Korean J. of Chem. Eng., **6**(2) (1989) *131-137*

ONE-FLUID MIXING RULES FOR CUBIC EQUATIONS OF STATE: III. SOLUBILITY OF PURE SOLIDS IN SUPERCRITICAL MIXED SOLVENTS

Youn Yong LEE, Hwayong KIM, Huen LEE*, and Won-Hi HONG*

Division of Chemical Engineering, Korea Advanced Institute of
Science and Technology P.O. Box 131, Cheongryang, Seoul, Korea
*Department of Chemical Engineering, Korea Institute of Technology, 400,
Kusong-dong, Yusung-gu, Taejon-shi, Chung-chong nam-do, Korea

(Received 21 June 1988 • accepted 4 November 1988)

Abstract—Three cubic equations of state are carefully examined to evaluate their capability for correlating the solubility of pure solids in supercritical mixed solvents. After obtaining the pure solute-solvent interaction parameters, the solid solute-cosolvent interaction parameters were directly calculated from the experimental ternary solubility data. The Redlich-Kwong, Soave, and Peng-Robinson equations of state correlate well the solubility data of 32 ternary systems producing AAD(%) errors of 12.54, 12.50 and 12.67% respectively.

INTRODUCTION

The potential application of supercritical fluid extraction in chemical separation processes has been of considerable research interest for the past decade. For rational process design of supercritical fluid extraction it would be highly desirable to have the simple and accurate estimation method for predicting the supercritical solubility data in various systems. In this connection, two previous studies [1,2] have been carried out to test the capability of the commonly used equations of state in correlating the binary solubility data of pure solids in supercritical pure solvents and the ternary solubility data of solid mixtures in supercritical pure solvents.

Recently, the experimental solubility studies for the ternary systems consisting of one solid soute and two mixed solvents have been appeared in the literature [3-6]. The results of these studies suggest that the solubility of certain solids could be increased significantly in either supercritical carbon dioxide or supercritical ethane by adding small amounts of various cosolvents. For instance, the addition of only 3.5 mol% methanol in the system of 2-aminobenzoic acid-carbon dioxide raised the solute's solubility over 600% [5]. In this study, the applicable cubic equations of state using simple one-fluids mixing rules are evaluated regarding their ability to quantitatively describe the solubility of solid solutes in supercritical mixed solvents.

EQUATIONS OF STATE EXAMINED

Various procedures [7-10] have been proposed in the literature to predict the solubility of non-volatile liquids or solids in supercritical fluids. The most computationally straightforward and thermodynamically consistent method for modeling high-pressure phase equilibria is to apply an equation of state with the appropriate mixing rules. In this study, the commonly used three cubic equations of state were adopted to test their predictive power in the solid-fluid equilibria. The Redlich-Kwong [11], Soave [12], and Peng-Robinson [13] equations of state are presented as follows;

Redlich-Kwong(RK):

$$P=\frac{RT}{\nu-b}-\frac{a(T)}{\nu(\nu+b)} \tag{1}$$

or

$$Z^3-Z^2+(A-B-B^2)Z-AB=0 \tag{2}$$

where

$$a(T)=0.42747\frac{R^2T_c^2}{P_c}\left[\frac{T_c}{T}\right]^{1/2}$$

$$b=0.08664\,RT_c/P_c$$

$$A=\frac{aP}{(RT)^2}$$

$$B=\frac{bP}{RT}$$

Soave (SRK):

$$P=\frac{RT}{v-b}-\frac{a(T)}{v(v+b)} \qquad (3)$$

or

$$Z^3-Z^2+(A-B-B^2)Z-AB=0 \qquad (4)$$

where

$$a(T)=0.42747\frac{R^2T_c^2}{P_c}\alpha(T)$$

$$b=0.08664\,RT_c/P_c$$

$$\alpha(T)=[1+m(1-T_r^{0.5})]^2$$

$$m=0.480+1.574\omega-0.176\omega^2$$

$$A=\frac{aP}{(RT)^2}$$

$$B=\frac{bP}{RT}$$

Peng and Robinson (PR):

