Polar Mixed-Solid Solute Systems in Supercritical Carbon Dioxide: Entrainer Effect and Its Influence on Solubility and Selectivity

Shobha Ravipaty,*,† Karl J. Koebke, and David J. Chesney

Department of Chemistry, Michigan Technological University, Houghton, Michigan 49931

The equilibrium solubilities of benzoic acid (BA), salicylic acid (SAL), and acetylsalicylic acid (ASA) were determined in binary (solute + CO_2), ternary (two solutes + CO_2), and quaternary systems (three solutes + CO_2) at temperatures ranging from (308 to 328) K and pressures ranging from (10.1 to 28.0) MPa. Solubility data were obtained using a dynamic approach with a simple and reliable apparatus. Polar mixed-solid solute systems demonstrated solubility enhancements, which were consistent with the entrainer effect. In all the polar ternary systems studied, at least one component exhibited solubility enhancements. In the polar quaternary system studied, the solubility of each component increased in comparison to each binary system; the solubility of ASA, SAL, and BA was enhanced up to 484 %, 248 %, and 43 %, respectively. The high solubility enhancements observed in our study indicate that solute–solute interactions are significant in the supercritical fluid (SCF) phase. The solubility enhancements observed in the polar mixed-solid solute systems studied resulted in a decrease in selectivity of SCF CO_2. However, in a quaternary system consisting of BA, SAL, and fluoranthene (FLU), the selectivity of SCF CO_2 for SAL versus FLU increased by a factor of 2.7 due to specific solute–solute interactions. This study showed that solute−solute interactions in mixed solid solute systems can result in an increase in the solubility of solutes and also the selectivity of SCF CO_2.

Introduction

Supercritical fluid carbon dioxide (SCF CO_2) is an attractive solvent and has been used in a large variety of applications. However, low polarity and low selectivity of SCF CO_2 have been the major impediments preventing the more widespread use.[1] A small amount of liquid cosolvent (an entrainer) is commonly added to SCF CO_2 to increase solubility of the solutes.[2] A cosolute in a mixed solute system can also act as an entrainer.[2] Most of the mixed-solid solute systems exhibit solubility enhancement where each component behaves as a cosolvent and enhances the solubility of the other component in the mixture in proportion to its concentration in the SCF (the entrainer effect).[3–12] The entrainer effect in mixed-solid solute systems is of considerable interest because the use of entrainers can open up new possibilities in SCF technology. Furthermore, since real processes are multicomponent in nature, investigation of mixed solute solubilities is vital. Studies on mixed-solid solute systems have suggested that greater potential for solubility enhancement exists for a mixture of polar solutes containing hydrogen bonding sites.[11] However, the studies pertaining to polar mixed-solid solute solubilities are relatively scarce, and to the best of our knowledge, there has been only one report in the literature concerning solubilities of polar solid solutes in a quaternary system.[9]

The primary objectives of the present study were to investigate the entrainer effect in polar mixed-solid solute systems and to gain a perspective on the nature and the effect of solute–solute interactions on solubility of the solutes. Benzoic acid (BA), salicylic acid (SAL), and acetylsalicylic acid (ASA) are industrially important compounds, and they are also substructures of many biologically active substances. We chose BA, SAL, and ASA as our model solutes on account of their hydrogen bonding capability and low solubility in SCF CO_2. We reasoned that for these solutes of low solubility one would expect negligible enhancements in the fluid phase, and any increase in solubility if observed would clearly indicate the existence of solute−solute interactions. We investigated the solubilities of BA, SAL, and ASA in binary (solute + SCF CO_2), ternary (two solutes + SCF CO_2), and quaternary systems (three solutes + SCF CO_2) over a range of temperatures [(308 to 328) K] and pressures [(10.1 to 28.0) MPa]. In addition, we sought to explore the effect of a polar cosolute (entrainer) on the selectivity of SCF CO_2 for a pair of solid solutes with similar volatility but different chemical functionality. As a model system, we have investigated the solubilities of BA (polar), SAL (polar), and fluoranthene (FLU) (nonpolar) in a quaternary system at 318 K in the pressure range of (12.0 to 28.0) MPa. A binary system (FLU + SCF CO_2) and a ternary system (FLU + BA + SCF CO_2) have also been studied at 318 K in the pressure range of (12.0 to 28.0) MPa.

Experimental Section

Materials. “Bone-dry”, industrial-grade CO_2 (> 99.9 %) was obtained from Superior Water & Welding (Pelkie, MI). Histological grade methanol was obtained from Fisher Scientific (Pittsburgh, PA) and was used for sample dilutions. Reagent grade potassium monobasic phosphate was obtained from Fisher Scientific. HPLC grade methanol was obtained from Fisher Scientific, and HPLC grade acetonitrile was obtained from EM Science (Gibbstown, NJ). The HPLC grade acetonitrile was dried over 3A molecular sieves (Aldrich, Milwaukee, WI) to remove water. The sources, purities, and melting points of the

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* Author to whom correspondence should be addressed. Tel.: (812)-855-0987. Fax: (812)-855-8300. E-mail address: sravipat@indiana.edu.

