Solubilities of Hexadecanoic and Octadecanoic Acids in Supercritical CO_2 With and Without Cosolvents

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The solubilities of hexadecanoic acid (palmitic acid) and octadecanoic acid (stearic acid) in supercritical carbon dioxide without cosolvents and with two cosolvents, namely, ethanol and 3-methyl-1-butanol, were determined at (308 and 318) K at pressures varying from (12.8 to 22.6) MPa. The solubility data, in both the absence and presence of cosolvents, were correlated by a model proposed by Mendez-Santiago and Teja.

Introduction

Supercritical fluids (SCFs) have diffusivities between that of a gas and a liquid, compressibilities comparable to a gas, densities comparable to a liquid, and negligible surface tension. These properties make them attractive solvents for many separation processes.[1] Supercritical carbon dioxide ($SCCO_2$) is commonly used because it is inert, nontoxic, and nonflammable. Due to its lack of polarity, polar substances are poorly soluble in $SCCO_2$, but these solubilities can be enhanced by adding cosolvents.[2,3]

The solubilities of saturated fatty acids in $SCCO_2$ are of considerable industrial importance. Hexadecanoic and octadecanoic acid are naturally available saturated fatty acids. The determination of solubilities of fatty acids in $SCCO_2$ is important because these compounds are extensively used in cosmetic, pharmaceutical, and surfactant industries.[4−6] For example, these fatty acids are reacted with ethanol[7] and 3-methyl-1-butanol,[8] and the resulting product esters are used as pharmaceutical products[7] and as food flavors.[8] Therefore, determination of the solubilities of these fatty acids in supercritical carbon dioxide with these cosolvents is important. In this study, the solubilities of hexadecanoic and octadecanoic acids at (308 and 318) K at various pressures have been investigated without cosolvents as well as in the presence of two cosolvents, namely, ethanol and 3-methyl-1-butanol.

Experimental Section

Materials. CO_2 (CAS No. 124-38-9) purchased from Vinayaka Gases (India) was purified to 99.9 %, by passing the gas through a bed of silica gel. Ethanol (CAS No. 64-17-5, 99.9 %), hexadecanoic acid (CAS No. 57-10-3, 98 %), octadecanoic acid (CAS No. 57-11-4, 98 %), and 3-methyl-1-butanol (CAS No. 123-51-3, 98 %) were purchased from Merck Inc. (India).

Apparatus and Procedure. A flow apparatus based on the principles of the saturation method[9] was used to measure solubilities of fatty acids in $SCCO_2$ with and without cosolvents. The experimental apparatus has been discussed in detail previously.[10] A schematic diagram of the apparatus is provided in Figure S1 (see Supporting Information). The high pressure saturation columns of inner diameter 14 mm and length of 300 mm were filled with solute and packed with glass wool and a porous frit at either end. These columns were kept in a thermostat, which maintained the temperature within ± 0.1 K. CO_2 was pressurized using a syringe pump (Jasco model PU-1580-CO_2), whereas the cosolvent was compressed by a high pressure pump (Jasco model PU-2080, intelligent HPLC pump). CO_2 and the cosolvent were mixed and fed through the saturation columns from the bottom. The exiting stream was collected in a trap and gravimetrically measured. By ascertaining