$$P=\frac{RT}{v-b}-\frac{a(T)}{v(v+b)+b(v-b)} \qquad (5)$$

or

$$Z^3-(1-B)Z^2+(A-2B-3B^2)Z$$

$$-(AB-B^2-B^3)=0 \qquad (6)$$

where

$$a(T)=0.45724\frac{R^2T_c^2}{P_c}\alpha(T)$$

$$b=0.07780\frac{RT_c}{P_c}$$

$$\alpha(T)=[1+\kappa(1-T_r^{0.5})]^2$$

$$\kappa=0.37464+1.54226\omega-0.26992\omega^2$$

$$A=\frac{aP}{(RT)^2}$$

$$B=\frac{bP}{RT}$$

The classical van der Waals one-fluid mixing rules have been adopted to extend these equations to mixtures as follows:

$$\theta_m=\sum_i\sum_j y_i y_j \theta_{ij} \qquad (7)$$

When θ may be either a or b, and the cross parameter θ_{ij} is given by

$$a_{ij}=(a_{ii}a_{jj})^{0.5}(1-k_{ij}) \qquad (8)$$

and

$$b_{ij}=(b_{ii}+b_{jj})/2 \qquad (9)$$

CALCULATION OF SUPERCRITICAL SOLUBILITY

The solubility of a solid solute i in a supercritical solvent is given by

$$y_i=\frac{P_i^o\phi_i^o\exp[v_i^s(P-P_i^o)]}{\phi_i P} \qquad (10)$$

where P is the total pressure, P_i^o is the sublimation pressure of the pure solid, v_i^s is the molar volume of the solid, ϕ_i^o is the fugacity coefficient of the saturated pure vapor of the solid solute which is very close to unity in view of the small vapor pressures and ϕ_i is the fugacity coefficient of the solid in the fluid phase. The most important variable ϕ_i for the supercritical solubility enhancement is given by

$$RT\ln\phi_i=\int_V^\infty[(\frac{\partial P}{\partial n_i})_{T,V,n_j\neq n_i}-\frac{RT}{V}]dV-RT\ln Z \qquad (11)$$

where $Z=Pv/RT$. The equation of state is used to find the fugacity of component i in the vapor phase, ϕ_i. The basic physical properties of the supercritical solvents and solid solutes are presented in Table 1 and 2 respectively. However, the experimental values of critical constants for some substances are not reported in the literature. For these solid solutes, the Ambrose method [16] was used to estimate critical constants.

In applying an equation of state to predict the solubility of solid solutes in supercritical mixed solvents, the three k_{ij} parameters must be determined. Among three binary interaction parameters involved in the equations of state, only two of them, k_{12} and k_{23}, are considered to be the key parameters influencing the supercritical solubility enhancement. The solid solute-solvent binary interaction parameter, k_{12}, can be obtained directly from binary solubility data for the individual solids in the supercritical solvent. The solid solute-cosolvent binary interaction parameter, k_{23}, representing the cosolvent-induced solubility enhancement, is determined from the ternary solubility data. However, the solvent-cosolvent binary interaction parameter, k_{13}, is considered to have no significant effect on the solubility enhancement and therefore can be set to be zero.

First, a nonlinear regression method coupled with polynomial roots searching method has been applied to determine the values of k_{12} of three equations of state for each solute-solvent system from experimental solubility data of binary systems. The objective function

$$F=\sum_{i=1}^{N}|(y_{2i}^{cal}-y_{2i}^{exp})/y_{2i}^{exp}| \qquad (12)$$

Table 1. Physical constants of solvents used in this study

Compd	MW	T_c, K	P_c, bar	v_c, cm^3/mol	Z_c	ω
Carbon dioxide	44.010	304.19	73.8	94.04	0.274	0.225
Methanol	32.042	512.6	80.9	118.00	0.224	0.556
Acetone	58.080	508.1	47.0	209	0.232	0.304
Ethane	30.070	305.5	49.1	141.7	0.274	0.098
n-Pentane	72.151	469.7	33.7	304	0.263	0.251
n-Octane	114.232	568.8	24.9	492	0.259	0.398
n-Undecane	156.313	638.8	19.7	660	0.24	0.535
Benzene	78.114	562.2	48.9	259	0.271	0.212
Cyclohexane	84.162	553.5	40.7	308	0.273	0.212
Methylene chloride	84.933	510.0	60.8	185	0.265	0.192