† Present address: Department of Chemistry, Indiana University, 800 E. Kirkwood Ave., Bloomington, IN 47405-7102.

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Table 1. Sources, Purities, and Melting Points (T_m) of the Solutes Used in This Work

substance	source	purity	T_m/K
benzoic acid	Matheson Coleman & Bell (Norwood, OH)	99 %	395
salicylic acid	Aldrich (Milwaukee, WI)	99 %	432
acetylsalicylic acid	Eastman (Rochester, NY)	99 %	408 to 409
fluoranthene	Aldrich (Milwaukee, WI)	98 %	380 to 383

solutes used in the study are shown in Table 1. All chemicals were used as received without further purification.

Apparatus and Method. A dynamic method was used to determine solubilities of the solutes in SCF CO_2. A detailed description of the apparatus and the method is given elsewhere.[13] Briefly, in this method, SCF CO_2 is allowed to flow through a bed of solute. A known volume of the saturated SCF CO_2 solution is then sampled, and the amount of solute is determined.

In a typical experiment, a 1.6 mL equilibration cell with stainless steel frits at each end was packed with ground solid solute (~700 mg). Glass wool plugs were placed at both ends of the equilibration cell to prevent clogging of the frits. For ternary and quaternary solubility studies, equal amounts of the selected solutes were weighed, mixed, and ground to get a uniform composition of the solid mixture before packing into the equilibration cell. To determine solubility of the solutes, SCF CO_2 was passed through an equilibration cell, and the saturated SCF CO_2 solution exiting the equilibration cell was allowed to flow through a 120 μL sample loop of the microsampling valve. After about (35 to 60) s (sufficient time to obtain an equilibrated sample), the sample loop was depressurized into a trapping solvent and collected off-line in a collection tube. The loop was rinsed with additional methanol to collect any precipitated solute. The contents of the collection tube were then transferred and diluted with methanol in a volumetric flask for analysis by HPLC. Then, solubility of the solutes was calculated and is expressed here as mole fraction solubility (y). Density values for SCF CO_2 were taken from those reported by Schmitt and Reid.[14] During the experiment, the pressure and temperature of the system were maintained constant to within ± 0.1 MPa and ± 1 K, respectively. After determining solubility at a desired condition, the equilibration cell was bypassed, and the rest of the system including the sample loop was purged with CO_2. This ensured that the methanol was removed from the sample loop and also prevented sample carry over problems between runs.

To ensure that only solid−fluid equilibria existed under the experimental conditions used for solubility studies, the phase behavior of all the systems was checked visually using a phase monitor (Supercritical Fluid Technologies, Inc.; Newark, DE). The phase behavior study involved the visual determination of the lower critical end point[11] for each system and verifying the absence of a liquid phase due to a depression in the melting point of the solutes.

Analysis. The collected samples were analyzed by HPLC. An HPLC pump (Waters; model 590; Milford, MA), an injection valve (Rheodyne; model 7125; Rohnert Park, CA) with a 20 μL injection loop volume, a UV–vis detector (Waters; model 481, Milford, MA), an integrator (Dionex; model 4270; Sunnyvale, CA), and an HPLC column (Waters Spherisorb ODS-2; 5 μm; 25 cm × 4.6 mm; Milford, MA) were used. For the analysis of BA, SAL, and ASA, the column was operated at a flow rate of 1.0 mL·min^{-1} using a mobile phase of 0.010 M phosphate buffer (pH 2.8) and methanol (55:45). For FLU, the column was operated at a flow rate of 1.0 mL·min^{-1} using a mobile phase of 0.010 M phosphate buffer and acetonitrile (20:80). For all solutes, the detector was set at 275 nm.

Table 2. Solubilities of BA, SAL, and ASA in SCF CO_2 (Binary Systems)

		BA	SAL	ASA
p/MPa	ρ/mol·cm^{-3}	10^3y^a	10^3y^a	10^3y
		T = 308 K		
10.1	0.01610	1.07	0.165	0.0572
12.0	0.01724	1.56	0.207	0.0732
15.1	0.01855	1.95	0.268	0.0998
16.0	0.01886	2.10	0.287	0.108
20.0	0.01968	2.49	0.332	0.136
24.0	0.02040	2.86	0.409	0.169
28.0	0.02090	3.13	0.422	0.193
		T = 318 K		
12.0	0.01497	1.32	0.218	0.0735
15.1	0.01692	2.25	0.319	0.122
16.0	0.01730	2.49	0.349	0.136
20.0	0.01848	3.33	0.450	0.183
24.0	0.01930	3.82	0.533	0.226
28.0	0.01996	4.24	0.615	0.261
		T = 328 K		
15.1	0.01493	2.27	0.350	0.124
16.0	0.01548	2.61	0.400	0.151
20.0	0.01720	4.07	0.583	0.231
24.0	0.01825	5.04	0.732	0.302
28.0	0.01907	5.95	0.875	0.375

[a] y = mole fraction solubility.

The stock solutions for BA and SAL and FLU were prepared in methanol. The ASA stock solution was prepared in dried acetonitrile to minimize hydrolysis[15] and stored in the refrigerator. Standard dilutions of ASA were prepared fresh daily in methanol.

