity coefficient γ_2 can be obtained, the solubility x_2 can be calculated.

2. Derivation of Activity Coefficient Equation

Generally, the correlative equation of activity coefficient contains more than one system characteristic parameter, which should be evaluated by using experimental data. To get a better activity coefficient equation, only if the characteristic parameter is appropriate can the activity coefficient be predicted accurately. The Wilson equation, which is applied widely for binary and more systems, is obtained in terms of the local composition concept. It only needs two interaction parameters for binary system so as to forecast the phase equilibrium for a ternary system and so on, which is different from other equations that need more parameters.

2-1. Binary System

The Wilson equation is generalized on the base of the Flory-Huggins equation at first:

$$G^E/RT = -x_1 \ln(x_1 + A_{21}x_2) - x_2 \ln(x_2 + A_{12}x_1) \quad (7)$$

Using a standard thermodynamics method, it can be shown that the activity coefficient correlative equation is given by

$$G^E/RT = - \sum_{i=1}^K x_i \ln \left(\sum_{j=1}^K A_{ji} x_j \right) \quad (8)$$

and

$$\ln \gamma_i = 1 - \ln \sum_{j=1}^K A_{ji} x_j - \sum_{j=1}^K \left(A_{ji} x_j / \sum_{k=1}^K A_{kj} x_k \right) \quad (9)$$

This equation is applied to binary systems and so on. For a binary system, the Wilson equation is as follows:

$$\ln \gamma_2 = - \ln(A_{12}x_1 + x_2) + x_1 \left[\frac{A_{12}}{x_2 + A_{12}x_1} - \frac{A_{21}}{A_{21}x_2 + x_1} \right] \quad (10)$$

where A_{12} , A_{21} are binary interaction parameters given by

$$A_{12} = \frac{V_1^L}{V_2^L} \exp \left[- \frac{(\lambda_{12} - \lambda_{22})}{RT} \right] \quad \text{and} \quad A_{21} = \frac{V_2^L}{V_1^L} \exp \left[- \frac{(\lambda_{21} - \lambda_{11})}{RT} \right]$$

2-2. Ternary System

For a ternary system with cosolvent (component 3), if, $A_{ii}=1$ one has

$$\begin{aligned} \ln \gamma_2 = & - \ln(x_1 A_{12} + x_2 A_{21} + x_3 A_{32}) + 1 - \frac{x_1 A_{21}}{x_1 + x_2 A_{21} + x_3 A_{32}} \\ & - \frac{x_2}{x_1 A_{12} + x_2 + x_3 A_{32}} - \frac{x_3 A_{23}}{x_1 A_{13} + x_2 A_{23} + x_3} \end{aligned} \quad (11)$$

A_{23} and A_{32} are interaction parameters of solid solute and cosolvent. For the present case, A_{13} and A_{31} reflect the interactions of solvent (1) and cosolvent (3). Physically, it is expected that the interactions between cosolvent (3) and solid (2) as well as solvent (1) and solid (2) are stronger than that between solvent (1) and cosolvent (3), and hence we assume $A_{13}=A_{31}\approx 0$ in Eq. (11), which leads to the following equation:

$$\begin{aligned} \ln \gamma_2 = & - \ln(x_1 A_{12} + x_2 + x_3 A_{32}) + 1 - \frac{x_1 A_{21}}{x_1 + x_2 A_{21}} \\ & - \frac{x_2}{x_1 A_{12} + x_2 + x_3 A_{32}} - \frac{x_3 A_{23}}{x_2 A_{23} + x_3} \end{aligned} \quad (12)$$

The validity of the above assumption will be verified by the predictive ability of the measured thermodynamic variables with the model. From the equation above, we see that the calculation of activity coefficient of ternary system is calculated on the base of interaction parameters of solvent and solid (component 1 and 2) for a binary system (without cosolvent), i.e., to calculate interaction parameters of cosolvent and solid (component 2 and 3) using the results of Eq. (12).