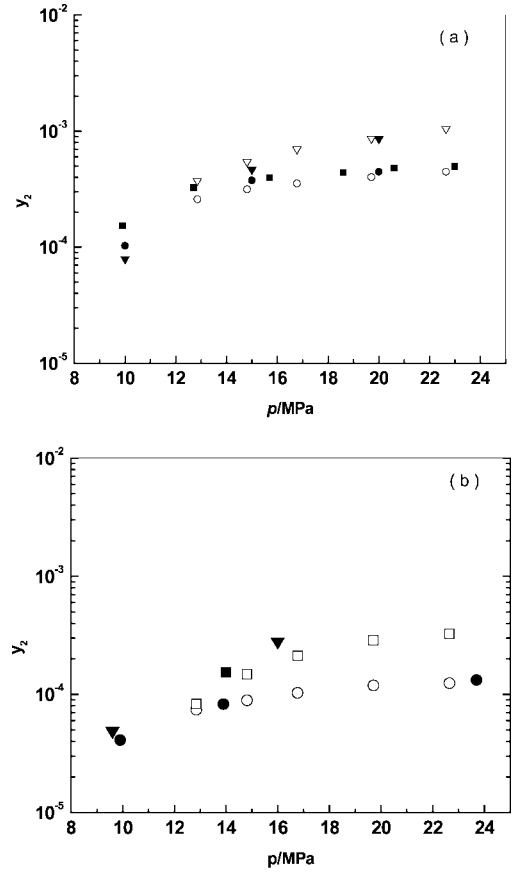

Figure 1. Solubility (y_2) of (a) hexadecanoic acid at 308 K (○, this work; ●, ref 6; ■, ref 16) and at 318 K (▽, this work; ▼, ref 6) and of (b) octadecanoic acid at 308 K (○, this work; ●, ref 13) and at 318 K (□, this work; ▼, ref 14; ■, ref 15) in $SCCO_2$ without cosolvents.

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Table 1. Solubility of Hexadecanoic Acid ($y_2 \cdot 10^4$) at (a) $T = 308$ K and (b) $T = 318$ K

	T/K = 308		
(a)	0 mol %	0.73 mol %	0.73 mol %
p/MPa	cosolvent	3-methyl-1-butanol	ethanol
12.8	2.58	4.14	5.29
14.8	3.14	4.86	6.16
16.7	3.53	5.33	6.72
19.7	4.01	5.88	7.36
22.6	4.45	6.35	7.91

	T/K = 318					
(b)	0 mol %	0.73 mol %	1.98 mol %	0.73 mol %	1.98 mol %	4.16 mol %
p/MPa	cosolvent	3-methyl-1-butanol	3-methyl-1-butanol	ethanol	ethanol	ethanol
12.8	3.74	6.57	10.76	8.53	13.00	27.18
14.8	5.44	9.05	14.81	11.60	17.69	36.94
16.7	6.98	11.18	18.29	14.20	21.66	45.23
19.7	8.65	13.30	21.76	16.74	25.54	53.33
22.6	10.45	15.52	25.40	19.39	29.58	61.77

Table 2. Solubility of Octadecanoic Acid ($y_2 \cdot 10^4$) at (a) $T = 308$ K and (b) $T = 318$ K

	T/K = 308		
(a)	0 mol %	0.73 mol %	0.73 mol %
p/MPa	cosolvent	3-methyl-1-butanol	ethanol
12.8	0.74	1.38	1.81
14.8	0.89	1.64	2.16
16.7	1.03	1.81	2.39
19.7	1.19	2.02	2.67
22.6	1.24	2.20	2.91

	T/K = 318					
(b)	0 mol %	0.73 mol %	1.98 mol %	0.73 mol %	1.98 mol %	4.16 mol %
p/MPa	entrainer	3-methyl-1-butanol	3-methyl-1-butanol	ethanol	ethanol	ethanol
12.8	0.83	2.19	4.05	2.83	4.92	12.92
14.8	1.48	3.07	5.67	3.98	6.92	18.20
16.7	2.12	3.84	7.10	4.99	8.69	22.80
19.7	2.87	4.63	8.55	6.04	10.50	27.57
22.6	3.24	5.46	10.10	7.14	12.42	32.62

Table 3. Temperature-Independent Correlation Parameters for Binary and Ternary Systems Obtained Using the Equations of Mendez-Santiago and Teja

system	temperature-independent constants			AARD (%)
hexadecanoic acid−$SCCO_2$	$A = 2750$	$B = 149100$		0.74
hexadecanoic acid−$SCCO_2$−3-methyl-1-butanol	$C = 2900$	$D = 133000$	$F = 12500$	1.48
hexadecanoic acid−$SCCO_2$−ethanol	$C = 3050$	$D = 130000$	$F = 10700$	1.96
octadecanoic acid−$SCCO_2$	$A = 2960$	$B = 144600$		3.93
octadecanoic acid−$SCCO_2$−3-methyl-1-butanol	$C = 3150$	$D = 138000$	$F = 15600$	1.90
octadecanoic acid−$SCCO_2$−ethanol	$C = 3220$	$D = 140000$	$F = 14100$	2.14

an adequate contact time, it was ensured that the exiting stream was saturated with the solute. Experiments were conducted with different flow rates between ($3 \cdot 10^{-6}$ and $30 \cdot 10^{-6}$) $m^3 \cdot s^{-1}$. Because no changes in solubilities were observed below $18 \cdot 10^{-6}$ $m^3 \cdot s^{-1}$, all experiments were conducted with $12 \cdot 10^{-6}$ $m^3 \cdot s^{-1}$. At this flow rate, the solubilities were determined after 1800 s, 3600 s, 7200 s, etc. After 3600 s, the solubilities were invariant, and thus the experiments were conducted for 7200 s. Each experimental data point was measured at least three times, and the deviation was less than 3 %.