Area−concentration calibration curves were used to determine the concentration of the collected analytes. A new calibration curve was generated each time an analysis of the sample solutions was conducted. Each reported solubility data point in the tables is an average of at least three replicate measurements with relative standard deviation less than 5 %. The reproducibility of the solubility measurements was also checked by performing solubility measurements on different days separated by several months, where the total number of replicates ranged from n = 3 to 11.

Results and Discussion

The reliability and efficiency of the solubility measurement technique were previously established by measuring the solubility of naphthalene in SCF CO_2 at 308 K and different pressures, as was described before.[13]

The phase behavior investigation of all the systems in the present study confirmed that the operating conditions for solubility measurements were well above the critical region of CO_2, and the data presented represent solid−fluid equilibria with no liquid phase present.

Binary Solubility of Polar Solutes. To establish a baseline from which to determine solubility enhancements, the individual solubilities of BA, SAL, and ASA in SCF CO_2 were measured at (308, 318, and 328) K over a pressure range of (10.1 to 28.0) MPa. Solubility measurements were carried out at CO_2 (liquid) flow rates ranging from (1.0 to 2.5) mL·min^{-1}. Variation of the flow rate within this range was found to have no effect on the observed solubilities, thereby confirming that solubility measurements were made under equilibrium conditions.

Experimental binary solubility data for BA, SAL, and ASA are listed in Table 2. It can be seen from the data that an

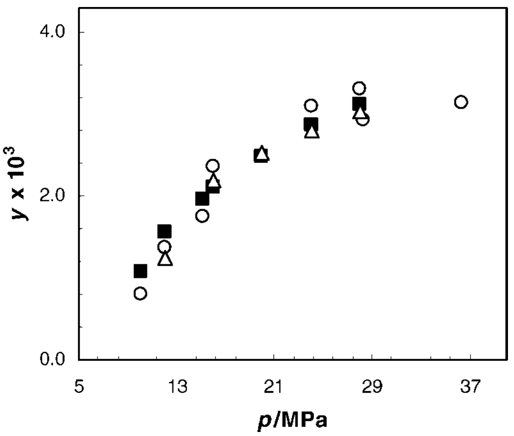

Figure 1. Solubility isotherms of BA in SCF CO_2 at 308 K: ■, this work; ○, Schmitt and Reid;[14] △, Dobbs et al.[16]

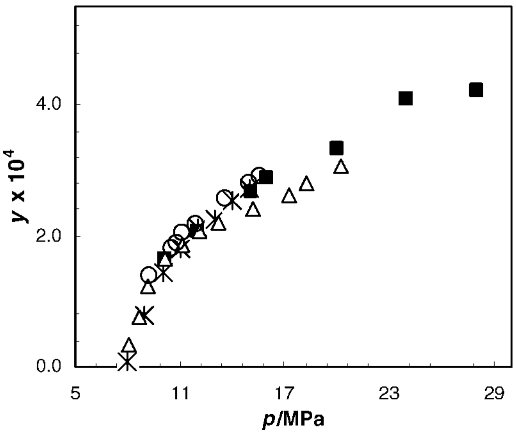

Figure 2. Solubility isotherms of SAL in SCF CO_2 at 308 K: ■, this work; △, Gurdial and Foster;[19] ○, Ke et al.;[20] *, Bristow et al.[21]

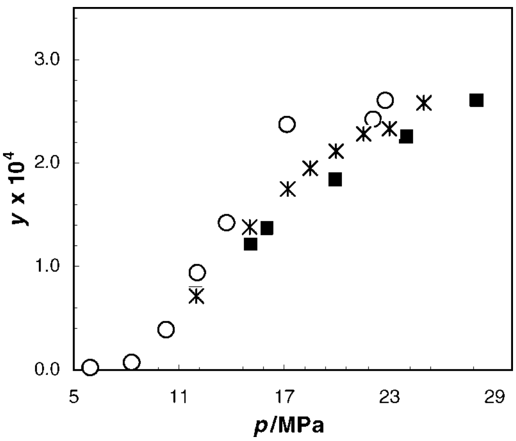

Figure 3. Solubility isotherms of ASA in SCF CO_2 at 318 K: ■, this work; ○, Tavana and Randolph;[24] *, Huang et al.[25]

isothermal increase in pressure increases the solubility of all the solutes correlating with the increase in CO_2 solvent density. An increase in temperature at constant pressure also increases the solubility due to a corresponding increase in solute vapor pressure. BA has an order of magnitude higher mole fraction solubility (10^{-3}) than SAL (10^{-4}) and ASA (10^{-5} to 10^{-4}). This is in accordance with the general observation that increasing the number of polar functional groups decreases the solubility in SCF CO_2.

The BA solubilities at 308 K reported herein are consistent with those reported by Schmitt et al.[14] and Dobbs et al.[16] (Figure 1). Notable, however, is the smooth trend exhibited by our solubility data which may reflect the inherently smaller sampling error associated with our procedure. Dobbs et al.[17] presented a convincing argument for the advantages of the microsampling technique over the gravimetric approach. The sampling errors associated with the microsampling technique are different in nature and smaller in magnitude than those associated with other methods of determining solubility.

