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Fluid Phase Behavior of Close Molecular Weight Fine Chemicals with Supercritical Carbon Dioxide

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Supercritical fluid phase equilibrium behavior of binary and ternary systems has been ascertained for separation of three pairs of aromatic chemicals having close molecular weights, namely, decalin + tetralin, anisaldehyde + anisic acid, and menthol + thymol. The respective fluid–liquid equilibrium and solid–fluid equilibrium phase compositions have been measured over a pressure range of 55–160 bar and temperature range of 323–373 K with carbon dioxide. The selectivity of separation is higher at lower temperature but increases with pressure up to a certain pressure beyond which it decreases. Apparent selectivities for the tetralin + decalin system from the binary data are comparable to experimental selectivities from the ternary data. Binary results may be used for assessing the selectivity of separation for systems having minimal chemical interaction. Supercritical carbon dioxide is a selective solvent for all three binary pairs of aromatic compounds studied.

Introduction

Separation of aromatic chemicals is considered commercially important as they are starting raw materials, often required in the purest form, for several high value fine chemicals. A supercritical fluid (SCF) solvent, such as carbon dioxide (CO_2), is known to have the capability of separating such difficult mixtures by virtue of its adaptable molecular association with the components. The solvent power and selectivity of separation can be manipulated by small variations in the operating conditions, such as temperature, pressure, and cosolvent (McHugh and Krukonis, 1986). In order to optimally utilize the potential of the supercritical CO_2 solvent by striking a balance between the solvent capacity and selectivity, it is imperative to study the fluid–liquid phase equilibria of the systems. Information on fluid phase behavior also facilitates effective design of the separation process. High-pressure phase equilibrium of binary mixtures has been extensively investigated in recent years (Yau and Tsal, 1992), though much less work has been done on ternary mixtures (Yu et al., 1993). The phase behavior of binary mixtures of supercritical CO_2 and the solute depicts the nature of solute–solvent interactions whereas the phase equilibrium behavior of a ternary system includes the influence of solute–solute interactions as well. Classical thermodynamic and molecular dynamic models are often inadequate to predict their behavior due to chemical association between the components (Reilly et al., 1992). It is thus important to carry out experimental measurements of the fluid phase equilibria (Donohue and Vimal Chand, 1988; Deiter and Gerard, 1993). In the present study, attention has been focused on separation of three binary pairs, namely, (i) decalin + tetralin, (ii) anisaldehyde + anisic acid, and (iii) menthol + thymol with supercritical CO_2 as the extracting solvent. Fluid phase equilibrium measurements have been performed on all the binary systems and one ternary system with CO_2 as the common component. In this paper, we analyze the effect of temperature and pressure on the distribution coefficients and the apparent selectivities calculated from the binary data and investigate their utility in assessing the feasibility of the desired separation based on the ternary data.

Experimental Section

An autoclave made of SS 316 having a 1 L internal volume and provision for rocking was used as the high-pressure equilibrium cell. It contained one inlet port for high-pressure CO_2 and two electrically heated sampling ports for the equilibrated phases, as shown schematically in Figure 1. The equilibrium cell was provided with an electrical heating mantle of 1.5 kW capacity, and the temperature of the cell was controlled by a PID controller to within ±0.5 °C. The equilibrium temperature was measured within ±0.1 °C by a chromel–alumel thermocouple inserted into the thermowell of the cell. The pressure was measured with a Bourdon pressure gauge with a precision of ±0.5 bar. A freezing mixture bath was used for cooling and liquefying CO_2 after it was purified by an adsorbent bed of molecular sieves. A liquid CO_2 pump (Haskel) was used as the pressure intensifier of CO_2 which was later stored and heated in a surge vessel of 1/2 L capacity at the supercritical condition. For each experimental run, the cell was charged with about 500 cm^3 of the desired liquid and supercritical CO_2 from the surge vessel to attain the desired condition. It was then rocked for 6 h while the operating pressure and temperature were kept constant followed by settling for 2 h.

