

ONE-FLUID MIXING RULES FOR CUBIC EQUATIONS OF STATE: II. SOLUBILITY OF SOLID MIXTURES IN SUPERCRITICAL FLUIDS

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Abstract—Three cubic equations of state are carefully examined to evaluate their capability for correlating the solubility of solid mixtures in supercritical fluids. After obtaining the pure solute-solvent interaction parameters, the solute-solute interaction parameters were directly calculated from the experimental ternary solubility data. The Redlich-Kwong, Soave, and Peng-Robinson equations of state correlate well the ternary data. However, the Redlich-Kwong equation of state gives the best result among them.

INTRODUCTION

Over the past few years, supercritical fluid extraction has received significant interest as a separation technology. Previous our studies of the solubility of solids in supercritical fluids have been limited to pure solids[1]. More generally, the simple method for correlating the solubility of multicomponent solids in supercritical fluids should be developed in order to apply this noble technology to separation processes.

Experimental solubility data of solid mixtures in supercritical fluids are now available from the literature for a few ternary systems within a very limited temperature range. In this study, the applicable cubic equations of state using simple one-fluids mixing rules are evaluated regarding their ability to quantitatively describe the experimental solubility data.

EQUATIONS OF STATE EXAMINED

Various procedures[2-5] 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[6], Soave[7], and Peng-Robinson[8]

equations of state are presented as follows;

Redlich-Kwong(RK):

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

or

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

where

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

$$b = 0.08664 RT_c / P_c$$

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

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

Soave (SRK):

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

or

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

where

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

$$b = 0.08664 RT_c / P_c$$

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

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

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

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

Peng and Robinson (PR):

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b) + b^2(v-b)}$$

or

$$Z^3 - (1-B)Z^2 + (A-2B-3B^2)Z - (AB-B^2-B^3) = 0 \tag{6}$$

where

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

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

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

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

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

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

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

$$b_m = \sum_i \sum_j y_i y_j \theta_{ij} \tag{7}$$

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

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

and

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

CALCULATION OF SUPERCRITICAL SOLUBILITY

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

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

where P is the total pressure, P_i^o is the sublimation pressure of the pure solid, ν_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 is given by

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

where $Z = P\nu/RT$. 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 solutes and supercritical solvents are presented in Table 1. However, the experimental values of critical constants for 1,10-decanediol are not reported in the literature. In this solute, the Lydersen's method[9] was used to estimate critical constants. Antoine vapor pressure equation used has the form of

$$\ln P_i^o [\text{bar}] = A - B/(T^*K) + C \tag{12}$$

The Antoine constants are also included in Table 1.

In applying an equation of state to predict the

Table 1. Physical properties of the solvents and solutes used in this study

Compd	Formula	MW	v_s cm ³ /g-mole	T_c K	P_c bar	ω	Antoine constants		
							A	B	C
Naphthalene	C ₁₀ H ₈	128.19	125.03	748.4	40.5	0.302	7.2144	2926.6	-35.8
Pher.anthrene	C ₁₄ H ₁₀	178.24	167.6	890	32.9	0.429	9.6310	4873.4	0
Benzoic acid	C ₇ H ₆ O ₂	122.13	96.5	752	45.6	0.620	9.408	4618.1	0
2,3-Dimethylnaphthalene	C ₁₂ H ₁₂	156.23	154.7	785	32.2	0.424	9.0646	4302.5	0
2,6-Dimethylnaphthalene	C ₁₂ H ₁₂	156.23	154.7	777	32.2	0.420	9.4286	4419.5	0
Anthracene	C ₁₄ H ₁₀	178.24	142.6	883	33.1	0.455	7.1464	4397.6	0
1,10-Decanediol	C ₁₀ H ₂₂ O ₂	174.29	158.4	720.4*	23.7*	1.325	12.234	5043.1	-52.9
Carbon dioxide	CO ₂	44.01		304.19	73.8	0.225			
Ethylene	C ₂ H ₄	28.05		282.40	50.4	0.085			

* Estimated by Lydersen's method [9]

solubility of solid mixtures in supercritical solvents, a binary interaction parameter, k_{ij} , appears which is introduced to account for molecular interactions between species i and j . Thus, for a ternary system containing two solids, 2 and 3, and a supercritical fluid, 1, the three k_{ij} parameters must be determined: Two of them, k_{12} and k_{13} , are obtained from binary solubility data for the individual solids in the supercritical fluid and the third, k_{23} , representing the solute-solute interaction from ternary solubility data for the solid mixtures in the supercritical fluid.