The solubility of SAL has been studied extensively.[8,18–23] The superimposition of the binary solubility data of SAL at 308 K from the present measurements and the selected literature sources is presented in Figure 2. This figure clearly shows the agreement between the different sets of data except for the data obtained from Gurdial et al.,[19] which are lower at higher pressures. A similar finding has been reported by Reverchon et al.[22]

Solubility of ASA has previously been reported by Tavana and Randolf at 318 K.[24] Huang et al. also reported the solubility of ASA in SCF CO_2.[25] Figure 3 shows that the data reported by Tavana and Randolf are significantly higher than our data and the data reported by Huang et al. The method used by Tavana and Randolph involved the collection of solute over a period of time with subsequent gravimetric analysis. The advantage of the sampling-valve approach is apparent, as evidenced by the smooth trend of our solubility data.

These binary solubility studies, in addition to providing data for establishing solubility enhancements, also served to provide a validation of our experimental method.

Ternary Solubility of Polar Solutes. To understand the solute–solute interactions in polar solid solute systems, three ternary systems (SAL + BA, ASA + BA, and ASA + SAL) were investigated at (308, 318, and 328) K over a pressure range of (10.1 to 28.0) MPa. At each temperature and pressure, solubility enhancements were determined from the measured binary and ternary solubilities. Solubility enhancement is defined as the percent relative increase of the ternary solubility relative to the binary solubility of the component at the same temperature and pressure.[9]

$$\text{solubility enhancement} = (y_{\text{ternary}} - y_{\text{binary}})/(y_{\text{binary}}) \cdot 100\ \% \tag{1}$$

An average value of solubility enhancement was then calculated for a given temperature and a defined range of pressures from individual values. A positive value of solubility enhancement represents a true enhancement, whereas a negative value indicates a decrease in solubility in the ternary system relative to the binary system (solubility diminution). Since the experimental precision for solubility measurements presented in this work is within ± 5 %, an average solubility enhancement in this range is therefore considered to be within the limits of experimental precision and does not constitute any significant increase or decrease in solubility.

The solubility data for the ternary systems, SAL + BA, ASA + BA, and ASA + SAL, at three temperatures are presented in Table 3. The tabulated results also show the corresponding solubility enhancements relative to the binary solubility data. In the three ternary systems studied, the ternary isotherms exhibited trends similar to binary isotherms, i.e., an increase in solubility with an increase in pressure at constant temperature and an increase in solubility with the increase in temperature at constant pressure. In each case, at least one of the solutes in the selected ternary systems exhibited solubility enhancement. The data from replicate solubility measurements are presented in all the figures.

Table 3. Solubilites of SAL + BA, ASA + BA, and ASA + SAL in SCF CO_2 (Ternary Systems)

	SAL + BA ternary system				ASA + BA ternary system				ASA + SAL ternary system			
	SAL		BA		ASA		BA		ASA		SAL	
p/MPa	10^3y[a]	SE[b] (%)	10^3y[a]	SE[b] (%)	10^3y[a]	SE[b] (%)	10^3y[a]	SE[b] (%)	10^3y[a]	SE[b] (%)	10^3y[a]	SE[b] (%)
						T = 308 K						
10.1	0.345	109	1.12	4.7	0.167	192	1.15	7.48	0.0778	36.0	0.200	21.2
12.0	0.473	129	1.56	0.0	0.257	251	1.66	6.41	0.117	59.8	0.255	23.2
15.1	0.657	145	1.95	0.0	0.366	267	2.23	14.4	0.172	72.3	0.335	25.0
16.0	0.706	146	2.05	−2.4	0.418	287	2.43	15.7	0.192	77.8	0.359	25.1
20.0	0.856	158	2.59	4.0	0.553	307	3.05	22.5	0.246	80.9	0.449	35.2
24.0	1.00	144	2.97	3.8	0.680	302	3.53	23.4	0.294	74.0	0.507	24.0
28.0	1.12	165	3.29	5.1	0.769	298	3.85	23.0	0.342	77.2	0.601	42.4
average		142		2.2		272		16.1		68.3		28.0
						T = 318 K						
12.0	0.461	111	1.29	−2.3	0.219	198	1.45	9.85	0.112	52.4	0.248	13.8
15.1	0.730	129	2.21	−1.8	0.424	248	2.55	13.3	0.206	68.9	0.401	25.7
16.0	0.803	130	2.43	−2.4	0.487	258	2.83	13.7	0.223	64.0	0.430	23.2
20.0	1.11	147	3.28	−1.5	0.716	291	3.79	13.8	0.318	73.8	0.606	34.7
24.0	1.36	155	4.00	4.7	0.904	300	4.56	19.4	0.403	78.3	0.724	35.8
28.0	1.53	149	4.43	4.5	1.17	348	5.41	27.6	0.495	89.7	0.854	38.9
average		137		0.20		274		16.3		71.2		28.7
						T = 328 K						
15.1	0.733	110	2.14	−5.7	0.436	252	2.63	17.6	0.207	66.9	0.410	17.1
16.0	0.865	116	2.56	−1.9	0.535	254	3.09	18.4	0.252	66.9	0.486	21.5
20.0	1.39	138	3.89	−4.4	0.940	307	4.90	20.4	0.421	82.3	0.749	28.5
24.0	1.86	154	5.11	1.4	1.35	347	6.33	25.6	0.552	82.8	0.997	36.2
28.0	2.26	158	6.07	2.0	1.95	420	8.68	45.9	0.667	77.9	1.19	36.0
average		135		−1.7		316		25.6		75.4		27.9

[a] y = mole fraction solubility. [b] SE = solubility enhancement.