The equilibrium cell was provided with arrangements for trapping of the equilibrated phases one at a time by cracking the valve for a moment. The fluid phase from the top of the cell was trapped in an evacuated 50 cm^3 bomb, which was later allowed to expand by means of an electrically heated needle valve connected to a glass separator. The pressure in the cell was not allowed to drop by more than 0.5 bar. The released gas was measured by means of a precalibrated wet test meter with an accuracy of ±10 cm^3. However, for sampling of the liquid phase, a small amount was trapped in 5 cm^3 evaculated tubing between two needle valves, which was later depressurized to 1 bar by another electrically heated needle valve. The CO_2 gas released from the glass separator was collected over an air tight water reservoir while water was displaced from it, and its volume was known from the volume of the displaced

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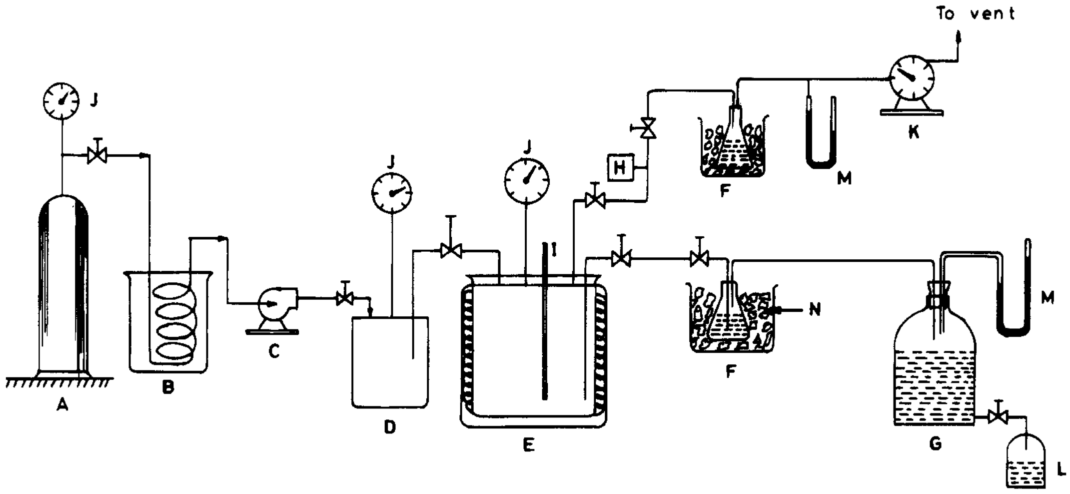


Figure 1. Schematic flow diagram of the experimental setup: (A) CO_2 cylinder; (B) cooling bath; (C) liquid CO_2 pump; (D) surge tank; (E) equilibrium cell; (F) separator; (G) jar; (H) bomb; (I) temperature controller, (J) pressure gauge; (K) wet test meter; (L) collector; (M) manometer; (N) freezing mixture.

Table 1. Physical Properties and Structures of the Compounds Used in This Study

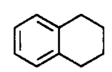
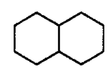
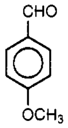
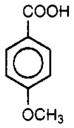
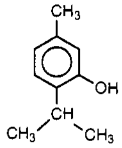
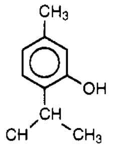
compound	MW	t_b/°C	t_f/°C	n_D	ρ/(g·cm^{-3})	structure
tetralin	132	207	−35	1.544	0.973	
decalin	138	190	−43	1.470	0.870	
p-anisaldehyde	136	248		1.574	1.119	
p-anisic acid	152		180			
thymol	150	232	50		0.965	
menthol	156	212	35		0.890	
methanol	36	65		1.325	0.880	CH_3OH

Table 2. Solubility of Various Aromatic Compounds in Supercritical CO_2[a]