Table 2. Physical constants of solid solutes used in this study

Compd	Formula	MW	v_s	T_c	P_c	ω	P_s,bar × 10^{-7}
			cm^3/mol	K	bar		
Benzoic acid	$C_7H_6O_2$	122.13	96.5	752	45.6	0.620	35(35°C),78(45°C),216(55°C),891(70°C)
2-Aminobenzoic acid	$C_7H_7NO_2$	137.14	97.1	851*	49.0*	0.820	1.2(35°C)
Phthalic anhydride	$C_8H_4O_3$	148.12	96.8	810	47.6	0.388	18(35°C)
Naphthalene	$C_{10}H_8$	128.19	125.0	748	40.5	0.302	2920(35°C),7026(45°C)
2-Naphthol	$C_{10}H_8O$	244.17	118.5	823*	46.8*	0.502	6.8(35°C)
Hexamethylbenzene	$C_{12}H_{18}$	162.28	152.7	752*	23.8*	0.498	50(35°C)
Acridine	$C_{13}H_9N$	179.22	178.8	883	31.9	0.498	2.1(35°C)
Phenanthrene	$C_{14}H_{10}$	178.24	167.6	890	32.9	0.429	6.5(35°C), 42.3(55°C)
Anthracene	$C_{14}H_{10}$	178.25	142.6	883	33.1	0.455	0.26(35°C)

*calculated from Ambrose method (ref. 16).

has been minimized in searching for a binary parameter of each binary system. Here, N stands for the number of experimental data points and 2 the solid component in the vapor phase. The values of overall regressed binary interaction parameters at individual isotherm are presented in Table 3. The solute-cosolvent interaction parameters, k_{23}, were then calculated from the experimental ternary solubility data using the same objective function presented in eq.(12). Again, when determined the value of k_{23}, the k_{12} obtained from the binary solubility data and the zero-value of k_{13} were used. The resulting k_{23} values of 44 ternary systems are summarized in Table 4. For a few systems the regressed k_{23} values determined from the original Redlich-Kwong equation of state are a little higher than those for the other systems. It can be thus said from this fact that an additional parameter accounting for the entrainer effect might be introduced for the better qualitative correlation of supercritical fluid-entrainer-solid solubility data. The quality of the calculated supercritical solubility is expressed in terms of on average absolute percent deviation (AAD%) defined as,

$$AAD(\%) = (100/N)\sum_{i=1}^{N} \left| (y_{2i}^{cal} - y_{2i}^{exp})/y_{2i}^{exp} \right| \quad (13)$$

RESULTS AND DISCUSSIONS

The effect of cosolvents on the solubility of solid solutes has been extensively examined in this work. The solubility data of pure solids in the supercritical mixed solvents were well correlated with the three commonly used cubic equations of state, RK, SRK and PR. The results show that there is no significant difference in the overall AAD(%) among them (RK-12.54%, SRK-12.50% and PR-12.67%) for 32 systems except the systems with two data points and therefore all of them can be successfully applied to correlate the supercritical solubility data of binary and ternary

Table 3. Solute(2)-solvent(1) binary parameters and AAD(%)