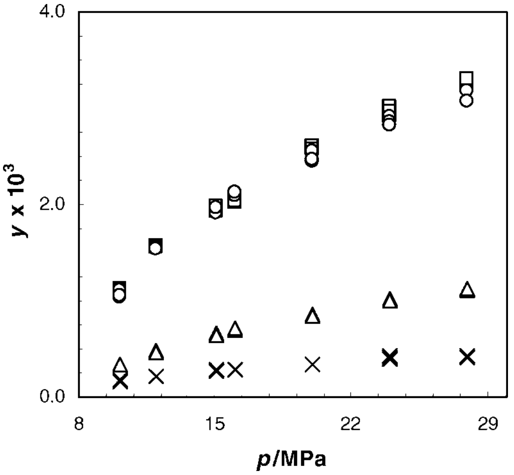

Figure 4. Comparison of binary and ternary solubilities of SAL and BA at 308 K: ×, SAL (binary); △, SAL (ternary); ○, BA (binary); □, BA (ternary).

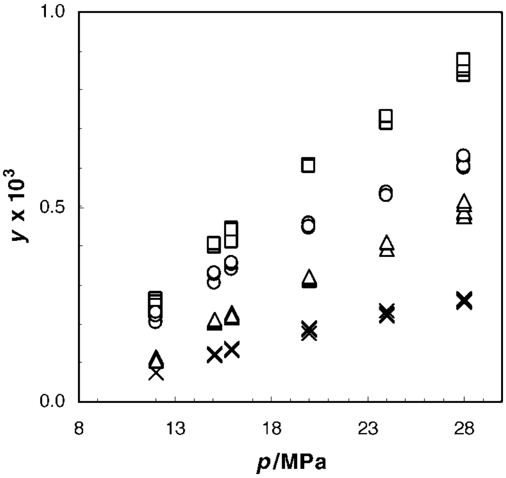

Figure 5. Comparison of binary and ternary solubilities of ASA and SAL at 318 K: ×, ASA (binary); △, ASA (ternary); ○, SAL (binary); □, SAL (ternary).

SAL + BA Ternary System. Under the conditions studied, the solubility of SAL in the presence of BA was enhanced up to 165%. However, there was no significant change in the solubility of BA relative to its binary solubility (solubility enhancement within ± 5%). The ternary solubility of BA therefore reconfirmed the accuracy of binary solubility data.

The pattern of solubility enhancement in the SAL + BA ternary system is consistent with the entrainer effect and is evident from Figure 4. The solubility of SAL is enhanced due to greater entraining effect of BA, but does not influence the solubility of BA in return, due to its low solubility. Furthermore, at constant temperatures the solubility enhancement of SAL seems to increase with pressure and remains relatively constant at higher pressures. This effect of pressure on solubility enhancement can be explained in terms of an increase in the solubility of entraining solute (BA) with pressure. Similar trends have been observed in other solute systems such as *o*-hydroxybenzoic acid + *p*-hydroxybenzoic acid.[8,9] However, a decrease in solubility enhancement with pressure has been reported in other solute systems such as 2,6-dimethyl naphthalene + 2,7-dimethyl naphathalene.[7]

ASA + BA Ternary System. Under the conditions studied, the solubility of ASA was enhanced up to 420 %, and that of BA was enhanced up to 46 %. The ASA + BA ternary system supports Dobbs and Johnston's postulate[12] that a more soluble solute (BA) causes a more significant increase in the solubility of a less soluble component (ASA) than vice versa. There is also a clear trend toward an increasing relative solubility enhancement for ASA with an increasing BA solubility in the fluid phase (Table 3).

ASA + SAL Ternary System. Figure 5 illustrates the solubility enhancements for ASA and SAL relative to their binary solubilities at 318 K. The low solubilities of ASA and SAL (relative to BA) are reflected in their solubility enhance-

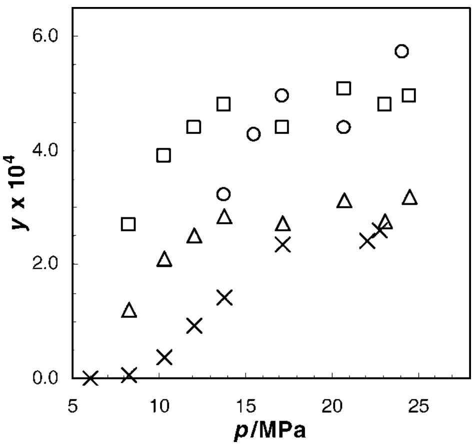

Figure 6. Binary and ternary solubilities of ASA and SAL, data from Tavana and Randolph:[24] ×, ASA (binary); △, ASA (ternary); ○, SAL (binary); □, SAL (ternary).

ments, which are lower in comparison to the two ternary systems previously discussed. Under the conditions studied, the solubility of ASA was enhanced up to 90 %, and that of SAL was enhanced up to 42 %.