P/bar	x_1	y_1	10^3K_2	K_1
		Carbon Dioxide (1) + Decalin (2)		
		T = 323 K		
100	0.791	0.9889	53.10	1.25
90	0.689	0.9940	19.20	1.44
80	0.500	0.9973	5.40	1.99
70	0.387	0.9990	1.63	2.58
60	0.281	0.9992	1.11	3.55
		T = 343 K		
130	0.728	0.9741	95.20	1.36
110	0.579	0.9889	26.30	1.70
100	0.521	0.9908	19.20	1.90
90	0.441	0.9950	8.94	2.26
75	0.312	0.9971	4.21	3.20
55	0.258	0.9977	3.10	3.87
		Carbon Dioxide (1) + Tetralin (2)		
		T = 323 K		
110	0.740	0.9916	32.30	1.34
95	0.620	0.9975	4.31	1.61
90	0.597	0.9986	3.48	1.67
85	0.520	0.9990	2.08	1.92
80	0.494	0.9993	1.38	2.02
52	0.322	0.9997	0.44	3.10
		Carbon Dioxide (1) + Anisaldehyde (2)		
		T = 323 K		
115	0.7949	0.9970	58.00	1.25
106	0.7815	0.9916	38.40	1.28
100	0.7661	0.9945	23.20	1.30
90	0.726	0.9980	7.30	1.37
80	0.6802	0.9993	2.19	1.49
72	0.5987	0.9997	0.75	1.67
55	0.3022	0.9998	2.29	3.31
		T = 373 K		
137	0.6420	0.9860	39.10	1.53
125	0.6300	0.9918	22.10	1.57
104	0.5500	0.9956	9.77	2.11
90	0.4705	0.9980	3.77	2.63
69	0.3307	0.9994	0.89	3.02
55	0.1827	0.9996	0.49	5.47

[a] x_1 is the mole fraction of carbon dioxide in the liquid phase, and y_1 is the mole fraction in the vapor phase.

water. Each glass separator was provided with a diffuser at the end of the inlet which was dipped into methanol to avoid entrainment losses. Each sampling bomb, after depressurization, was thoroughly washed with methanol. The washings along with the contents of the glass separators were weighed in a Shimadzu (Japan) balance with an accuracy of ±0.0001 g. The composition was systematically determined using a UV spectrophotometer with an accuracy of better than 10 ppm. The accuracy of the equilibrium vapor and liquid phase compositions was estimated to be within ±1%, as depicted by the agreement of the experimental data reported on the carbon dioxide (1) + tetralin (2) system (Kim et al., 1989).

The materials in the present study were used as they were supplied (De, 1994). Tetralin and decalin, both having a minimum purity of 99% (by mass), were supplied by Merck, Germany. Anisaldehyde, thymol, and menthol with a stated minimum purity of 99% (by mass) were obtained from S.D. Fine Chemicals, India. Anisic acid of 98% purity (by mass) was supplied by SISCO Research Laboratory, Bombay, and CO_2 gas of 99 mol % purity by Metro Trading Corp., Bombay. Methanol (99.99 mol % purity) used was of UV spectroscopic grade and was supplied by Spectrochem India Ltd. The physical properties of these chemicals are given in Table 1.