Systems	T,°C	P,bar	No. Data	RK		SRK		PR		Data Source
				k_{12}	y_2,AAD(%)	k_{12}	y_2,AAD(%)	k_{12}	y_2,AAD(%)	
Benzoic acid-CO_2	35	101-364	9	-0.17198	12.16	0.02405	16.22	0.02137	18.85	4
	45	101-363	12	-0.17437	11.65	0.01197	17.84	0.01035	20.26	4
	55	101-363	12	-0.18014	8.01	-0.00535	24.28	-0.00511	25.22	4
	70	101-364	7	-0.19335	4.20	-0.02692	26.13	-0.02280	25.03	4
Benzoic acid-Ethane	55	55-362	7	-0.22443	21.26	-0.02785	24.98	-0.02400	26.39	4
2-Aminobenzoic acid-CO_2	35	120-350	6	-0.06014	18.07	0.17431	19.42	0.16517	21.42	5
Phthalic anhydride-CO_2	35	120-350	5	-0.11926	10.49	-0.01240	11.90	-0.01180	13.76	5
Naphthalene-CO_2	35	78-334	13	0.03630	8.48	0.10228	12.33	0.09843	14.49	14
	45	88-314	13	0.03652	8.18	0.09532	16.21	0.09235	17.11	14
2-Naphthol-CO_2	35	100-350	9	-0.06546	20.69	0.07583	22.62	0.07360	25.11	5
Hexamethylbenzene-CO_2	35	150-350	3	-0.03481	22.95	0.10361	21.86	0.09698	14.81	3
Acridine-CO_2	35	120-350	6	-0.01374	4.96	0.12058	7.33	0.11385	11.94	5
Phenanthrene-CO_2	35	100-350	7	0.02172	5.33	0.12813	6.53	0.12211	9.20	3
	55	120-280	5	0.00196	2.15	0.10095	17.94	0.09679	19.54	15
Phenanthrene-Ethane	55	71-355	6	-0.06927	9.15	0.04572	16.50	0.04730	20.25	4
Anthracene-CO_2	35	120-200	3	-0.01048	8.26	0.10671	9.48	0.09948	11.05	6

systems. At the present time, it should be pointed out that the RK equation of state is somewhat superior to the SRK and PR equation of state when applied to binary solid-supercritical solvent equilibria and ternary two solid mixture-supercritical solvent equilibria. The overall discussion of this conclusion can be found in the two previous papers [1,2].

The solubilities of the solids are increased more by the presence of several mol% of cosolvent them by changes in the pressure of several hundred bar. For example, the solubility enhancement of phenanthrene by adding cosolvent is 1.6 for 3.5 mol% pentane and 3.6 for 3.5 mol% undecane as shown in Figure 1. These values are less influenced by pressure change than by mole% change of cosolvent. In comparison, an increase in the pressure from 150 to 350 bar raises the solubility by a factor of only 1.7 in pure CO_2. In addition, the solubility enhancement may be achived by increasing mol% of cosolvent. At 350 bar, the solubility of 2-naphthol in carbon dioxide with methanol cosolvent increases by a factor of 8 as the cosolvent concentration is increased from 3.5 to 9 mol% on a solute-free basis as shown in Figure 2. The same behavior is also found in CO_2-phenanthrene-n-octane (cosolvent) system as shown in Figure 3. However, it should be noted that the cubic equations of state does not correlate well the solute solubility in polar cosolvent as shown in Figure 2. This example indicates that a polar effect such as hydrogen-bonding association must be

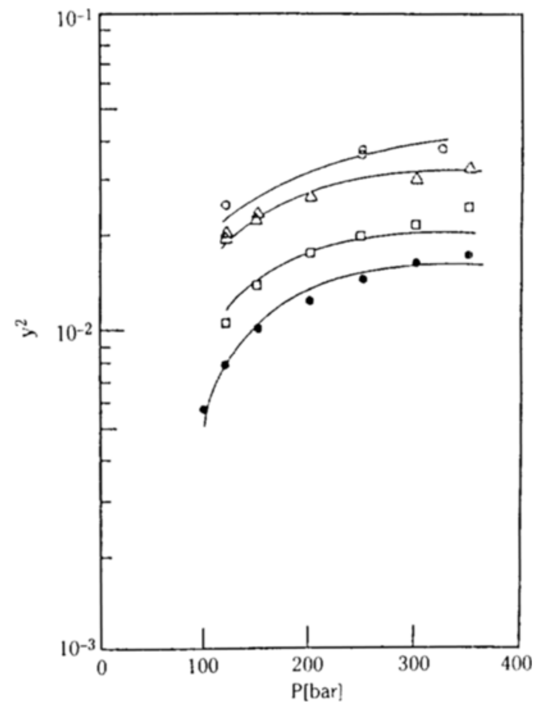

Fig. 1. Solubility of phenanthrene in carbon dioxide with 3.5 mol% various cosolvents at 35°C.
●, pure CO_2; □, n-pentane + CO_2; △, n-octane + CO_2; ○, n-undecane + CO_2; —, predicted by using RK equation of state.