3. The Calculation of Infinite Dilute Activity Coefficient

3-1. Binary System

Analyzing binary interaction parameters A_{12} and A_{21} yields

$$A_{12} = \frac{V_1^L}{V_2^L} \exp \left[- \frac{(\lambda_{12} - \lambda_{22})}{RT} \right] = \frac{\rho_2}{\rho_1} \exp \left[- \frac{(\lambda_{12} - \lambda_{22})}{RT} \right] = \frac{1}{\rho_1} * G_{12}(T) \quad (13)$$

$$\text{where } G_{12}(T) = \rho_2 \exp \left[- \frac{(\lambda_{12} - \lambda_{22})}{RT} \right].$$

In the same way one has

$$A_{21} = \frac{\rho_1}{\rho_2} \exp \left[- \frac{(\lambda_{21} - \lambda_{11})}{RT} \right] = \rho_1 * G_{21}(T) \quad (14)$$

Because the amount of solid component 2 is negligibly small in the mixture, it can be assumed that $\rho_1=\rho$. Thus

$$\ln \gamma_2^\infty = - \ln \frac{G_{12}(T)}{\rho} - \rho * G_{21}(T) + 1 \quad (15)$$

That is

$$\ln \gamma_2^\infty = \ln \rho - \rho * G_{21}(T) - \ln[G_{12}(T)] + 1 \quad (16)$$

Standardized form is as follows:

$$y = \ln(x) - G_{21} * x - \ln(G_{12}) + 1 \quad (17)$$

where $y=\ln \gamma_2^\infty$, $x=\rho$.

From Eq. (6), one has

$$\ln \gamma_2 = \frac{-\Delta H_f}{R} \left(\frac{1}{T} - \frac{1}{T_f} \right) - \ln(x_2) \quad (18)$$

From the equation above, $\ln \gamma_2$ can be obtained by the data of solubility x_2 at different temperatures and pressures.

Because the solubility of solid solute in SC CO₂ is negligibly small, the solution can be viewed as infinite dilute solution. As a result, the activity coefficient γ_2 can be thought of as an infinite dilute activity coefficient γ_2^∞ . The $\ln \gamma_2$ obtained from Eq. (18) at different temperature and pressure is equal to y in Eq (17). So binary interaction parameters G_{12} and G_{21} can be obtained by non-linear regression based on Eq. (17).

3-2. Ternary System

Eq. (12) could be rewritten as the following:

$$\ln \gamma_2 = -\ln(x_1 A_{12} + x_2 + x_3 A_{32}) + 1 - \frac{x_1 A_{21}}{x_1 + x_2 A_{21}} - \frac{x_2}{x_1 A_{12} + x_2 + x_3 A_{32}} - \frac{x_3 A_{23}}{x_2 A_{23} + x_3}$$

where

$$A_{23} = \frac{V_2^l}{V_3^l} \exp\left[-\frac{(\lambda_{23} - \lambda_{33})}{RT}\right] = \frac{\rho_3}{\rho_2} \exp\left[-\frac{(\lambda_{23} - \lambda_{33})}{RT}\right] = \rho_3 * G_{23}(T)$$

$$\text{and } A_{32} = \frac{1}{\rho_3} * G_{32}(T).$$

In the same way, we treat a binary system as a infinite dilute system in view of the solid solute, i.e., $x_2 \rightarrow 0$ and $x_1 + x_3 \rightarrow 1$, one has

$$\ln \gamma_2 = -\ln(x_1 A_{12} + x_3 A_{32}) + 1 - A_{21} - A_{23} \quad (19)$$

That is

$$\ln \gamma_2 = -\ln\left(x_1 \frac{G_{12}}{\rho_1} + x_3 \frac{G_{32}}{\rho_3}\right) + 1 - \rho_1 G_{21} - \rho_3 G_{23} \quad (20)$$

Standardized form is as follows:

$$y = 1 - G_{21}x - \rho_3 G_{23} - \ln\left(x_1 \frac{G_{12}}{x} + \frac{x_3 G_{32}}{\rho_3}\right) \quad (21)$$

In the same way, we assume that $y = \ln \gamma_2$, $x = \rho$ and $\rho \approx \rho_1$.

Because x_1 , x_3 , ρ_3 , G_{12} and G_{21} are all known, binary interaction parameters G_{23} and G_{32} can be obtained by a non-linear regression procedure.