Tavana and Randolph[24] have previously reported the solubility data for the ASA + SAL ternary system at 318 K (Figure 6). There is considerable inconsistency in the experimental solubility data obtained by these authors and the present work. According to their data, the solubility enhancement for ASA is high (>400 %) at very low pressures and decreases considerably with increasing pressure; moreover, SAL exhibits solubility diminution. These results clearly contradict our observations. Also notable are the smooth solubility trends observed in our study. Further, the binary solubility data for SAL reported by these authors are significantly higher than those reported by other investigators.[19,26] The observed discrepancies could be a result of the experimental technique used in their study, which involved the collection of the solute over a period of time, with subsequent derivatization and chromatographic analysis. Also, details regarding the accuracy of the experimental measurements and the purity of ASA and SAL were not provided.

Quaternary Solubility of Polar Solutes. The solubilities of ASA, SAL, and BA in a quaternary system were determined at (308, 318, and 328) K over a pressure range of (10.1 to 28.0) MPa. Our objective was to evaluate the individual solubilities of the solutes in the presence of the other two solutes and determine if solubility enhancement patterns differed from those observed in the ternary systems.

Quaternary solubilities of the three solutes and their corresponding solubility enhancements are shown in Table 4. The quaternary solubility isotherms of all three solutes displayed patterns similar to binary and ternary systems. The solubility of each solute and the corresponding solubility enhancement increased with an increase in pressure at a given temperature.

Solubilities of all the solutes were enhanced relative to their respective binary systems. For ASA and SAL, the solubilities were enhanced beyond those observed in the ternary systems, due to the presence of an additional entrainer in the system. However, for BA, the solubility was not enhanced beyond that observed in the two ternary systems despite the combined presence of ASA and SAL.

Under the conditions studied, the solubilities of ASA, SAL, and BA were enhanced up to 484 %, 248 %, and 43 %, respectively. Comparison of solubility enhancements in the quaternary system with those of the ternary enhancements indicates that the less-soluble solutes in a quaternary system may interact independently of each other and that the enhancements may be additive. For example, the quaternary solubility enhancement for ASA at 308 K and 28.0 MPa is 352 % which is approximately the sum of its ternary enhancements with BA (298 %) and SAL (77 %).

Table 4. Solubilities of ASA + SAL + BA in SCF CO_2 (Quaternary System)

	ASA		SAL		BA	
p/MPa	10^3y^a	SE^b (%)	10^3y^a	SE^b (%)	10^3y^a	SE^b (%)
			$T = 308$ K			
10.1	0.169	195	0.349	112	1.12	4.67
12.0	0.298	307	0.524	153	1.67	7.05
15.1	0.415	316	0.710	165	2.31	18.5
16.0	0.473	338	0.761	165	2.52	20.0
20.0	0.642	372	0.987	197	3.12	25.3
24.0	0.760	350	1.13	176	3.54	23.8
28.0	0.872	352	1.31	210	4.07	30.0
average		319		168		18.5
			$T = 318$ K			
12.0	0.250	240	0.480	120	1.41	6.82
15.1	0.491	302	0.855	168	2.52	12.0
16.0	0.563	314	0.981	181	2.84	14.1
20.0	0.872	377	1.37	204	3.80	14.1
24.0	1.13	400	1.73	225	4.75	24.3
28.0	1.39	433	2.08	238	5.56	31.1
average		344		189		17.1
			$T = 328$ K			
15.1	0.480	287	0.848	142	2.45	7.93
16.0	0.610	304	1.06	165	3.03	16.1
20.0	1.09	372	1.78	205	4.80	17.9
24.0	1.67	453	2.55	248	6.76	34.1
28.0	2.19	484	2.85	226	8.48	42.5
average		380		197		23.7

^{a} y = mole fraction solubility. ^{b} SE = solubility enhancement.