First, a nonlinear regression method coupled with

polynomial roots searching method has been applied to determine the values of k_{12} and k_{13} of three equations of state for each solute-solvent system from experimental solubility data of 9 binary systems. The objective function

$$F = \sum_{i=1}^N |(y_{ji}^{cat} - y_{ji}^{exp}) / y_{ji}^{exp}| \quad j = 2, 3 \quad (3)$$

has been minimized in searching for a binary parameter of each binary system. Here, N stands for the number of experimental data points and j the solid components in the vapor phase. The values of overall regressed binary interaction parameters, which are in-

Table 2. Temperature-independent binary parameters and AAD(%) errors for 9 binary systems

Systems	T,K	P,bar	No Data	RK		SRK		PR		Data source
				k_{12}	AAD(%)	k_{12}	AAD(%)	k_{12}	AAD(%)	
CO ₂ -Naphthalene	308-328	77-319	40	0.03504	9.50	0.09735	16.32	0.09435	17.20	10
CO ₂ -Phenanthrene	318-338	118-276	15	0.02127	6.99	0.11980	13.90	0.11516	14.91	11
	308	100-350	7	0.02197	5.33	0.12835	6.54	0.12233	9.21	12
CO ₂ -Benzoic Acid	308-343	99-359	39	-0.17554	14.12	0.00994	25.75	0.00883	25.84	13
CO ₂ -2,3-DMN	308-328	97-276	15	-0.00625	8.57	0.10351	9.36	0.09901	11.25	11
CO ₂ -2,6-DMN	308-328	94-276	15	-0.00531	6.25	0.10203	9.21	0.09784	10.14	11
CO ₂ -Anthracene	308-318	139-277	9	0.03336	7.29	0.14454	5.65	0.13813	6.55	14
CO ₂ -1,10-Decanediol	318-328	131-303	15	-0.18178	8.99	0.16709	6.88	0.14329	7.33	16
Ethylene-2,3-DMN	308-328	76-276	18	-0.11285	19.45	0.01363	12.43	0.01680	11.06	11
Ethylene-2,6-DMN	308-328	77-276	18	-0.10625	14.52	0.01318	9.40	0.01684	7.62	11

Table 3. Temperature-dependent binary parameters and AAD(%) errors for 9 binary systems

Systems	T, K	P, bar	No Data	RK		SRK		PR	
				k_{12}	AAD(%)	k_{12}	AAD(%)	k_{12}	AAD(%)
CO ₂ -Naphthalene	308	79-334	13	0.03630	8.48	0.10228	12.33	0.09843	14.49
	318	88-314	13	0.03652	8.18	0.09532	16.21	0.09235	17.11
CO ₂ -Phenanthrene	308	100-350	7	0.02197	5.33	0.12835	6.54	0.12233	9.21
	318	120-280	5	0.01874	5.93	0.12240	11.19	0.11672	13.70
CO ₂ -Benzoic Acid	308	101-364	9	-0.17198	12.16	0.02405	16.22	0.02137	18.85
	318	101-363	12	-0.17437	11.65	0.01197	17.84	0.01035	20.26
CO ₂ -2,3-DMN	308	99-280	5	-0.01087	4.10	0.10303	1.93	0.09758	3.75
	318	99-280	5	-0.00627	1.81	0.10223	15.19	0.09779	17.43
CO ₂ -2,6-DMN	308	97-280	5	-0.00512	4.87	0.10511	5.89	0.09989	7.06
	318	98-280	5	-0.00568	9.33	0.10034	7.39	0.09623	9.39
CO ₂ -Anthracene	308	139-277	4	0.03328	11.05	0.14611	10.20	0.13915	8.54
	318	139-277	5	0.03343	4.36	0.14298	2.90	0.13712	4.56
CO ₂ -1,10-Decanediol	308			-0.18178**		0.16709**		0.14329**	
	318	205-307	3	-0.18534	5.68	0.17070	3.73	0.14697	1.03
Ethylene-2,3-DMN	308	77-280	6	-0.10321	11.49	0.01926	7.35	0.02136	7.12
Ethylene-2,6-DMN	308	80-280	6	-0.10267	10.71	0.01559	11.56	0.01804	11.70