EXPERIMENTAL

The experimental setup is shown in Fig. 1. We used the method of flowing to measure the solubility of solid in supercritical CO_2 with cosolvent. In experiments, CO_2 from a steel bottle was compressed to a certain pressure via a compressor 1 (NOVA 2A004) and its pressures were controlled to the desired range by a pressure regulator. After adjusting, the gas CO_2 flowed into mixer 3, in which it was mixed with the cosolvent that was provided by high-pressure

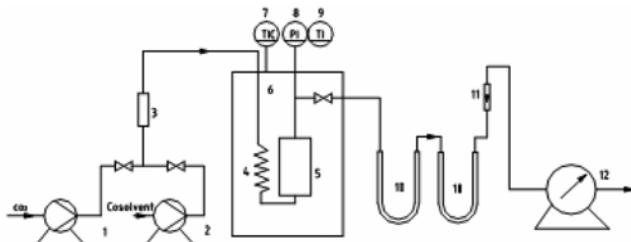


Fig. 1. Flow sheet for solubility measurements in SCF with and without cosolvent.

- | | |
|--|---------------------------|
| 1. Cosolvent pump | 7. Temperature controller |
| 2. High-pressure pump | 8. Manometer |
| 3. Mixer | 9. Thermometer |
| 4. Pre-heating equipment | 10. Sample collector |
| 5. Equilibrium pool | 11. Rotor flowmeter |
| 6. Container with constant temperature | 12. Wet-gas flowmeter |

measuring pump 2 (BACKMAN MODEL100A). Then, the mixture flowed into the extractive column from the bottom via a pipe with heating electric-wire. The function of the electric-wire is to keep supercritical CO_2 to be at certain temperature so as to make cosolvent exist at the non-liquid state. It is necessary to keep extractive column in a container with constant temperature (type CS503 of Chongqing Yinhe experiment equipment Co. Ltd, China), which could make the supercritical mixing gas contact with the solid solute for an effective extractive mass transfer [Chun et al., 1996]. After reaching equilibrium, the solute and solvent is discharged from the top of extractive column. Afterwards, the pressure of the solute and solvent was decreased to the common pressure by a decreasing valve. Within the two U-glass pipes in series, the solid solute is separated out of the deposit, while CO_2 and other remaining gas cosolvent were discarded through rotor and wet-gas flowmeter to the air, in which the rotor flowmeter is used to keep the flow rates of CO_2 stable.

Table 1. Comparison of solubility calculation for benzoic acid (without cosolvent) by the present model

T (K)	P (MPa)	Parameter		x_2^{exp} ($\times 10^3$)	x_2^{cal} ($\times 10^3$)	AAD%
		G_{12}	G_{21}			
308	12	0.00146	0.30307	1.25	1.274	1.92
308	16	0.00146	0.30307	2.19	2.220	1.37
308	20	0.00146	0.30307	2.53	2.382	5.85
308	24	0.00146	0.30307	2.81	2.823	0.46
308	28	0.00146	0.30307	3.03	3.272	7.99
323	13	0.00304	0.28833	1.03	1.186	15.4
323	15	0.00304	0.28833	1.80	1.686	6.11
323	16	0.00304	0.28833	2.08	1.934	7.08
323	20	0.00304	0.28833	3.34	2.921	12.5
323	25	0.00304	0.28833	4.11	4.172	1.54
323	30	0.00304	0.28833	4.92	5.455	10.9

Note: otherwise noted, $AAD = \frac{1}{N} \sum_{i=1}^N \left| \frac{x_i^{\text{cal}} - x_i^{\text{exp}}}{x_i^{\text{exp}}} \right| \times 100$, and for the present case the total average error of solubility of benzoic acid without cosolvent is 8.115%.

Table 2. Comparison of solubility calculation for benzoic acid with ethanol as cosolvent

T (K)	P (MPa)	Parameter		x_2^{exp} ($\times 10^3$)	x_2^{cal} ($\times 10^3$)	AAD%
		G_{12}	G_{21}			
308	13	0.14948	-0.0242	7.10	7.444	4.84
308	16	0.14948	-0.0242	8.83	8.545	3.23
308	20	0.14948	-0.0242	10.5	10.239	2.86
308	25	0.14948	-0.0242	11.6	11.417	1.32
308	30	0.14948	-0.0242	12.0	12.354	3.04
323	12	0.08409	-0.01944	4.63	5.366	15.8
323	16	0.08409	-0.01944	9.17	7.935	13.4
323	20	0.08409	-0.01944	12.8	11.143	13.0
323	25	0.08409	-0.01944	13.7	13.809	0.647
323	30	0.08409	-0.01944	14.7	16.741	13.9

Note: the total average error of solubility of benzoic acid with ethanol as cosolvent is 7.23%.