Ternary System. The presence of a cosolvent increases both the critical temperature and the pressure of the resulting mixture. The critical loci of supercritical carbon dioxide−ethanol and 3-methyl-1-butanol were obtained from the literature,[11,12] and all our experiments were conducted above the critical temperature and critical pressure of these mixtures.

Results and Discussion

The reliability of the apparatus was reported in our previous work,[10] which was further confirmed by comparing the experimental data with the existing results[6,13−16] (Figure 1). The solubilities of hexadecanoic and octadecanoic acids at (308 and 318) K at various pressures are shown in Table 1a and b and Table 2a and b.

The equation of state approach (EOS) has been successfully used to model the solubilities of several fatty acids in $SCCO_2$ without cosolvent. Solubilities of several fatty acids in $SCCO_2$ without cosolvents[17] and the solubilities of dodecanoic acid and tetradecanoic acid in $SCCO_2$ with and without cosolvents have been modeled[10] using the Peng−Robinson EOS with appropriate mixing rules. Thus, the Peng−Robinson EOS using mixing rules with two binary interaction parameters, k_{ij} and l_{ij}, was examined to correlate the experimental data. The critical properties of carbon dioxide, hexadecanoic acid, octadecanoic acid, ethanol, and 3-methyl-1-butanol were taken from the literature.[11,12,18] Correlating the experimental solubility data requires an optimization process where the two binary interaction parameters, k_{ij} and l_{ij}, are obtained for each binary pair. The three-component system of $SCCO_2$, cosolvent, and solute requires six interaction parameters, k_{12}, l_{12}, k_{13}, l_{13}, and k_{23}, l_{23}, where the subscripts

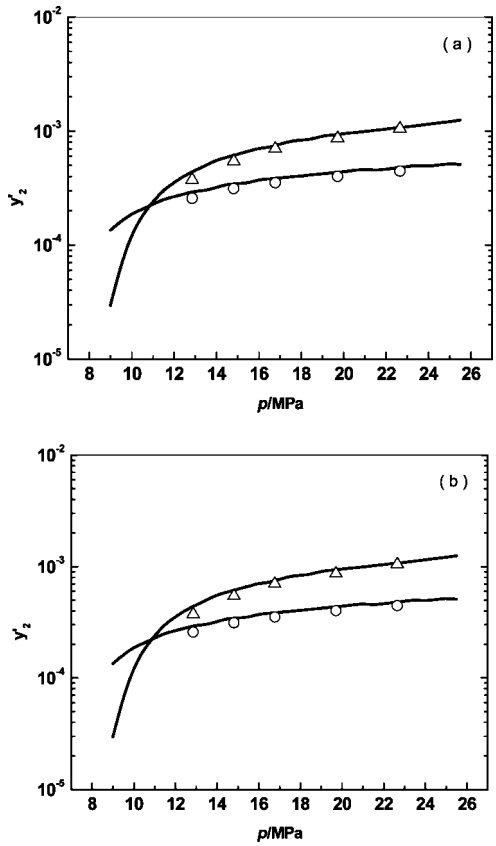

Figure 2. Experimental solubility (y_2) of (a) hexadecanoic acid (b) octadecanoic acid (○, 308 K; Δ, 318 K) in $SCCO_2$ without cosolvents. The lines are model predictions based on eq 1, and the temperature-independent correlation parameters are given in Table 3.

1, 2, and 3 represent CO_2, solute (saturated fatty acid), and cosolvents (alcohol), respectively. The parameters k_{12} and l_{12} are determined based on the experimental data of solubility of fatty acids in $SCCO_2$ in the absence of cosolvent. The parameters k_{13} and l_{13} were obtained independently from VLE data of CO_2−ethanol[11] and CO_2−3-methyl-1-butanol.[12] The absolute average relative deviation exceeded (15 and 80) % for the solubilities of hexadecanoic acid and octadecanoic acid with cosolvents (see Supporting Information) indicating that the correlations were not satisfactory.