Table 4. Solute(2)-cosolvent(3) binary parameters and AAD(%)

Systems	T,°C	P,bar	No. Data	RK		SRK		PR		Data Source
				k_{23}	y_2,AAD(%)	k_{23}	y_2,AAD(%)	k_{23}	y_2,AAD(%)	
CO_2-Benzoic acid-Methanol(3.5 mol%)	35	90-350	10	-0.91388	16.32	-0.25248	17.25	-0.26449	19.63	5
	45	120-200	5	-1.26036	7.52	-0.46268	11.37	-0.49770	12.02	6
	55	120-200	3	-1.11110	10.65	0.17322	20.28	0.17710	21.06	6
CO_2-Benzoic acid-Acetone(3.5 mol%)	35	100-330	7	-0.38452	14.30	-0.03045	15.02	-0.03890	17.12	5
CO_2-Benzoic acid-n-Octane(3.5 mol%)	35	100-300	5	-0.36855	12.00	-0.01692	9.66	-0.02287	12.28	5
CO_2-2-Aminobenzoic acid-Methanol(3.5 mol%)	35	90-300	6	-1.44517	24.40	-0.66022	21.28	-0.69263	22.50	5
CO_2-2-Aminobenzoic acid-Acetone(3.5 mol%)	35	90-300	6	-0.65373	15.56	-0.22506	14.80	-0.24787	16.47	5
CO_2-Phthalic anhydride-Acetone(3.5 mol%)	35	200-300	4	-0.33833	3.44	-0.12064	3.59	-0.12267	5.62	5
CO_2-2-Naphthol-Methanol(3.5 mol%)	35	120-350	6	-1.00947	18.55	-0.51770	16.78	-0.52735	19.38	5
CO_2-2-Naphthol-Methanol(7.0 mol%)	35	120-350	5	-0.89396	11.89	-0.36189	15.03	-0.37368	17.64	6
CO_2-2-Naphthol-Methanol(9.0 mol%)	35	200-350	6	-0.92203	21.49	-0.39870	11.57	-0.41747	10.09	6
CO_2-Hexamethylbenzene-Methanol(3.5 mol%)	35	100-350	5	0.11289	26.83	0.25849	28.88	0.19005	23.66	5
CO_2-Hexamethylbenzene-Acetone(3.5 mol%)	35	100-350	10	0.06642	24.64	0.20912	25.23	0.15316	20.11	5
CO_2-Hexamethylbenzene-n-Pentane(3.5 mol%)	35	100-350	6	-0.16837	20.22	0.01808	20.17	-0.01596	14.82	3
CO_2-Hexamethylbenzene-n-Octane(3.5 mol%)	35	120-350	6	-0.25208	17.84	-0.02669	19.90	-0.04147	13.61	3
CO_2-Hexamethylbenzene-n-Undecane(3.5 mol%)	35	120-350	4	-0.30655	19.47	-0.04416	23.93	-0.05587	16.69	3
CO_2-Acridine-Methanol(3.5 mol%)	35	120-350	8	-0.52075	10.23	-0.17177	8.73	-0.16664	12.11	5
CO_2-Acridine-Acetone(3.5 mol%)	35	120-350	7	-0.24323	4.41	-0.01717	3.92	-0.02100	8.45	5
CO_2-Phenanthrene-n-Pentane(3.5 mol%)	35	120-350	6	-0.09170	6.81	0.06375	6.47	0.05909	1.95	3
CO_2-Phenanthrene-n-Octane(3.5 mol%)	35	120-350	7	-0.22455	3.38	-0.01183	1.98	-0.02087	5.61	3
CO_2-Phenanthrene-n-Octane(5.25 mol%)	35	120-350	5	-0.21713	4.03	-0.00834	6.80	-0.01674	1.36	3