Table 3. Comparison of solubility calculation for benzoic acid with propanol as the cosolvent

T (K)	P (MPa)	Parameter		x_2^{exp} ($\times 10^3$)	x_2^{cal} ($\times 10^3$)	AAD%
		G_{12}	G_{21}			
308	13	0.15376	-0.01485	7.10	7.444	4.84
308	16	0.15376	-0.01485	8.83	8.545	3.23
308	20	0.15376	-0.01485	10.5	10.239	2.86
308	25	0.15376	-0.01485	11.6	11.417	1.32
308	30	0.15376	-0.01485	12.0	12.354	3.04
323	13	0.12317	-0.02505	5.95	6.502	9.27
323	16	0.12317	-0.02505	8.32	8.131	2.22
323	18	0.12317	-0.02505	10.8	9.688	10.4
323	25	0.12317	-0.02505	13.9	13.526	2.55
323	30	0.12317	-0.02505	15.0	16.117	7.16

Note: the total average error of solubility of benzoic acid with propanol as cosolvent is 7.35%.

Table 4. Comparison of solubility calculation for benzoic acid at 50 °C and 323 K with butanol and pentanol as the cosolvents

Cosolvent	P (MPa)	Parameters		x_2^{exp} ($\times 10^3$)	x_2^{cal} ($\times 10^3$)	AAD%
		G_{23}	G_{32}			
Butanol	16	0.1969	-0.03113	8.95	9.365	4.64
	20	0.1969	-0.03113	12.6	11.862	5.86
	25	0.1969	-0.03113	14.0	13.642	2.42
	30	0.1969	-0.03113	14.8	15.349	4.06
Note: the total average error of solubility of benzoic acid with butanol as cosolvent is 4.24%.						
Pentanol	16	0.25312	-0.02908	9.44	9.742	3.24
	20	0.25312	-0.02908	12.3	11.812	3.81
	25	0.25312	-0.02908	13.4	13.108	1.89
	30	0.25312	-0.02908	13.8	14.167	2.66
Note: the total average error of solubility of benzoic acid with pentanol as cosolvent is 2.90%.						

Table 5. Comparison of experimental and calculated solubility data with the present model for n-hexadecane in SC CO₂

Cosolvent	T (K)	G_{12}	G_{21}	G_{23}	G_{32}	P (MPa)	ρ	$x_2 \times 10^3$		AAD%							
								Experimental data	Calculated data								
Without	308	0.00033	0.36747			9.20	15.74	1.46	1.385	5.14							
								11.38	17.31	6.95							
								13.40	18.26	3.97							
								15.38	18.70	2.12							
								16.55	19.00	2.92							
								17.50	19.25	4.02							
								20.37	19.64	5.90							
Average								4.43									
Without	318	0.00447	0.24251			8.55	6.189	1.06	0.984	7.17							
								11.34	13.82	1.87							
								13.30	15.68	7.86							
								15.38	16.82	2.60							
								17.48	17.69	1.86							
								20.13	18.36	2.40							
								3.96									
Without	323	0.00089	0.33919			8.55	5.657	0.41	0.394	3.90							
								11.27	11.89	6.30							
								13.38	14.89	2.60							
								15.44	16.14	5.17							
								17.48	17.20	0.17							
								20.06	17.98	1.42							
								8.73									
Average								3.26									
Total average								3.89									

COMPARISON OF CALCULATED RESULTS OF LIQUID MODEL WITH DATA

1. The Calculation of the Experimental Data

In our experiments, the solubility of benzoic acid in SC CO₂ without cosolvent and with cosolvent of ethanol, propanol, butanol, pen-

tanol, etc. was measured. The concentrations of a component were reported by using molar fraction of species i which is defined as

$$x_i = \frac{\text{moles of species } i}{\text{Total moles of mixture}} \quad (22)$$

Using the liquid model proposed above, the solubility of ben-

Table 6. Comparison of the model results in this work and in literature for n-hexadecane

Model	Character	Numbers of parameters	AAD/%		
			308 (K)	318 (K)	323 (K)
Model in this work	Correlative	2	4.43	3.96	3.26
Model 1 [Yau et al., 1992]	Correlative	2	14.69	8.00	4.15
Model 2 [Yau et al., 1992]	Correlative	3	13.49	9.49	6.99
Model 3 [Yau et al., 1992]	Correlative	3	16.94	4.37	8.01