**Values regressed from experimental data of Ref. 16.

dependent of temperature, are presented in Table 2. For comparison, the values of isothermal binary interaction parameters, which vary with temperature, are presented in Table 3 for all the same systems listed in Table 2. In this table, the experimental solubility data of a binary system 1,10-decanediol-CO₂ measured at 318, 323 and 328 K were regressed to obtain the binary interaction parameters at 308 K since no experimental data at this isotherm exist in the literature. The solute-solute interaction parameters, k_{23} , were then calculated from the experimental ternary solubility

data using the objective function defined as,

$$F = \sum_{i=1}^N \{ |(y_{2i}^{cal} - y_{2i}^{exp}) / y_{2i}^{exp}| + |(y_{3i}^{cal} - y_{3i}^{exp}) / y_{3i}^{exp}| \} \quad (14)$$

The resulting k_{23} values of 10 ternary systems are reported in Table 4, when calculated from the overall data, and Table 5, when calculated from the isothermal data. The quality of the calculated supercritical solubility is expressed in terms of on average absolute deviation (AAD) defined as,

Table 4. Temperature-independent solute-solute binary parameters and AAD(%) errors for 10 ternary systems

Systems	T, K	P, bar	RK			SRK			PR			Data source
			k_{23}	$y_{2,AAD}$ (%)	$y_{3,AAD}$ (%)	k_{23}	$y_{2,AAD}$ (%)	$y_{3,AAD}$ (%)	k_{23}	$y_{2,AAD}$ (%)	$y_{3,AAD}$ (%)	
CO ₂ -Phenanthrene-Naphthalene	308	120-280	-0.19519	2.66	2.99	0.12183	1.98	14.12	0.09528	4.09	14.34	12
CO ₂ -Phenanthrene-Benzoic Acid	308	120-280	-0.62191	3.15	12.05	0.41398	3.86	17.70	0.31167	3.17	17.93	12
CO ₂ -Phenanthrene-2,3-DMN	308-318	120-280	13.38458	96.47	61.38	10.51066	95.78	60.26	10.19480	95.69	59.29	12
CO ₂ -Phenanthrene-2,6-DMN	308	120-280	-0.42948	2.63	8.68	0.26497	2.45	7.14	0.22843	6.63	7.95	12
CO ₂ -Naphthalene-Benzoic Acid	308-318	120-280	-0.42499	3.92	11.65	0.07620	16.62	18.47	0.04427	18.27	18.57	12
CO ₂ -Naphthalene-2,3-DMN	308	120-280	-0.20507	7.00	0.58	0.08127	9.79	1.50	0.07380	10.38	5.47	12
CCl ₂ -2,3-DMN-2,6-DMN	308-318	120-280	-0.21603	2.98	3.84	0.16269	3.72	5.67	0.14554	4.17	5.77	12
Ethylene-2,3-DMN-2,6-DMN	308	120-280	-0.18935	2.66	2.19	0.15351	5.14	5.73	0.13686	7.99	8.65	12
CCl ₂ -Phenanthrene-Anthracene	308-318	104-242	-0.02499	8.89	18.55	0.12855	13.38	10.56	0.09509	7.74	8.40	10
CO ₂ -1,10-Decanediol-Benzoic Acid	308-318	164-307	-1.43798	17.25	6.22	-0.02145	9.34	19.76	-0.06031	9.59	18.96	11

Table 5. Temperature dependent solute-solute binary parameters and AAD(%) errors for 10 ternary systems