Therefore, the solubilities of saturated fatty acids with and without cosolvents were correlated by the equations proposed by Mendez-Santiago and Teja.[19,20] The solubility of the fatty acid, y_2, without cosolvent was correlated with

$$T \ln E = A + B\rho \tag{1}$$

where E is the enhancement factor given by

$$E = \frac{y_2 p}{p^{\text{sub}}} \tag{2}$$

where p and T are the system pressure in MPa and temperature in K; p^{sub} is the sublimation pressure of the solid solutes in MPa (obtained from Huang et al.[18]); and ρ is the density of $SCCO_2$ (calculated from the 27 parameter equation of state[21]) in mol·mL^{-1}. The values of A and B for hexadecanoic acid and octadecanoic acid along with the absolute average relative deviation (AARD) are presented in Table 3.

Solubilities of Solids in SCCO$_2$ + Cosolvent. The solubility of the fatty acid with cosolvent, y_2', was correlated with

$$T \ln E' = C + D\rho + Fx_3 \tag{3}$$

where x_3 is mole fraction of the cosolvent and E' is the enhancement factor with cosolvent given by

$$E' = \frac{y_2' p}{p^{\text{sub}}} \tag{4}$$

where C, D, and F are constants that are obtained by correlation with experimental data and reported in Table 3.

The solubilities of hexadecanoic acid and octadecanoic acid in $SCCO_2$ are shown in Figure 2a and b. The solubilities of hexadecanoic acid in $SCCO_2$ + ethanol and $SCCO_2$ + 3-methyl-1-butanol ternary systems are shown in Figures 3a and b. The solubilities of octadecanoic acid in $SCCO_2$ and $SCCO_2$ + ethanol and $SCCO_2$ + 3-methyl-1-butanol ternary systems are shown in Figures 4a and b.

Cosolvent Effect. An enhancement in solubility is observed as a result of the cosolvent. The solubility enhancement effect can be quantified by e, which is defined as the ratio of the solubility obtained with cosolvent to that obtained without cosolvent. The average cosolvent enhancement factors (over all pressures) are listed in Table 4. From e values, it is apparent that ethanol is a better cosolvent than that of 3-methyl-1-butanol. This may be due to the hydrogen bonding of ethanol compared to that of 3-methyl-1-butanol.[22] The solubilities of the saturated fatty acids are enhanced significantly by the presence of the cosolvent compared to the effect

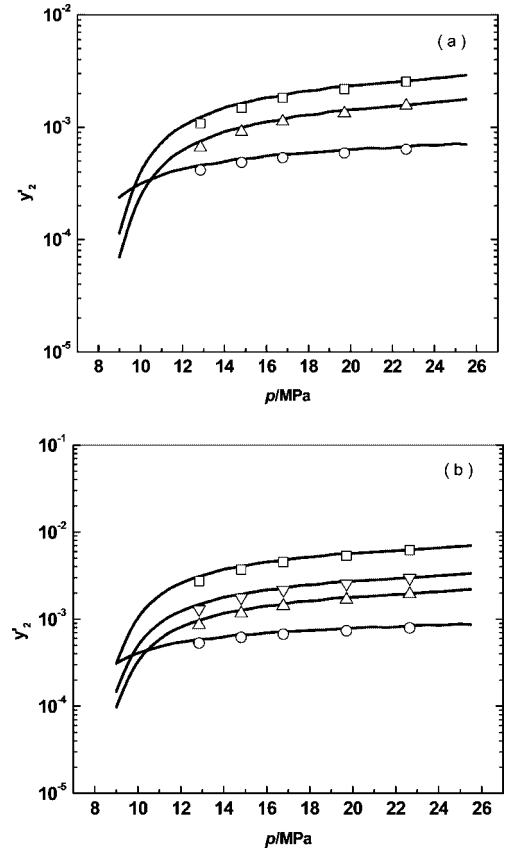

Figure 3. Experimental solubility (y_2') of hexadecanoic acid with (a) 3-methyl-1-butanol and (b) ethanol. Legends for (a): ○, 308 K with 0.73 mol % of 3-methyl-1-butanol; Δ, 318 K with 0.73 mol % of 3-methyl-1-butanol; □, 318 K with 1.98 mol % of 3-methyl-1-butanol. Legends for (b): ○, 308 K with 0.73 mol % of ethanol; Δ, 318 K with 0.73 mol % of ethanol; ∇, 318 K with 1.98 mol % of ethanol; □, 318 K with 4.16 mol % of ethanol. The lines are model predictions based on eq 3, and the temperature-independent correlation parameters are given in Table 3.