Table 7. Comparison of experimental and calculated solubility data by the present model for eicosanoic acid in SC CO₂

Cosolvent	T/K	G ₁₂	G ₂₁	G ₂₃	P/MPa	ρ	$x_2 \times 10^3$		AAD%
							Experimental data	Calculated data	
Without	308.2	7.76×10^{-6}	0.4776		7.171	17.54	0.232	0.244	5.17
					13.85	18.33	0.359	0.342	4.74
					16.30	18.96	0.469	0.446	4.90
					18.71	19.51	0.568	0.565	0.53
					20.95	19.86	0.623	0.656	5.30
					20.37	19.64	4.95	4.658	5.90
Average									4.42

Table 8. Comparison of the model results in this work and in literature for eicosanoic acid

Model	Character	Numbers of parameters	AAD/%
Model in this work	Correlative	2	4.42
Model [Yau et al., 1994]	Correlative	3	15.17

zoic acid is calculated, and the results of experimental and calculated results are shown in Tables 1-4. It is seen from the tables that the new model works quite well.

2. The Verification of Literature Data to the Model in this Work

In order to verify the correction of the model generalized in this work, we use the data published in the literature [Yau et al., 1992; 1994; Dobbs et al., 1987]. Tables 5, 7 and 9 show the comparison of experimental data and literature data of solubility with n-hexadecane, eicosanoic acid, benzoic acid separately. We see that the error is less than 5%. Tables 6, 8 and 10 show the precision com-

parison of literature model and the model in this work. Again, we see that the model in this work is better than the literature model.

In order to compare more clearly, the experimental data and calculated data in this work are compared in Figs. 1 and 2 with n-hexadecane in SC CO₂ and with benzoic acid at 308 K (with cosolvent of 3.5% methanol (mol/mol)), respectively. From the figures, we see that it is in accordance with calculated and experimental data, and the precision of the model in this work is better than that of the literature model.

CONCLUSION

An “expanded liquid” model was developed for predicting the solubility of solid solute, where the activity coefficient is obtained via the Wilson Equation through a regression procedure. Based on 46 data points of 8 materials, it is demonstrated that the relative error between experimental data and the calculated results by the model

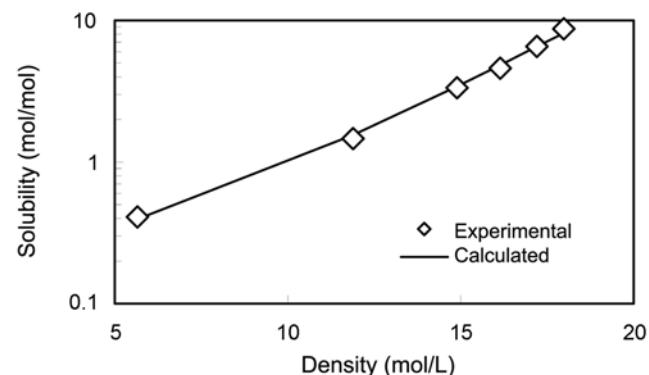


Fig. 2. Comparison of experimental and calculated solubility data with the present model for n-hexadecane in SC CO₂ at 323 K.

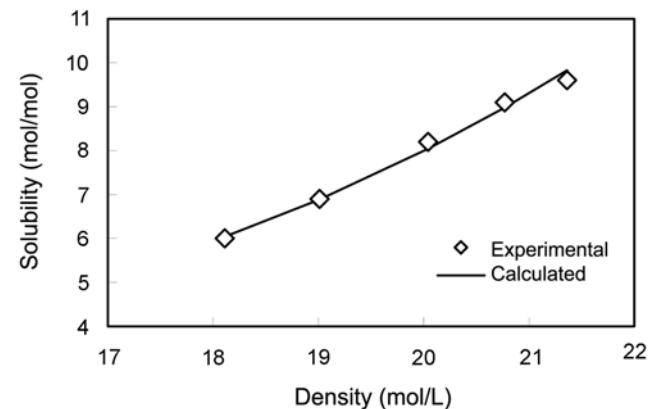


Fig. 3. Comparison of experimental and calculated solubility data with the present model for benzoic acid in SC CO₂ at 308 K (with the cosolvent of 3.5% methanol in mol/mol).

