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An Equilibrium Model for the Correlation of the Solubility of Solids in Supercritical Fluids with Cosolvent

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ABSTRACT

Solubility of solids in supercritical fluids was studied by chemical association reaction method in this work, where both cases of with and without cosolvent were considered. Based on the thermodynamic and association reaction equilibrium theories, a model for the solubility of solids in supercritical fluids under association reactions was developed, which reduces to normal solubility calculation model when there are no cosolvent and association reactions. The model was tested with the experimental data collected from the literature, and the results show that it is more accurate than other models.

Key Words: Solubility; Supercritical fluid; Chemical association reaction; Cosolvent.

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1. INTRODUCTION

One of the most important research fields of supercritical fluid technology is the solubility of solids in supercritical fluid.[1,2] Although many investigations have been carried out for pure solvents,[3–5] very few reports have been published on supercritical fluid systems with cosolvents. In the existing literatures, equations of state[6–9,14–16] and grid models[10,11] are usually used, and the calculation accuracy is low. When pressure is high, especially with polar substances, the phase equilibria change a lot by the effect of association among molecules. Many researchers have studied the chemical association reaction theory in which the nonideality of the solvent is attributed to the effect of chemical association.[12,13] In this work, solubility of solutes in the supercritical fluids with cosolvent was studied by chemical association method, and a model of high accuracy was developed.

2. THEORY

At low pressure, normal gases can be taken as ideal gases, however, some polar gases, such as carboxylic acids and mellows depart far from ideal gas behavior in spite of low pressure. Supercritical fluid extractions are usually operated at high pressure and low temperature, and the cosolvents are normally polar substances. So, we assume that solute B exists in an associating state. In the supercritical fluid A with cosolvent C, the association reactions are assumed as follows:

$$B + nA \rightleftharpoons BA_n \tag{1}$$

$$B + mc \rightleftharpoons BC_m \tag{2}$$

Since the solubility calculation is not affected by whether the association reactions occur in the solute or solvent phase, for the convenience of calculation, we suppose that the association reactions are in the supercritical fluid phase, and we denote B in solid state as B(S), and B in supercritical state as B(F), etc. So, the association reaction equations are:

$$B(S) \rightleftharpoons B(F) \tag{3}$$

$$B(F) + nA(F) \rightleftharpoons BA_n(F) \tag{4}$$

$$B(F) + mC(F) \rightleftharpoons BC_m(F) \tag{5}$$

Combining Eqs. (3), (4), and (5), one obtains:

$$\mathrm{B(S)} + \mathrm{nA(F)} \rightleftharpoons \mathrm{BA_n(F)} \tag{6}$$

$$\mathrm{B(S)} + \mathrm{mC(F)} \rightleftharpoons \mathrm{BC_m(F)} \tag{7}$$

The equilibrium constants for Eqs. (6) and (7) are K_1 and K_2, respectively, so

$$K_1 = \frac{\hat{f}_{BA_n}^{(F)}}{\hat{f}_B^{(S)}(\hat{f}_A^{(F)})^n} \tag{8}$$

$$K_2 = \frac{\hat{f}_{BC_m}^{(F)}}{\hat{f}_B^{(S)}(\hat{f}_C^{(F)})^m} \tag{9}$$

The fugacity for each component can be calculated with the following equations:

$$\hat{f}_A^{(F)} = y_A \hat{\varphi}_A P \tag{10}$$

$$\hat{f}_B^{(F)} = y_B \hat{\varphi}_B P \tag{11}$$

$$\hat{f}_C^{(F)} = y_C \hat{\varphi}_C P \tag{12}$$

$$\hat{f}_{BA_n}^{(F)} = y_{BA_n} \hat{\varphi}_{BA_n} P \tag{13}$$

$$\hat{f}_{BC_m}^{(F)} = y_{BC_m} \hat{\varphi}_{BC_m} P \tag{14}$$

where, y_i ($i = A, B, C, BA_n, BC_m$) is mole fraction of each component in the supercritical fluid phase, and