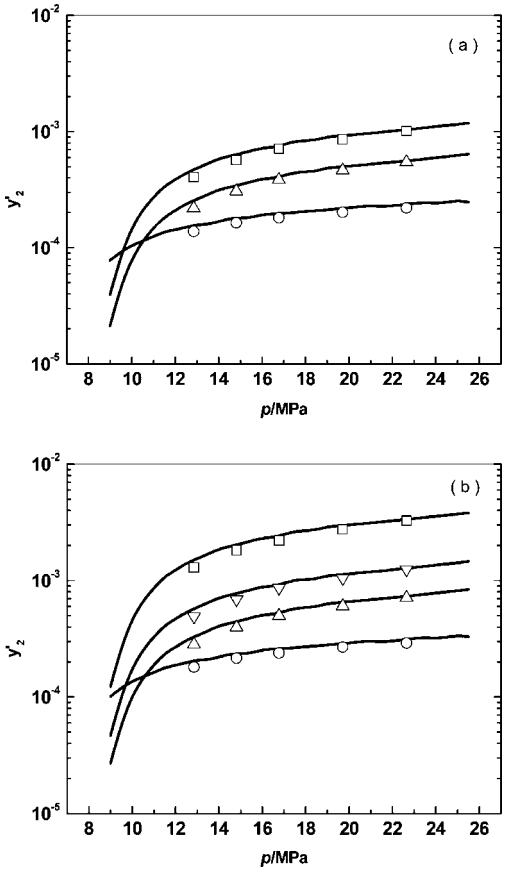

Figure 4. Experimental solubility data (y'_2) of octadecanoic acid with (a) 3-methyl-1-butanol and (b) ethanol. Legends for (a): ○, 308 K with 0.73 mol % of 3-methyl-1-butanol; Δ, 318 K with 0.73 mol % of 3-methyl-1-butanol; □, 318 K with 1.98 mol % of 3-methyl-1-butanol. Legends for (b): ○, 308 K with 0.73 mol % of ethanol; Δ, 318 K with 0.73 mol % of ethanol; ∇, 318 K with 1.98 mol % of ethanol; □, 318 K with 4.16 mol % of ethanol. The lines are model predictions based on eq 3, and the temperature-independent correlation parameters are given in Table 3.

Table 4. Average Cosolvent Effect (*e*) for the Fatty Acids

	e			
	T/K = 308		*T*/K = 318	
	hexadecanoic acid			
(a)	cosolvent mol % (solute free basis)			
cosolvent	0.73 mol %	0.73 mol %	1.98 mol %	4.16 mol %
ethanol	1.91	2.04	3.12	6.52
3-methyl-1-butanol	1.51	1.61	2.60	
	octadecanoic acid			
(b)	cosolvent mol % (solute free basis)			
	0.73 mol %	0.73 mol %	1.98 mol %	4.16 mol %
ethanol	2.35	2.55	4.43	11.65
3-methyl-1-butanol	1.78	1.96	3.63	

of increasing pressure. For example, the solubility enhancement of octadecanoic acid at 318 K by adding cosolvent is 11.65 times for 4.16 % ethanol, as shown in Table 2b. In comparison, in the absence of a cosolvent, an increase in the pressure from (12.8 to 22.6) MPa increases the solubility only by a factor of 3.9 at 318 K.

Conclusions

The solubilities of hexadecanoic acid and octadecanoic acid in $SCCO_2$ and in $SCCO_2$ + ethanol and $SCCO_2$ + 3-methyl-1-butanol at (308 and 318) K and (12.8 to 22.6) MPa were determined. The results obtained indicate that the solubilities of hexadecanoic acid and octadecanoic acid are higher in the $SCCO_2$ + ethanol system compared with that of $SCCO_2$ + 3-methyl-1-butanol. The experimental data were correlated by the equations proposed by Mendez-Santiago and Teja, and the overall deviations between the experimental data and correlated results were less than 4 % in all cases.

Supporting Information Available:

Figure S1 shows the schematic diagram of the apparatus used for measuring solubilities. The appendix A1 discusses the derivation of the fugacity coefficient using the Peng−Robinson equation of state with appropriate mixing rules. Table S1 shows the adjustable binary interaction parameters for the ternary systems obtained using the PR EOS. This material is available free of charge via the Internet at http://pubs.acs.org.

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