Table 9. Comparison of experimental and calculating solubility data with the present model for benzoic acid in SC CO₂

Cosolvent	T (K)	G ₁₂	G ₂₁	G ₂₃	G ₃₂	P (MPa)	ρ	$x_2 \times 10^3$		AAD%
								Experimental data	Calculating data	
Without	308	0.00146	0.30307			12	17.46	1.25	1.274	1.92
						16	18.81	2.19	2.22	1.37
						20	19.67	2.53	2.382	5.85
						24	20.34	2.81	2.823	0.46
						28	20.92	3.03	3.272	7.99
Average										3.52
Acetone 3.5%	308			0.13494	-0.01795	10	17.23	3.34	3.416	2.28
						12	18.04	3.90	3.916	0.41
						15	18.81	4.49	4.449	0.91
						20	19.79	5.37	5.214	2.91
						25	20.49	5.92	5.819	1.71
						33	21.33	6.4	6.606	3.22
Average										1.9
Methanol 3.5%	308			0.10137	-0.03417	9	16.52	4.8	4.81	0.252
						12	18.11	6.0	6.04	0.655
						15	19.01	6.9	6.89	0.016
						20	20.04	8.2	8.04	1.97
						25	20.77	9.1	8.98	1.33
						30	21.36	9.6	9.83	2.38
Average										1.12
Octane 3.5%	308			0.23945	-0.0046	10	16.29	2.9	3.031	4.52
						15	17.60	4.31	4.026	6.59
						25	18.99	5.55	5.468	1.48
						30	19.45	5.82	6.057	4.07
Average										4.16

Table 10. Comparison of the model results in this work and in literature for benzoic acid

Model	Character	Numbers of parameters	AAD/%		
			Acetone	Methanol	n-Octane
Model in this work	Correlative	2	1.90	1.12	4.16
Model 1 [Dobbs et al., 1987]	Correlative	3	5.0	12.0	2.5
Model 2 [Dobbs et al., 1987]	Predictive		7.0	32.0	51.0

is less than 5%, even less than 2% in some cases, indicating that the model in this work has higher precision than the model in the literature. Moreover, the model contains only two parameters in order to calculate the solubility of a ternary system, which is less than the model of literature with 4 parameters.

ACKNOWLEDGMENT

The financial support of the Ministry of Education of China (Contract: 00017) and the Ministry of Science and Technology of China (Contract: G2000048) is greatly appreciated.

NOMENCLATURE

f : fugacity [Pa]

January, 2006

ΔH : melting enthalpy [J/mol]

P : system pressure [Pa]

R : gas constant [J/(mol·K)]

T : system temperature [K]

V : molar volume [m³/mol]

x : molar fraction

Greek Letters

γ : fugacity coefficient

ρ : density [mol/m³]