$$y_A + y_B + y_C + y_{BA_n} + y_{BC_m} = 1 \tag{15}$$

As pointed out before, solute B exists mainly in an associating state, so it is a good approximation to assume that y_B is far smaller than 1; then Eq. (15) becomes:

$$y_A = 1 - y_C - y_{BA_n} - y_{BC_m} \tag{16}$$

and

$$\hat{f}_A^{(F)} = (1 - y_C - y_{BA_n} - y_{BC_m})\hat{\varphi}_A P \tag{17}$$

Substitution of Eq. (8) for Eqs. (13) and (17) yields

$$\frac{y_{BA_n}}{(1-y_C-y_{BA_n}-y_{BC_m})^n}=\frac{K_1\hat{f}_B^{(s)}\hat{\varphi}_A^n P^{n-1}}{\hat{\varphi}_{BA_n}} \tag{18}$$

Substituting Eq. (9) for Eqs. (11), (12), and (14) after arrangement, we obtain:

$$\frac{y_{BC_m}}{(1-y_C-y_{BA_n}-y_{BC_m})^n}=\frac{K_2\hat{f}_B^{(S)}P^{m-1}(y_C\hat{\varphi}_C)^m}{(1-y_C-y_{BA_n}-y_{BC_m})^n\cdot\hat{\varphi}_{BC_m}} \tag{19}$$

Combining Eqs. (18) and (19), one obtains:

$$\frac{y_{BA_n}+y_{BC_m}}{(1-y_C-y_{BA_n}-y_{BC_m})^n}=\frac{K_1\hat{f}_B^{(S)}\hat{\varphi}_A^n P^{n-1}}{\hat{\varphi}_{BA_n}}+\frac{K_2\hat{f}_B^{(S)}P^{m-1}(y_C\hat{\varphi}_C)^m}{(1-y_C-y_{BA_n}-y_{BC_m})^n\cdot\hat{\varphi}_{BC_m}} \tag{20}$$

The solubility of solute B is:

$$y=y_B+y_{BA_n}+y_{BC_m} \tag{21}$$

Because solute B mainly exists in an associating state and y_B is small, we assume:

$$y=y_{BA_n}+y_{BC_m} \tag{22}$$

Supposing that the standard state of solute B is the pure solute under system pressure and temperature, then:

$$\hat{f}_B^{(S)}=a_B f^0{}_{\mathrm{B}}=x_B\gamma_B f^0{}_{\mathrm{B}} \tag{23}$$

Since:

$$d(\ln f_B)=\frac{V_B}{RT}dP \tag{24}$$

after integration, one obtains:

$$f_B^0\approx f_B^*\exp\left[\frac{V_B}{RT}(P-P_B^*)\right] \tag{25}$$

Substituting Eq. (23) for Eq. (25), one obtains,

$$\hat{f}_B^{(S)}=x_B\gamma_B f_B^*\exp\left[\frac{V_B}{RT}(P-P_B^*)\right] \tag{26}$$

Eq. (20) is substituted for Eqs. (21) and (26), after arrangement:

$$\frac{y}{(1-y_C-y)^n} = P^{-1}x_B\gamma_B f_B^* \exp\left[\frac{V_B}{RT}(P-P_B^*)\right] \times \left[\frac{K_1(\varphi_A\hat{P})^n}{\varphi_{\hat{B}A_n}} + \frac{K_2(y_C\hat{\varphi}_C P)^m}{(1-y_C-y)^n\hat{\varphi}_{BC_m}}\right] \tag{27}$$

Eq. (27) is the general solubility calculation equation proposed in this work, where m and n can be integer or decimal fraction.

Eq. (27) is not only applicable in that the extracted phase is pure liquid, but also applicable in that the extracted phase is pure solid. For pure solid, x_B and γ_B are equal to 1, and the solubility calculation equation for pure solid can be simplified further as follows:

$$\frac{y}{(1-y_C-y)^n} = P^{-1}f_B^* \exp\left[\frac{V_B}{RT}(P-P_B^*)\right] \times \left[\frac{K_1(\hat{\varphi}_A P)^n}{\hat{\varphi}_{BA_n}} + \frac{K_2(y_C\hat{\varphi}_C P)^m}{(1-y_C-y)^n\hat{\varphi}_{BC_m}}\right] \tag{28}$$

Eq. (28) is the model for the calculation of the solid solubility in the supercritical fluids with cosolvent.