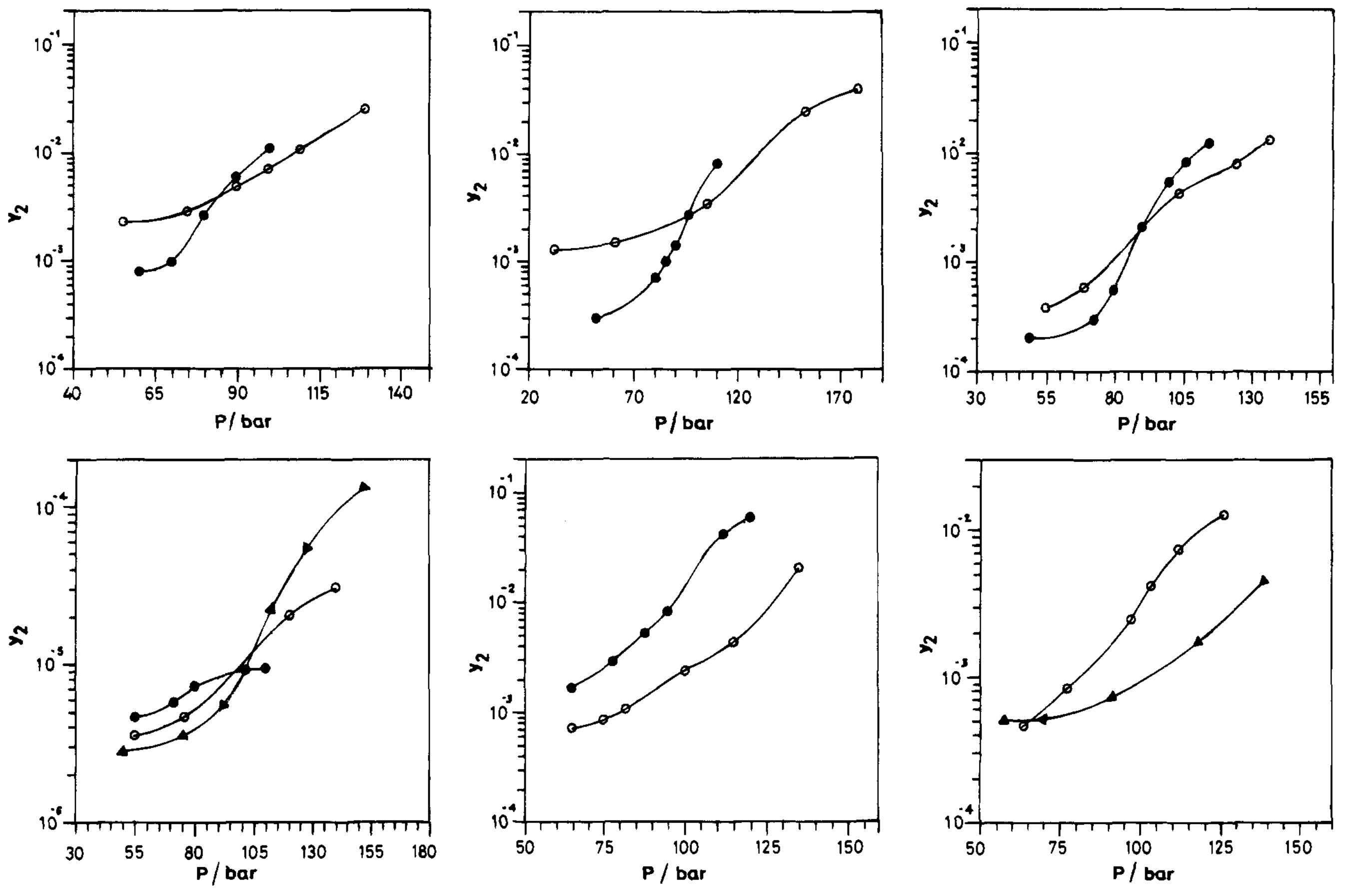


Figure 2. (a, top left) Pressure–composition diagram for carbon dioxide (1) + decalin (2): (●) 323 K; (○) 343 K. (b, top middle) Pressure–composition diagram for carbon dioxide (1) + tetralin (2): (●) 323 K; (○) 343 K. (c, top right) Solubility of anisaldehyde (2) in supercritical carbon dioxide (1): (●) 323 K, (○) 373 K. (d, bottom left) Solubility of anisic acid (2) in supercritical carbon dioxide (1): (●) 323 K; (○) 343 K; (▲) 373 K. (e, bottom middle) Solubility isotherms of menthol (2) + carbon dioxide (1): (●) 323 K; (○) 343 K. (f, bottom right) Solubility isotherms of thymol (2) + carbon dioxide (1): (○) 323 K; (▲) 343 K.

Table 3. Solubility of Anisic Acid in Supercritical Carbon Dioxide

P/bar	10^6y_2	P/bar	10^6y_2
	$T = 323$ K		
110	9.64	71	5.78
100	9.21	55	4.61
80	7.35		
	$T = 343$ K		
140	32.00	75	4.58
120	21.02	55	3.57
100	10.20		
	$T = 373$ K		
151	137.30	92	5.56
130	59.03	75	3.65
112	22.67	50	2.87

Table 4. Solubility of Menthol and Thymol in Supercritical CO_2

menthol		thymol	
P/bar	10^3y_2	P/bar	10^3y_2
	$T = 323$ K		
120	57.83	127	12.56
112	42.31	113	7.21
95	8.127	104	4.14
88	5.331	98	2.44
78	2.890	78	0.83
65	1.720	65	0.47
	$T = 343$ K		
135	22.08	140	4.49
115	7.29	119	1.71
100	3.40	90	0.44
82	1.02	70	0.51
75	0.88	57	0.54
65	0.72		