Λ : binary interaction parameters

Superscripts

cal : calculated value

exp : experimental value

L, S : liquid and solid phases, respectively

Subscripts

i, j : component i and j

1, 2, 3 : SCF, solute, cosolvent components, respectively

REFERENCES

- Ashour, I., Almehaideb, R., Fateen, S. E. and Aly, G., "Representation of solid-supercritical fluid phase equilibria using cubic equation of state," *Fluid Phase Equilibrium*, **167**, 41 (2000).
- Baek, J. K., Kim, S., Lee, G. S. and Shim, J. J., "Density correlation of solubility of C.I. disperse orange 30 dye in supercritical carbon dioxide," *Korean J. Chem. Eng.*, **21**, 230 (2004).
- Bamberger, T., Erickson, J. C. and Cooney, C. L., "Measurement and model prediction of solubilities of pure fatty acids, pure triglycerides, and mixtures of triglycerides in supercritical carbon dioxide," *J. Chem. Eng. Data*, **33**, 327 (1988).
- Bush, D. and Echert, C. A., "Prediction of solid-fluid equilibria in supercritical carbon dioxide using linear solvation energy relationships," *Fluid Phase Equilibrium*, **150-151**, 479 (1998).
- Chen, P., Tang, M. and Chen, Y., "Calculations of the solubility of solids in supercritical fluids using the Peng-Robinson equation of state and a modified mixing model," *Ind. Eng. Chem. Res.*, **34**, 332 (1995).
- Chrastil, J., "Solubility of solids and liquids in supercritical gases," *J. Phys. Chem.*, **86**, 3016 (1982).
- Chun, B.-S., Lee, H.-G., Cheon, J.-K. and Wilkinson, G., "Mass transfer in a countercurrent spray column at supercritical conditions," *Korean J. Chem. Eng.*, **13**, 234 (1996).
- Dobbs, J. M., Wong, J. M. and Lahiere, R. J., "Modification of supercritical fluid phase behavior using polar cosolvents," *Ind. Eng. Chem. Res.*, **26**(1), 56 (1987).
- Gurdial, G. S. and Foster, N. R., "Solubility of O-hydroxybenzoic acid in supercritical carbon dioxide," *Ind. Eng. Chem. Res.*, **30**, 575 (1991).
- Hwang, J., Kim, C. H. and Lim, G. B., "Experimental studies and discrete thermodynamic modeling on supercritical CO₂ extractions of a hexadecane and crude oil," *Korean J. Chem. Eng.*, **12**, 244 (1995).
- Hu, Y., *Molecule thermodynamics of fluid*, High Education Press, Beijing, pp. 310-464 (1982).
- Johnston, K. P. and Eckert, C. A., "Modeling supercritical mixtures: How predictive is it?" *Ind. Eng. Chem. Res.*, **28**, 1115 (1989).
- Kim, Y.-H., Lee, Y.-W. and Park, J.-K., "Supercritical carbon dioxide debinding in metal injection molding (MIM) process," *Korean J. Chem. Eng.*, **19**, 986 (2002).
- Li, Q., Zhang, Z., Zhong, C., Liu, Y. and Zhou, Q., "Solubility of solid solutes in supercritical carbon dioxide with and without cosolvents," *Fluid Phase Equilibrium*, **207**, 183 (2003a).
- Li, Q., Zhong, C., Zhang, Z., Liu, Y. and Zhou, Q., "An equilibrium model for the correlation of the solubility of solids in supercritical fluids with cosolvent," *Sep. Sci. & Tech.*, **38**, 1705 (2003b).
- Li, Q., Zhong, C., Zhang, Z. and Zhou, Q., "Modeling of the solubility of solid solutes in supercritical CO₂ with and without cosolvent using solution theory," *Korean J. Chem. Eng.*, **21**, 1173 (2004).
- Mendez-Santiago, J. and Teja, A. S., "The solubility of solids in supercritical fluids," *Fluid Phase Equilibrium*, **158-160**, 501 (1999).
- Noh, M. J., Kim, T. G., Hong, I. K. and Yoo, K. P., "Measurements and correlation of effect of cosolvents on the solubilities of complex molecules in supercritical carbon dioxide," *Korean J. Chem. Eng.*, **12**, 48 (1995).
- Reid, R. C., Prausnitz, J. M. and Poling, B. E., *The properties of gases and liquid*, 4th Edition, McGraw-Hill, New York, pp. 102-151 (1987).
- Soave, G., "A simple model for the supercritical extraction of solids," *Journal of Supercritical Fluids*, **19**, 19 (2000).
- Valderrama, J. O. and Silva, A., "Modified Soave-Redlich-Kwong equations of state applied to mixtures containing supercritical carbon dioxide," *Korean J. Chem. Eng.*, **20**, 709 (2003).
- Yau, J.-S. and Tsal, F.-N., "Solubility of 1-hexadecanol and 1-octadecanol in subcritical and supercritical carbon dioxide," *J. Chem. Eng. Data*, **37**, 285 (1992).
- Yau, J.-S. and Tsal, F.-N., "Solubility of 1-eicosanol and eicosanoic acid in supercritical carbon dioxide from 308.2 K at pressures to 21.26 MPa," *J. Chem. Eng. Data*, **39**, 827 (1994).
- Yoo, K.-P., Shin, H.-Y., Noh, M.-J. and You, S.-S., "Measurement and modeling solubility of bioactive coumarin and its derivatives in supercritical carbon dioxide," *Korean J. Chem. Eng.*, **14**, 341 (1997).
- Zhu, Z., *Supercritical fluid technology-principals and applies*, Chemical Engineering Press, Beijing, pp. 61-133 (2000).
- Zigger, D. H. and Eckert, C. A., "Correlation and prediction of solid-supercritical fluid phase equilibria," *Ind. Eng. Chem. Process Des. Dev.*, **22**, 582 (1983).