Systems	T, K	P, bar	Data source	RK			SRK			PR		
				k_{23}	$y_{2,AAD}$ (%)	$y_{3,AAD}$ (%)	k_{23}	$y_{2,AAD}$ (%)	$y_{3,AAD}$ (%)	k_{23}	$y_{2,AAD}$ (%)	$y_{3,AAD}$ (%)
CO ₂ -Phenanthrene-Naphthalene	308	120-280	9	-0.20381	2.36	4.47	0.02764	2.97	8.77	0.02159	6.05	10.13
CO ₂ -Phenanthrene-Benzoic Acid	308	120-280	5	-0.72245	3.41	11.81	-0.18274	3.36	13.65	-0.18908	5.46	15.09
CO ₂ -Phenanthrene-2,3-DMN	308	120-280	5	10.86103	98.44	39.83	8.66066	98.31	36.31	8.77745	98.40	32.73
	318	120-280	5	14.09082	93.76	79.13	11.07455	93.41	78.93	11.11555	93.51	78.84
CO ₂ -Phenanthrene-2,6-DMN	308	120-280	5	-0.46280	2.77	9.03	-0.10266	4.32	10.12	-0.07591	8.47	11.05
CO ₂ -Naphthalene-Benzoic Acid	308	120-280	5	-0.39881	2.49	10.04	-0.01248	11.88	11.66	-0.02707	13.15	13.3
	318	120-280	5	-0.47266	4.84	7.34	-0.01782	27.41	12.71	-0.02212	27.21	15.29
CO ₂ -Naphthalene-2,3-DMN	308	120-280	5	-0.16265	11.50	1.00	0.08330	5.26	1.01	0.08090	7.60	4.55
CO ₂ -2,3-DMN-2,6-DMN	308	120-280	9	-0.06204	2.71	2.84	0.17799	3.61	1.98	0.19136	3.87	4.41
	318	120-280	9	-0.23021	3.49	2.35	0.15054	2.53	3.73	0.14398	4.44	5.93
Ethylene-2,3-DMN-2,6-DMN	308	120-280	9	-0.26806	7.06	4.45	0.10128	7.32	6.83	0.09873	9.72	9.14
	318	120-280	9	-0.26806	7.06	4.45	0.10128	7.32	6.83	0.09873	9.72	9.14
CO ₂ -Phenanthrene-Anthracene	308	104-242	4	-0.15314	4.25	9.87	0.08448	4.90	8.07	0.07277	7.98	5.93
	318	104-242	4	0.	14.92	26.44	0.11613	3.38	11.27	0.08972	2.30	9.30
CO ₂ -1,10-Decanediol-Benzoic Acid	308	164-306	5	-2.31054	4.75	5.82	-0.10641	6.92	7.06	-0.30265	3.95	8.65
	318	164-307	5	-0.72069	7.55	9.07	-0.05573	8.31	11.86	-0.17275	8.78	13.68

$$AAD(\%) = (100/N) \sum_{i=1}^N |(y_{ji}^{cal} - y_{ji}^{exp}) / y_{ji}^{exp}| \quad (15)$$

$j = 2, 3$

RESULTS AND DISCUSSIONS

The overall results resulting from the Redlich-Kwong, Soave, Peng-Robinson equations of state are summarized in Table 6. As shown in Tables 4 and 5, the one ternary system, CO₂-phenanthrene-2,3-dimethylnaphthalene, could not be correlated with the three cubic equations of state used in this study. Thus, this ternary system was not included in the overall results presented in Table 6.

It should be noted that the solubility of a particular solid component in the ternary system is considerably higher than that in the pure solid system at the same temperature and pressure. The solubility data for the phenanthrene-naphthalene-CO₂ system are shown in Figures 1 and 2. Binary solubility data for the binary pure solid-solvent system are also shown for comparison. The solubility of phenanthrene from a binary solid mixture of phenanthrene and naphthalene in supercritical carbon dioxide increases by a maximum of 75% over that when no naphthalene is present. The

Table 6. AAD(%) errors resulting from three equations of state

	RK(AAD%)		SRK(AAD%)		PR(AAD%)	
	y ₂	y ₃	y ₂	y ₃	y ₂	y ₃
Overall(Table 4)	5.68	7.42	7.36	11.18	8.00	11.78
Isothermal(Table 5)	5.55	6.01	7.09	8.36	8.38	9.73

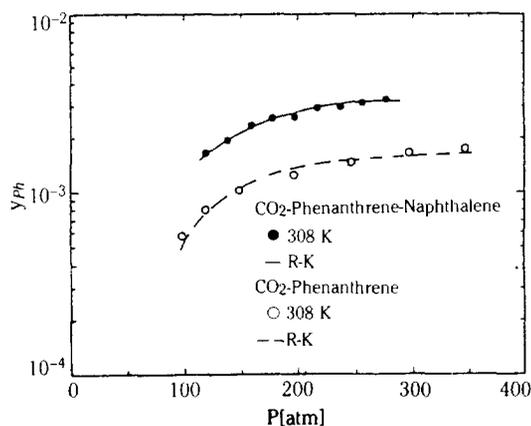


Fig. 1. Solubility of phenanthrene from a binary solid mixture of phenanthrene and naphthalene in supercritical carbon dioxide.