Results and Discussion

The fluid–liquid equilibrium (FLE) data have been generated by the static method for five binary systems (Figure 2a–e), namely, (i) decalin + CO_2 at 323 and 343 K, (ii) tetralin + CO_2 at 323 K, (iii) anisaldehyde + CO_2 at 323 and 373 K, (iv) menthnol + CO_2 at 323 and 343 K, and (v) thymol + CO_2 at 323 and 343 K, over pressures ranging from 55 to 160 bar. The solid–fluid equilibrium data (Figure 2f) for the solid component anisic acid in supercritical CO_2 have also been generated at the three temperatures 323, 343, and 373 K. The FLE data for the ternary system decalin + tetralin + CO_2 have been measured only at two temperatures, namely, 323 and 343 K, for an equimolar mixture of decalin + tetralin. The phase equilibrium compositions and the distribution coefficients for these systems are presented in Tables 2–5. The distribution coefficient, K_i, is defined as

$$K_i = y_i/x_i \qquad (1)$$

where y and x denote the mole fractions in the SCF phase and liquid phase, respectively. The solubilities of tetralin and decalin increase with pressure at all temperatures, but decrease with temperature beyond a certain pressure. The crossover pressure of decalin + CO_2 is found to be 85 bar whereas for tetralin + CO_2 it is 95 bar. The solubility of anisaldehyde also decreases with temperature at a constant pressure beyond a certain pressure (the crossover pressure being 90 bar) whereas the solubility of anisic acid, a solid,

Table 5. Fluid–Liquid Equilibria for Decalin + Tetralin + CO_2

P/bar	x_2	x_3	10^3y_2	10^3y_3	10^3k_2	10^3k_3
			T = 323 K			
72	0.2394	0.2503	0.66	0.41	2.75	1.63
84	0.1861	0.1945	1.08	2.50	5.79	1.29
90	0.1652	0.1727	1.93	0.40	11.69	2.34
100	0.1327	0.1696	4.80	1.10	36.17	6.49
110	0.0951	0.1215	6.00	1.70	60.90	13.99
			T = 343 K			
85	0.0955	0.0955	1.00	0.65	10.47	6.78
110	0.0808	0.1286	1.28	0.82	15.85	7.27
120	0.0751	0.1177	4.69	2.31	62.45	19.58
130	0.061	0.0958	7.40	6.33	121.14	66.07
135	0.0586	0.0919	9.09	8.77	161.49	95.42
140	0.0556	0.0871	11.98	11.53	199.47	132.37

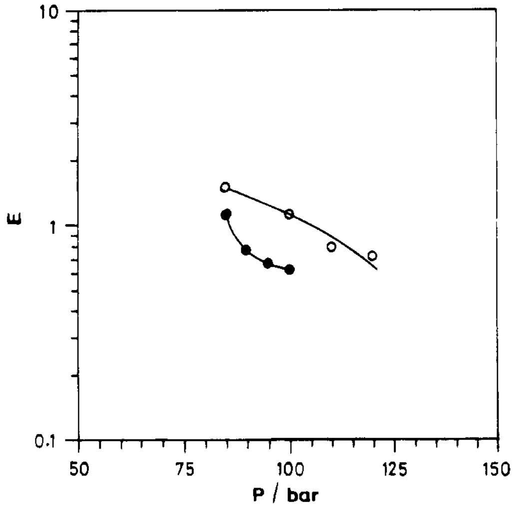


Figure 3. Enhancement factor (E) of decalin as a function of pressure: (●) 323 K; (○) 343 K.

shows a reverse trend; namely, it isobarically increases with temperature beyond 100 bar. The latter observation may be due to the fact that anisic acid melts at higher temperatures under CO_2 pressure. Similarly the solubility decreases with temperature for thymol and menthol beyond a certain pressure, with the only difference being that the crossover pressure occurs at a much lower pressure, e.g., 65 bar for thymol and a still lower pressure for menthol. The solubility of menthol at 323 K is 5 times higher than that of thymol in the pressure range of 25–120 bar and 4 times higher at 343 K in the pressure range of 90–135 bar. The variations of distribution coefficients with pressure and temperature also exhibit similar trends as do the solubilities. For assessing the ease of separation, the selectivity S_{ij} of component i with respect to the reference component j is calculated, which is dependent on temperature, pressure, composition, and the nature of molecular association among the components:

$$S_{ij} = \frac{K_i}{K_j} = \frac{y_i/x_i}{y_j/x_j} \tag{2}$$

In the absence of rigorous experimental results or reliable prediction methods, it is often customary to estimate the apparent selectivity from the binary values rather than the ternary or higher order data. The order of magnitude of the uncertainty in the estimation can be ascertained from the enhancement factor, E, which is defined as

$$E = \frac{K_i'(\text{from ternary data})}{K_i(\text{from binary data})} \tag{3}$$