CO_2-Phenanthrene-n-Octane(7.0 mol%)	35	120-350	6	-0.21514	2.35	-0.00946	2.85	-0.01602	2.71	3
CO_2-Phenanthrene-n-Undecane(3.5 mol%)	35	120-350	4	-0.25710	5.70	-0.01730	0.78	-0.01915	4.61	3
CO_2-Anthracene-Methanol(3.5 mol%)	35	120-350	5	0.03342	5.34	0.21600	6.39	0.22189	4.13	6
CO_2-Phenanthrene-Benzene(various)	55	111-305	7	0.02239	30.59	0.17159	26.01	0.14961	27.31	4
CO_2-Phenanthrene-Acetone(various)	55	200	4	-0.12026	3.68	0.09244	2.65	0.07954	2.31	4
CO_2-Phenanthrene-Cyclohexane(various)	55	202	2	-0.15620	1.35	0.06252	3.43	0.04798	2.86	4
CO_2-Phenanthrene-Methylene chloride(various)	55	202	2	-0.22814	15.05	0.05391	3.49	0.03930	4.06	4
CO_2-Benzoic acid-Benzene(various)	55	200	4	-0.43549	10.83	-0.02288	7.50	-0.04109	7.60	4
CO_2-Benzoic acid-Acetone (various)	55	202	2	-0.48123	7.37	-0.03339	9.50	-0.05099	8.64	4
CO_2-Benzoic acid-Cyclohexane(various)	55	202	2	-0.35682	14.32	0.02459	15.96	0.00571	15.21	4
CO_2-Benzoic acid-Methylene chloride(various)	55	202	2	-0.39646	18.57	-0.00822	12.32	-0.02318	13.02	4
Ethane-Phenanthrene-Benzene(various)	55	101-301	8	-0.21979	6.72	0.03176	9.77	0.02198	14.42	4
Ethane-Phenanthrene-Acetone(various)	55	182	2	-0.22799	0.01	0.03214	1.00	0.01106	0.11	4
Ethane-Phenanthrene-Cyclohexane(various)	55	182	2	-0.14241	0.44	0.08410	1.85	0.05861	1.04	4
Ethane-Phenanthrene-Methylene chloride(various)	55	182	2	-0.17400	11.29	0.06054	9.85	0.03830	9.12	4
Ethane-Benzoic acid-Benzene(various)	55	182	2	-0.37745	6.27	-0.05872	5.30	-0.07704	5.96	4
Ethane-Benzoic acid-Acetone(various)	55	182	2	-0.82533	11.34	-0.33623	10.88	-0.35517	11.43	4
Ethane-Benzoic acid-Cyclohexane(various)	55	182	2	-0.25019	3.71	0.03255	2.87	0.01132	3.45	4
Ethane-Benzoic acid-Methylene chloride(various)	55	182	2	-0.37367	5.77	-0.06181	4.98	-0.07852	5.60	4
CO_2-Naphthalene-Ethane(6.2 mol%)	35	99-364	8	-0.03854	1.68	0.09862	5.49	0.11177	8.69	4
	45	99-364	8	0.02573	15.14	0.16700	8.01	0.17783	10.54	4
CO_2-Benzoic acid-Ethane(6.2 mol%)	55	116-364	5	-0.14491	14.21	0.09109	11.61	0.10171	14.00	4
	70	116-364	5	-0.16782	10.93	0.09401	16.37	0.09051	16.58	4
Total					12.54		12.50		12.67	