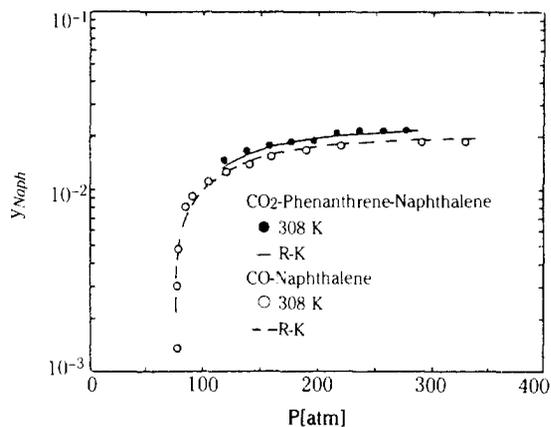


Fig. 2. Solubility of naphthalene from a binary solid mixture of phenanthrene and naphthalene in supercritical carbon dioxide.

corresponding increase for naphthalene is about 20%. The similar patterns of the solubility enhancement were also noticed for a number of ternary systems as also shown in Figures 3-6. The maximum solubility enhancements of the binary solid mixtures in supercritical CO₂ are given in parentheses: benzoic acid (280%)-naphthalene(107%), 2,3-dimethylnaphthalene (144%)-naphthalene(46%), and phenanthrene(-10%)-2,3-dimethylnaphthalene(-10%). However, the fundamental mechanism of the solubility enhancement appearing in the solid mixtures has been poorly understood. One possible explanation is that the upper critical end point for a ternary solid-fluid mixture is expected to occur at a temperature lower than those for either binary solid-supercritical fluid systems. Thus,

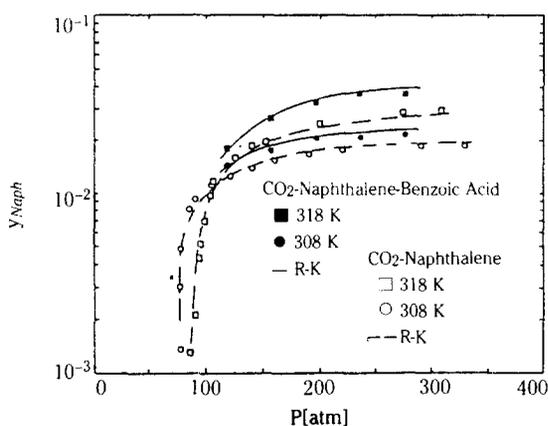


Fig. 3. Solubility of naphthalene from a binary solid mixture of naphthalene and benzoic acid in supercritical carbon dioxide.

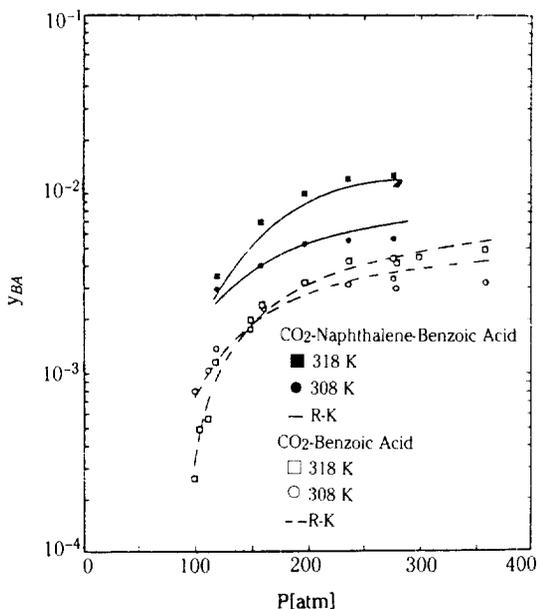


Fig. 4. Solubility of benzoic acid from a binary solid mixture of naphthalene and benzoic acid in supercritical carbon dioxide.