3. DISCUSSION AND SIMPLIFICATION OF THE MODEL FOR THE SOLID SOLUBILITY IN SUPERCRITICAL FLUIDS WITH COSOLVENT

The Case When There Are no Association Reactions Between Solute and Supercritical Fluid Molecules

In this case, Eq. (28) becomes:

$$y = P^{-1}f_B^* \exp\left[\frac{V_B}{RT}(P-P_B^*)\right]\left[\frac{1}{\hat{\varphi}_B} + \frac{K_2(y_C\hat{\varphi}_C P)^m}{\hat{\varphi}_{BC_m}}\right] \tag{29}$$

If there is also no cosolvent, then $y_C = 0$, $f_B^* = P_B^*$, Eq. (29) can be simplified further as:

$$y = \frac{P_B^*}{P\hat{\varphi}_B}\exp\left[\frac{V_B}{RT}(P-P_B^*)\right] \tag{30}$$

Eq. (30) is the normally used solubility calculation equation in the literature, where $\hat{\varphi}_B$ can be calculated by an EOS.

The Case When Solute Associates with Supercritical Fluid

In this case, n is not equal to zero, and we can define enhancement factor E as follows:

$$E = \frac{yP}{P_B^*} \tag{31}$$

Since $f_B^* = \phi_B^* P_B^* = P_B^*$, Eq. (28) changes to:

$$E = \exp\left[\frac{V_B}{RT}(P - P_B^*)\right]\left[\frac{K_1(\hat{\varphi}_A P)^n(1 - y_C - y)^n}{\hat{\varphi}_{BA_n}} + \frac{K_2(y_C\hat{\varphi}_C P)^m}{\hat{\varphi}_{BC_m}}\right] \tag{32}$$

The following two conditions are considered:

(1) When there is no cosolvent, y_C is equal to zero, Eq. (32) becomes:

$$E = \exp\left[\frac{V_B}{RT}(P - P_B^*)\right]\left[\frac{K_1(\hat{\varphi}_A P)^n(1 - y)^n}{\hat{\varphi}_{BA_n}}\right] \tag{33}$$

Furthermore,

$$\ln E = \frac{V_B}{RT}(P - P_B^*) + n\ln P + \ln K_1 + \ln\frac{(\hat{\varphi}_A)^n}{\hat{\varphi}_{BA_n}} + n\ln(1 - y) \tag{34}$$

$$\text{Since } P = ZRT\rho/M \tag{35}$$

$$\ln K_1 = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{36}$$

Upon substitution of Eqs. (35) and (36) into Eq. (34), one obtains:

$$\ln E = n\ln(\rho T) + \frac{ZV_B\rho}{M} + F(T, P, y) \tag{37}$$

with

$$F(T,P,y) = -\frac{V_B P_B^* + \Delta H^0}{RT} + \frac{\Delta S^0}{R} + n\ln\frac{ZR}{M} + \ln\frac{(\hat{\varphi}_A)^n}{\hat{\varphi}_{BA_n}} + n\ln(1 - y) \tag{38}$$

where ρ is the density of the supercritical phase. At supercritical state, ρ is a function of the pressure, temperature and components, and F is a very complex function. The following simplified empirical equation is proposed for convenience:

$$F(T, P, y) = k_2'\rho + k_3/T + k_4 \tag{39}$$

Substituting the above equation into Eq. (37), and after arrangement, we get:

$$\ln E = k_1 \ln(\rho T) + k_2\rho + k_3/T + k_4 \tag{40}$$

(2) When there is cosolvent, we suppose:

$$E_0 = \exp\left[\frac{V_B}{RT}(P - P_B^*)\right] \frac{K_1(\hat{\varphi}_A P)^n (1 - y_C - y)^n}{\hat{\varphi}_{BA_n}} \tag{41}$$

$$E_1 = \exp\left[\frac{V_B}{RT}(P - P_B^*)\right] \frac{K_2(y_C \hat{\varphi}_C P)^m}{\hat{\varphi}_{BC_m}} \tag{42}$$

From Eq. (32), we know $E = E_0 + E_1$. Generally, the concentration of cosolvent is about 3–5%[14,15] and n is small, so we suppose that $1 - y_C - y \approx 1 - y$.