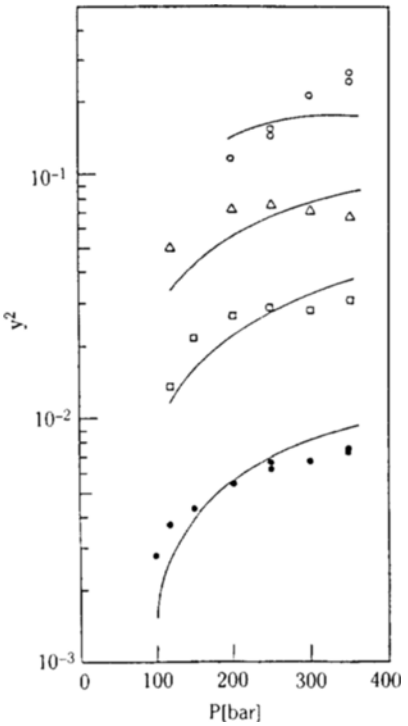

Fig. 2. Solubility of 2-naphthol in carbon dioxide with methanol cosolvent at 35°C.

●, pure CO_2; □, 3.5 mol% methanol; △, 7.0 mol% methanol; ○, 9.0 mol% methanol; —, predicted by using RK equation of state.

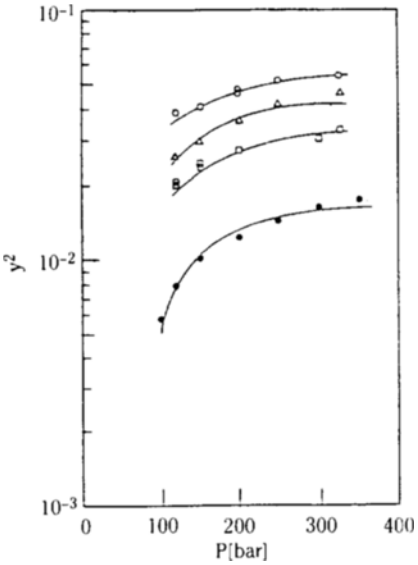

Fig. 3. Solubility of phenanthrene in carbon dioxide with n-octane cosolvent at 35°C.

●, pure CO_2; □, 3.5 mol% n-octane in CO_2; △, 5.25 mol% n-octane in CO_2; ○, 7.0 mol% n-octane in CO_2; —, predicted by using RK equation of state.

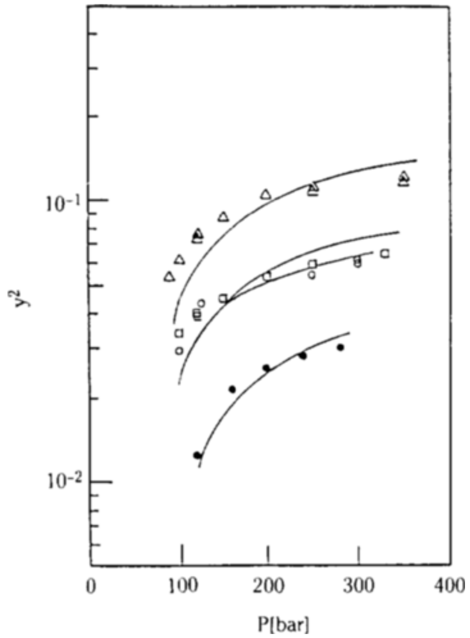

Fig. 4. Solubility of benzoic acid in carbon dioxide with 3.5 mol% various cosolvents at 35°C.

●, pure CO_2; □, acetone + CO_2; △, methanol + CO_2; ○, n-octane + CO_2; —, predicted by using RK equation of state.

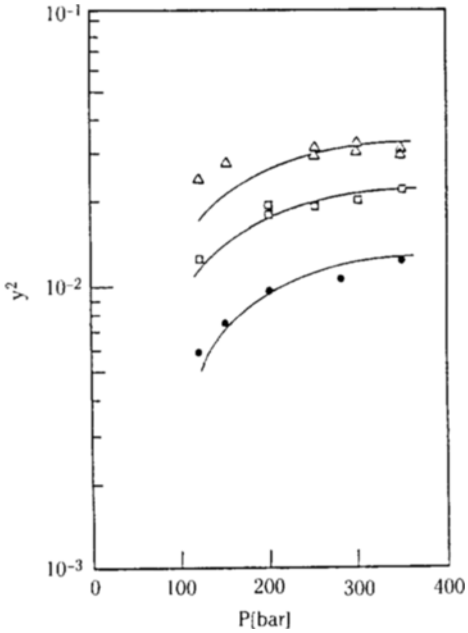

Fig. 5. Solubility of acridine in carbon dioxide with 3.5 mol% various cosolvents at 35°C.

●, pure CO_2; □, acetone + CO_2; △, methanol + CO_2; —, predicted by using RK equation of state.

considered for the systems including polar cosolvent. From the general pattern of behavior, it can be said that the logarithmic increase in the solute solubility is approximately linear to the mole fraction of the added cosolvent. The solubility increase of acridine and benzoic acid caused by the addition of 3.5 mol% nonpolar and polar cosolvents are presented in Figures 4 and 5 respectively.