when comparisons are made between ternary and binary solid-fluid systems at the same temperature, the ternary system is closer to the upper critical end point [16]. The other possible explanation can be stated as follows. In CO₂, naphthalene is much more soluble than phenanthrene. Consequently, in the ternary system naphthalene raises phenanthrene's solubilities 75%, while its solubility increases only 20%. Naphthalene and benzoic acid are both highly soluble in

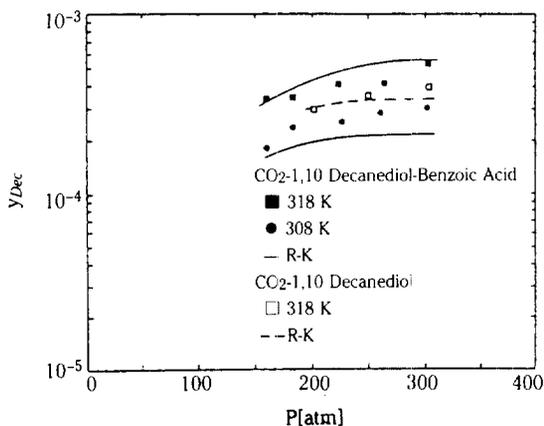


Fig. 5. Solubility of 1,10-decanediol from a binary solid mixture of 1,10-decanediol and benzoic acid in supercritical carbon dioxide.

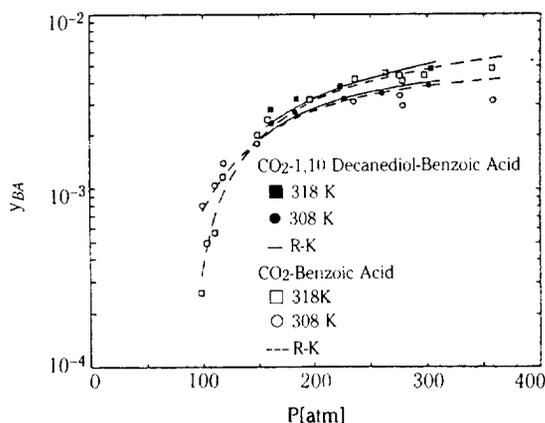


Fig. 6. Solubility of benzoic acid from a binary solid mixture of 1,10-decanediol and benzoic acid in supercritical carbon dioxide.

CO₂, and therefore both solubilities are increased over 100%. The solubilities of phenanthrene and 2,3-dimethylnaphthalene, which are low in the binary case, actually decrease in the ternary case [17].

An important point on the selectivity of solid mixtures by supercritical fluids can be drawn from the general results obtained in this study. The selectivity, α , defined as y_2/y_3 , of the solvent for a ternary system at low pressures is simply the ratio of the vapor pressures of two solids. At high pressures, the selectivity decreases sharply, and levels off at a value of unity. It must be noticed that the extracted-solute mixture cannot be separated with pure supercritical CO₂ unless the extractant composition in equilibrium can be altered by changing the process conditions. This is, in effect, azeotropic situation. The following conclusions can be drawn with great generality from the results reported herein:

(1) Although the three cubic equations of state correlate fairly well the solubility data of solid mixtures in supercritical fluid, the original Redlich-Kwong equation of state, which is the simplest type among them, gives the best results in accuracy for the both cases of overall temperature-independent binary parameters and isothermal temperature-dependent binary parameters. The regressed values of binary interaction parameters can be used for engineering applications down to three places of decimals without any harm of accuracy. One interesting point is that the overall AAD (%) errors are quite good enough for both cases. Therefore, the overall temperature-independent binary parameters can be used to correlate the ternary solubility data in any different temperature range.

(2) The one ternary system, CO₂-phenanthrene-2,3-DMN, was not able to be correlated with the three

equations of state used in this study. This system is the only one that the solute solubility decreases while in other systems the solute solubility increases. Therefore, the approach using the cubic equations of state should be tested further when the new ternary data become available.

(3) The solubility of a given solid in the ternary system will increase relative to that in the binary system in proportion to the solubility of the other solid in supercritical fluid.

(4) The selectivity of supercritical fluids for solute mixture is fairly independent of temperature, but heavily dependent upon pressure.

ACKNOWLEDGEMENT

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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.(13)
 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^s : 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

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