Then Eq. (41) is identical to Eq. (33). We can consider E_0 as the enhancement factor caused by supercritical fluid B, which can be calculated by Eq. (40). Using the same method for the derivation of Eq. (40), we can derive Eq. (43) from Eq. (42):

$$\ln E_1 = \ln(E - E_0) = n_1 \ln(y_3\rho T) + n_2\rho + n_3/T + n_4 \tag{43}$$

where, k_i and n_i $(i = 1 \backsim 4)$ are adjustable parameters, which can be obtained by fitting the solubility data.

Eqs. (40) and (43) are the solubility calculation models proposed by this work, which can be used to calculate the effect of cosolvent on solubility. The parameters are regressed by two steps. Firstly, we regress k_i by fitting the solubility data without cosolvent. Then, we can get n_i in Eq. (43) by fitting the solubility data with cosolvent. By this way, we can calculate the solubility of solids in supercritical fluids with and without cosolvent.

4. RESULTS AND DISCUSSION

In order to test the model, the experimental data published in the literature were collected, which are shown in Tables 1–3. Comparisons with

Table 1. Solubility of solutes in SCF CO_2 with cosolvent (comparison of this work with the HSVDW1 and HSVDW2 models).

					Parameters				AAD%[a]			
Solute + cosolvent	Temp. (K)	Pressure range (bar)	Mole fraction of cosolvent	No. of points	k_1	$k_2 \times 10^3$	k_3	k_4	This work	HSVDW1	HSVDW2	Data source
Benzoic acid + acetone	308	100 − 330	3.5	7	0.2891	0.4064	107.77	−0.085	1.5	5.0	7.0	(14)
Benzoic acid + methanol	308	90–350	3.5	10	0.3953	0.3541	358.82	−0.3411	2.3	12.0	32.0	(14)
Benzoic acid + n-octane	308	100–300	3.5	5	0.2239	0.5865	−564.01	0.5332	2.0	2.5	51.0	(14)
Acridine + acetone	308	120–350	3.5	6	0.1766	0.5003	321.59	0.4504	3.3	5.3	23.8	(14)
Acridine + methanol	308	120–350	3.5	8	0.5831	0.2757	416.44	0.3259	2.8	8.3	50.0	(14)
Benzoic acid + acetone	308	200–300	3.5	4	0.1638	0.4842	194.01	0.0170	1.3	3.8	28.2	(14)
2-Aminobenzoic acid + acetone	308	90–300	3.5	6	0.1261	0.5757	81.79	−0.4480	4.6	5.5		(14)
2-Aminobenzoic acid + methanol	308	90–350	3.5	6	0.4406	0.3749	322.68	−0.0359	4.1	21.0		(14)
Phenanthrene + n-pentane	308	120–350	3.5	6	0.2324	0.6340	−707.10	−0.0940	2.1	8.9	12.1	(15)
Phenanthrene + n-octane	308	100–350	3.5–7.0	18	2.1069	0.4998	−6542.1	−0.375	5.2	5.3	8.5	(15)
Phenanthrene + n-undecane	308	120–350	3.5	4	1.5189	0.5143	−4226.0	−0.4212	3.3	3.8	18.8	(15)
Hexamethylbenzene + n-pentane	308	100–350	3.5	6	0.1899	0.4258	166.65	0.0411	1.5	3.8	31.8	(15)
Hexamethylbenzene + n-octane	308	120–350	3.5	6	0.1649	0.4816	177.54	−0.0320	1.6	1.8	15.3	(15)
Hexamethylbenzene + n-undecane	308	120–350	3.5	4	0.1592	0.5299	93.570	0.0093	0.4	1.0	1.7	(15)
Average									2.9	6.7	22.3	

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

Table 2. Solubility of solutes in SCF CO_2 with cosolvent (comparison of this work with the SRK and PR EOSs).