The polar ternary and quaternary systems studied in this work exhibited trends consistent with the entrainer effect. In SAL + BA and ASA + BA ternary systems, the solubilities of SAL and ASA were enhanced by a factor of 2.7 and 4.5, respectively, because of the greater entraining effect of BA. Although SAL has slightly higher solubility than ASA, it does not cause any significant enhancement in BA solubility, and BA enhanced ASA to a greater extent (420 %) compared to SAL (165 %). The observed differences in solubility enhancement could be due to the differences in the functional groups and the strength of the interactions. The magnitude of the solubility enhancement was higher in the quaternary system where the solubility of SAL was enhanced by a factor of 4 and ASA was enhanced by a factor of 6. In spite of the low solubilities of the polar solutes in SCF CO_2, the high solubility enhancements observed in our study indicate that solute–solute interactions are significant in the SCF phase. In view of the potential hydrogen bonding sites, hydrogen bonding is a probable interaction between the polar solutes, as has been suggested for other polar mixed-solid solute systems.[9,11]

Selectivity in Mixed-Solid Solute Systems. In a majority of the mixed-solid solute systems, the overall result of solubility enhancement is a decrease in the selectivity (α) of an SCF solvent for a particular component ($\alpha = y_{\text{solute1}}/y_{\text{solute2}}$), ultimately leading to a decrease in the separation of solid solutes. The polar mixed-solid solute systems studied in this work also exhibited a decrease in selectivity of SCF CO_2. This can be illustrated by considering the example of the ASA + SAL ternary system. The selectivity of SCF CO_2 for SAL versus ASA can be defined as the ratio of respective mole fractions of the solutes in the fluid phase ($\alpha = y_{\text{SAL}}/y_{\text{ASA}}$). The selectivities

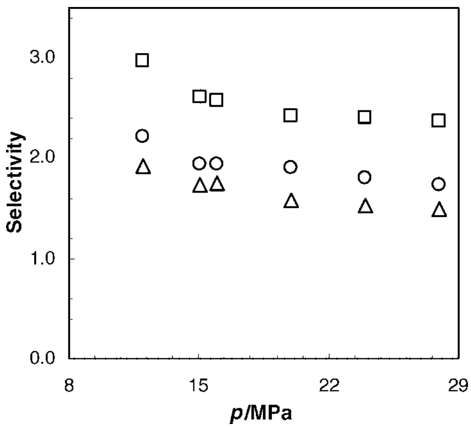

Figure 7. Selectivity of SCF CO_2 for SAL (1) versus ASA (2) at 318 K: □, y_1/y_2 in binary system; ○, y_1/y_2 in ASA + SAL ternary system; △, y_1/y_2 in ASA + SAL + BA quaternary system.

based on the binary, ternary, and quaternary data are presented in Figure 7 as a function of pressure. In each case, the selectivity is higher at lower pressures at the expense of lower solute concentrations in the fluid phase and decreases with increases in pressure. In the ASA + SAL ternary system, the increase in solubility of the solutes (entrainer effect) resulted in lower selectivities than those expected from binary solubility data. In the quaternary system, the presence of an additional polar entrainer (BA) resulted in a further decrease in the selectivities, since the solubility of ASA is enhanced to a greater extent than SAL.

It has been demonstrated that the selectivity of SCF CO_2 for polar versus nonpolar solids can be improved by the addition of a small amount of polar liquid cosolvent.[12] We theorized that a polar cosolute should also be able to increase the selectivity of SCF CO_2 through specific interactions with the solutes. However, to the best of our knowledge, a quaternary system with polar and nonpolar solid solutes and a polar cosolute (entrainer) has not been investigated. Therefore, to explore the possibility of increasing the selectivity of SCF CO_2 by addition of a polar cosolute, a quaternary system consisting of BA (polar entrainer), SAL (polar solute), and FLU (nonpolar solute) was studied at 318 K in the pressure range of (12.0 to 28.0) MPa. A binary system of FLU and a ternary system of FLU + BA were also studied for comparison.

The binary solubilities of FLU determined in this study were in agreement with those reported by Yamini and Bahramifar[27] (Figure 8). The ternary solubilities and corresponding solubility enhancements for a 50:50 wt % mixture of FLU and BA at 318 K are presented in Table 5. The weak solute–solute interactions (dispersion forces) between BA and FLU are reflected in their solubility enhancements; the solubility of FLU was enhanced up to 26 %, and BA was enhanced up to 20 %.

Quaternary solubilities of FLU, SAL, and BA, and their corresponding solubility enhancements, are presented in Table 6. Under the conditions studied, the solubility of SAL was enhanced up to 215 %, and FLU was enhanced to only 40 %. A comparison of quaternary solubilities of FLU and SAL with those of binary solubilities is illustrated in Figure 9. In the figure, quaternary and binary solubilities of BA have been omitted for clarity. The differences in the magnitude of the enhancements observed in this study indicate the differences in the nature of interactions between BA + SAL (strong polar interactions) and BA + FLU (weak dispersive forces) solute pairs. On the basis of the binary solubility data, the selectivity of SCF CO_2 for SAL vs FLU is essentially unity due to similar volatilities. However, in the presence of BA, the selectivity increased to a value of 2.7 indicating preferential interactions (Figure 10). In this study, BA (polar entrainer) enhanced the solvent power as well as the selectivity of SCF CO_2. This system demonstrated that polar solute–solute interactions are strong and can be potentially useful in increasing the selectivity of SCF CO_2 and enhancing the separation of solutes having similar volatilities.