CONCLUSIONS

The following conclusions can be drawn with great generality from the reported herein:

1. Among the three cubic equations of state (Redlich-Kwong, Soave-Redlich-Kwong and Peng-Robinson), the original Redlich-Kwong equation of state gave the best results in accuracy for both cases of the solubility of pure solids in pure supercritical solvents and the solubility of solid mixtures in pure supercritical solvents as can be seen in the two previous works [1,2]. However, in case of the solubility of solid solutes in supercritical mixed solvents, the three equations of state equally well correlate the experimental data of these ternary systems.
2. The solubility enhancement of the solids is more greatly influenced by the mol% of cosolvent than by the specific choice of cosolvent [4].
3. The addition of a cosolvent to the supercritical fluid decreases the compressibility of the mixed solvent, particularly at lower pressures and this effect also tends to increase the solubility of the solid solute.
4. The further experimental data are needed to develop a comprehensive thermodynamic model applicable to the actual supercritical fluid extraction processes using various cosolvents.

ACKNOWLEDGEMENT

The financial support of the Korea Science and Engineering Foundation is gratefully acknowledged.

NOMENCLATURE

A, B : variable defined in eqs.(2), (4) and (6)
a, b : parameter defined in eqs.(1), (3) and (5)
F : objective function defined in eq.(12)
k_{ij} : binary interaction parameter associated with a
m : parameter in the Soave equation of state
N : number of data points
P : total pressure
P_i^o : sublimation pressure of the solute, i
R : gas constant
T : temperature
v : molar volume
V : total volume
y : mole fraction
Z : compressibility factor
α : variable in eqs.(3) and (5)
κ : parameter in the Peng-Robinson equation of state
θ_{ij} : parameter that is to be mixed
ϕ : fugacity coefficient

REFERENCES

1. Lee, Y.Y., Kim, H., Lee, H., and Hong, W.: *Korean J. Chem. Eng.*, **5,** 76 (1988).
2. Lee, Y.Y., Kim, H., Lee, H., and Hong, W.: *Korean J. Chem. Eng.*, **5,** 116 (1988).
3. Dobbs, J.M., Wong, J.M., and Johnston, K.P.: *J. Chem. Eng. Data,* **31,** 303 (1986).
4. Schmitt, W.J. and Reid, R.C.: *J. Chem. Eng. Data,* **31,** 204 (1986).
5. Dobbs, J.M., Wong, J.M., Lahiere, R.J., and Johnston, K.P.: *Ind. Eng. Chem. Res.*, **26,** 56 (1987).
6. Dobbs, J.M. and Johnston, K.P.: *Ind. Eng. Chem. Res.*, **26,** 1476 (1987).
7. Ziger, D.H. and Eckert, C.A.: *Ind. Eng. Chem. Process Des. Dev.*, **22,** 582 (1983).
8. Allada, S.R.: *Ind. Eng. Chem. Process Des. Dev.*, **23,** 344 (1984).
9. Mart, C.J., Papadopoulos, K.D., and Donohue, M.D.: *Ind. Eng. Chem. Process Des. Dev.*, **25,** 394 (1986).
10. Gilbert, S.W. and Eckert, C.A.: *Fluid Phase Equilibria,* **30,** 41 (1986).
11. Redlich, O. and Kwong, J.N.S.: *Chem. Rev.*, **44,** 233 (1949).
12. Soave, G.: *Chem. Eng. Sci.*, **27,** 1197 (1972).
13. Peng, D.Y. and Robinson, D.B.: *Ind. Eng. Chem. Fundam.*, **15,** 59 (1976).
14. Tsekhanskaya, Y.V., Iomtev, M.B., and Mushkina, E.V.: *Russ. J. Phys. Chem.*, **38,** 1173 (1965).
15. Kurnik, R.T., Holla, S.J., and Reid, R.C.: *J. Chem. Eng. Data,* **26,** 47 (1981).
16. Reid, R.C., Prausnitz, J.M., and Poling, B.E.: "The Properties of Gases and Liquids", 4th ed., McGraw-Hill, New York, NY (1987).