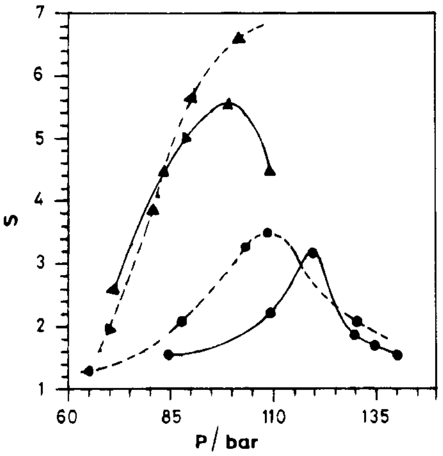


Figure 4. Selectivity (S) of decalin in the CO_2 + decalin + tetralin mixture as a function of pressure: (–) from ternary data; (- - -) from binary data; (▲) 323 K; (●) 343 K.

Table 6. Selectivity (S_{ij}) of Decalin from Ternary Data and Apparent Selectivity (S_{ij}(app)) from Pure Component Data

	T = 323 K		T = 343 K	
P/bar	S_{ij}	S_{ij}(app)	S_{ij}	S_{ij}(app)
140			1.55	
135			1.69	
130			1.83	2.13
120			3.18	
110	4.5		2.18	3.558
100	5.57	6.87		3.31
90	4.90	5.51		1.99
85			1.54	
84	4.49			
80		3.90		
72	2.60			
70		1.98		
65				1.22
60		1.67		

Table 7. Apparent Solubility Ratio (R_{ij}(app) of Menthol to Thymol from Binary Data

P/bar	R_{ij}(app)	P/bar	R_{ij}(app)
	T = 323 K		
120	5.25	78	3.49
112	6.12	65	2.71
95	5.64		
	T = 343 K		
135	4.76	70	1.89
115	4.86	65	1.55
90	3.37		

Figure 3 shows the variation with pressure of the enhancement factor E of decalin in the ternary mixture. E decreases with an increase in pressure. Thus, in the presence of a second component, K_i of the component is marginally suppressed at higher pressures due to greater association between them in the liquid phase. However, as the components to be separated are similar in nature, the supression of K_i for either component is of the same order of magnitude, making the apparent selectivity not much different from the selectivity (see Figure 4). On the basis of this validation, the values of the apparent selectivity have been calculated from the respective binary data and are presented in Table 6. Table 7 presents the behavior of the solubility ratio, R_{ij}, with pressure at two temperatures for menthol + thymol + CO_2, where

$$R_{ij} = y_i/y_j \tag{4}$$

The ratio, R_{ij}, decreases with temperature at constant pressure but increases with pressure at constant temperature up to a pressure beyond which the trend is reserved as does the selectivity, S_{ij}. Thus, in the absence of liquid phase compositions which are difficult to measure, the solubility ratio, R_{ij}, can be considered to assess the behavioral trends of the selectivity of the separation.

Conclusions

Supercritical CO_2 is a selective solvent for separation of binary pairs of aromatic compounds having close molecular weights. Out of the systems studied, namely, decalin + tetralin, anisaldehyde + anisic acid, and menthol + thymol, the selectivity of separation is the highest for anisaldehyde + anisic acid, the latter being a solid component in its pure state. The selectivity decreases with temperature at a constant pressure, but increases with pressure at a constant temperature up to a certain pressure. Similarly, the solubility increases with pressure, but the variation with temperature reverses in trend beyond a certain crossover pressure, which needs to be ascertained individually. In the absence of fluid phase equilibrium results on the ternary systems, the binary results may be utilized for ascertaining the order of magnitude and behavior of the selectivity of separation, but not as satisfactorily the crossover pressure. The enhancement of the distribution coefficients is dependent on pressure, passing through unity, thus indicating that at a certain pressure the selectivities and solubility ratios from binary and ternary data, respectively, are identical, having no difference in the molecular associations of the components with supercritical carbon dioxide.

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