Solute + cosolvent	Temp range (K)	Pressure range (bar)	Mole fraction of cosolvent	No. of points	Parameters				AAD%			Data source
					k_1	$k_2 \times 10^3$	k_3	k_4	This work	SRK	PR	
Naproxen + ethyl acetate	333	100.3–179.3	1.75–5.25	18	1.5826	0.3300	−12176.8	22.67	5.6	23.3	14.8	(16)
Naproxen + acetone	318–333	89.6–179.3	1.75–5.25	32	1.3005	0.3080	5905.2	−27.87	6.0	11.8	7.6	(16)
Naproxen + 1-propanol	333	110.3–197.3	1.75–5.25	15	1.4294	0.2227	5281.4	−25.08	2.8	17.0	25.0	(16)
Naproxen + methanol	323–333	110.3–193.1	1.75–5.25	26	1.3485	0.3387	6110.6	−28.68	7.9	12.0	16.2	(16)
Naproxen + ethanol	323–333	100.3–179.3	1.75–5.25	24	1.3489	0.2892	4201.3	−22.12	3.7	10.1	18.7	(16)
Naproxen + 2-propanol	323–333	100.3–179.3	1.75–5.25	22	1.4764	0.2712	4532.4	−24.13	4.1	13.2	23.1	(16)
Average									5.2	13.8	16.5	

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Table 3. Solubility of solutes in SCF CO_2 with cosolvent (comparison of this work with the APACT model).

Solute + cosolvent	Temp range (K)	Pressure range (bar)	Mole fraction of cosolvent	No. of points	Parameters				AAD%		Data source
					k_1	$k_2 \times 10^3$	k_3	k_4	This work	APACT	
Benzoic acid + propanol	308–318	100–320	3.48–3.61	11	0.5540	0.2359	7037.3	− 22.08	6.8	16.1	(17)
Benzoic acid + ethanol	308–318	100–320	3.48–3.80	11	0.6107	0.1787	5773.9	− 17.27	8.2	24.3	(17)
Benzoic acid + n-hexane	308–318	100–320	3.67–4.05	12	0.1255	0.3740	1321.8	− 1.33	2.4	17.0	(17)
Biphenyl + acetone	308–303	100–200	3.42–3.85	8	0.7834	0.5101	− 10764.0	24.95	3.0	7.0	(17)
Biphenyl + n-hexane	308–313	100–320	3.46–3.94	10	0.5719	0.4322	− 8697.5	22.99	4.4	5.2	(17)
Diphenylamine + acetone	308–313	100–260	3.16–4.08	10	0.2362	0.7964	− 1754.1	1.97	6.6	9.0	(17)
Diphenylamine + n-hexane	308–313	100–320	3.44–4.07	12	2.2987	0.4849	− 10566.2	11.24	7.2	7.7	(17)
Average									5.6	12.7	

literature models were also carried out. In Table 1, the correlated results of the proposed model as well as those from the HSVDW1 and HSVDW2 models[14,15] are given. Obviously, the proposed model shows much better accuracy than the other two models, with the average absolute deviation (AAD) of 2.94% against 6.70% and 22.3% for HSVDW1 and HSVDW2 models, respectively. Comparison with the SRK and PR EOSs[16] is given in Table 2, and that with the APACT (Associating Perturbed Anisotropic Chain Theory) model[17] is given in Table 3. From Tables 2 and 3, it is obvious that the proposed model is more accurate than the others. Of course, the fact that there are more adjustable parameters in the proposed model may cause better correlative accuracy, and the consideration of association reactions are more reasonable and closer to the real situation presented in the supercritical phase.