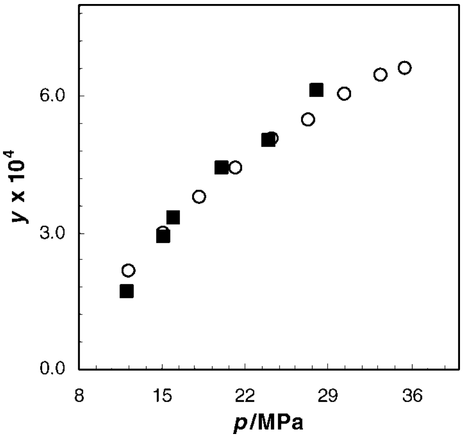

Figure 8. Solubility isotherms of FLU in SCF CO_2 at 318 K: ■, this work; ○, Yamini and Bahramifar.[27]

Table 5. Solubilities of FLU + BA in SCF CO_2 (Ternary System) at 318 K

	FLU		BA	
p/MPa	10^3y^a	SE^b (%)	10^3y^a	SE^b (%)
12.0	0.178	5.61	1.25	−5.19
15.1	0.356	23.1	2.44	8.47
16.0	0.372	11.7	2.70	8.25
20.0	0.509	15.6	3.71	11.5
24.0	0.613	22.4	4.61	20.7
28.0	0.772	26.0	4.99	17.6
average		17.4		10.2

[a] y = mole fraction solubility. [b] SE = solubility enhancement.

Table 6. Solubilities of FLU + SAL + BA in SCF CO_2 (Quaternary System) at 318 K

	FLU		SAL		BA	
p/MPa	10^3y^a	SE^b (%)	10^3y^a	SE^b (%)	10^3y^a	SE^b (%)
12.0	0.200	18.5	0.532	144	1.32	−0.30
15.1	0.369	27.7	0.853	167	2.38	5.74
16.0	0.398	19.4	0.995	185	2.65	6.25
20.0	0.548	24.5	1.42	215	3.62	8.74
24.0	0.701	39.9	1.66	212	4.53	18.6
28.0	0.763	24.5	1.88	205	5.20	22.7
average		25.8		188		10.3

[a] y = mole fraction solubility. [b] SE = solubility enhancement.

Conclusions

Binary, ternary, and quaternary solubilities of BA, SAL, and ASA were investigated at pressures ranging from (10.1 to 28.0) MPa and at temperatures ranging from (308 to 328) K. This study re-examined the published data for binary solubility of BA, SAL, and ASA and ternary solubility of the ASA + SAL system and emphasized the need for a reliable method of accurate solubility measurement.

The polar mixed-solid solute systems exhibited solubility enhancements consistent with the entrainer effect. This study confirmed that even in dilute solutions, solute–solute interactions are significant in the SCF phase. Solubility enhancement in polar mixed solute systems resulted in a decrease in the selectivity

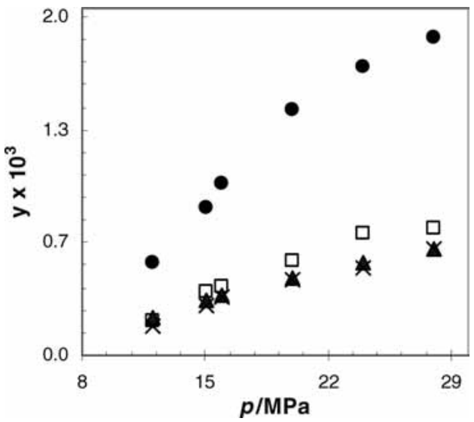

Figure 9. Comparison of binary and quaternary solubilities of FLU and SAL with BA as the entrainer at 318 K: ×, FLU (binary); □, FLU (quaternary); ▲, SAL (binary); ●, SAL (quaternary).

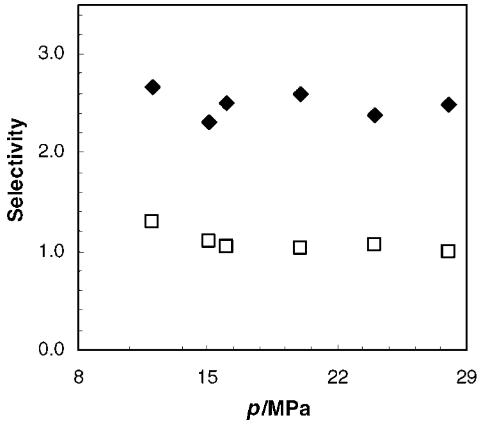

Figure 10. Selectivity of SCF CO$_2$ for SAL (1) versus FLU (2) at 318 K: □, y_1/y_2 in the binary system; ♦, y_1/y_2 in the FLU + SAL + BA quaternary system.

of SCF CO$_2$. However, study of the FLU + SAL + BA quaternary system demonstrated that solute–solute interactions can be specific and that these interactions can be utilized to improve the selectivity of SCF CO$_2$ for compounds of similar volatility but different polarity.

The large magnitude of the solubility enhancements observed for polar solutes in the present study indicates strong polar–polar interactions. It is probable that hydrogen bonding is the main interaction leading to high solubility enhancements.

To tailor the solvent power to achieve specific goals and exploit the solute–solute interactions, a still better understanding of the nature and the strength of molecular interactions in SCF solutions is warranted. Future investigations should involve more detailed solubility studies of polar multicomponent systems involving spectroscopic and computational methods.

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