The effect of the cosolvent on the enhancement factor for the system of benzoic acid + CO_2 + cosolvent is shown in Fig. 1, where both the experimental values and the calculated results from the proposed model are given. Obviously, the cosolvent effect on the solubility of benzoic acid in CO_2 is significant, and methanol shows larger effect than acetone, which may be caused by the stronger interactions between the benzoic acid and methanol molecules than that between the benzoic acid and acetone

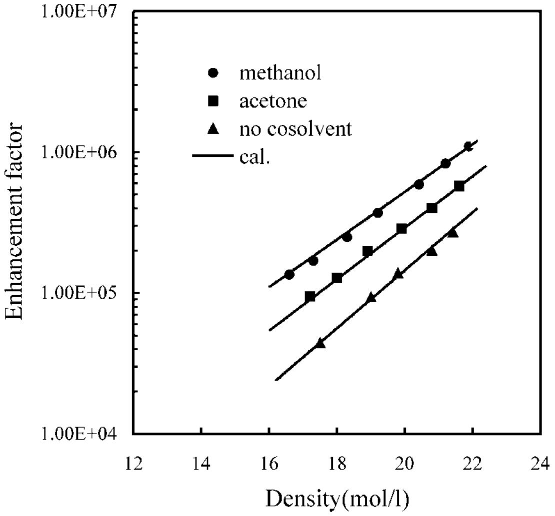

Figure 1. Experimental and calculated enhancement factor for the system of benzoic acid + CO_2 with and without cosolvent.

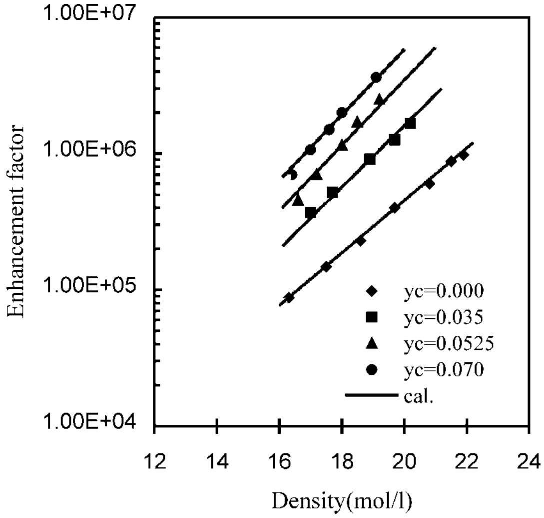

Figure 2. Effect of the cosolvent concentration on the enhancement factor for the system of phenanthrene + n-octane + CO_2.

molecules. On the other hand, the figure also shows that the proposed model correlates the solubility data quite well.

The effect of the cosolvent concentration on the enhancement factor for the system of phenanthrene + n-octane + CO_2 is shown in Fig. 2. It is clear that the effect increases with increasing the cosolvent concentration, and the calculated results show very good agreement with the experimental observation.

CONCLUSION

A new model was proposed for the correlation of the solubility of solids in supercritical fluids with cosolvent based on the chemical association reaction method. It takes association into account, which is more sound and accurate than the existing models. The proposed model can be used for systems with and without cosolvents, which reduces to the normal solid solubility calculation equation when association and cosolvent do not exist. The current work proposed an alternative method to correlate the solubility of solids in supercritical fluids with cosolvent, which may be useful for the representation of the solid solubility data.

SYMBOLS

A	Supercritical solvent
a	Activity
B	Solute
BA_n, BC_m	Association reaction product
C	Cosolvent
$\hat{f}_i$	Fugacity of component i
K_1,K_2	Association reaction equilibrium constant
k_i,n_i ($i = 1 \backsim 4$)	Model parameters
M	Molecular weight, kg/kmol
P	System pressure, MPa
R	Gas constant, J/(mol·K)
T	System temperature, K
V	Molar volume, m^3/mol
x	Molar fraction of extracted phase
y	Molar fraction of supercritical phase
Z	Compressibility factor

Greek Letters

ϕ	Fugacity coefficient
ρ	Density, mol/m^3
ΔH^0	Standard enthalpy difference, J/mol
ΔS^0	Standard entropy difference, J/(mol·K)

Superscripts

cal	Calculated value
exp	Experimental value
F	Supercritical fluid phase
S	Solid phase
0	Standard state
*	Pure state

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