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Solubility of 1-Octadecanol and Stearic Acid in Supercritical Carbon Dioxide

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By use of a continuous flow facility, the solubility of 1-octadecanol [$CH_3(CH_2)_{16}CH_2OH$] and stearic acid [$CH_3(CH_2)_{16}COOH$] in dense supercritical carbon dioxide has been established at 318, 328, and 338 K and pressures ranging from 140 to 467 bar. Maximum solubilities were observed for both systems at 318 K and pressures of 280–300 bar. The results of the 1-octadecanol–carbon dioxide system at 328 and 338 K and those for the stearic acid–carbon dioxide system at 338 K were correlated with the mole fraction of the solute and the reduced density of the pure solvent. This approach yielded deviations of 5.85% (13 points) for 1-octadecanol and 3.39% (5 points) for stearic acid. The Hansen three-dimensional solubility parameter was also applied to the Flory–Huggins theory for the development of a different model which yielded deviations of 24.0% (17 points) for 1-octadecanol and 5.14% (17 points) for stearic acid.

Supercritical extraction presently continues to receive considerable attention as a separation scheme and promises in the near future to be a valuable method for the purification of newly developed specialty chemicals. One of the significant advantages of this method resides in that the solvent can be easily, quickly, and completely separated from the accompanying solute and thus significantly reduce the contamination of valuable compounds with a residual solvent. In this regard, the pharmaceutical and food industries are currently examining the application of supercritical separation processes since there exists the possibility of employing cheap and safe solvents such as carbon dioxide and nitrogen. Background established on supercritical extraction obtained in the past decade now permits the improvement of mechanical design and the performance of continuously operated high-pressure compressors, pressure regulators, and emergency relief systems that make the operation of these processes less troublesome and safer to use. In this regard, it should be noted that a pilot plant for the continuous separation of lecithin from soya oil, as reported by Peters et al. (*1*), is now successfully operational. Based on the results of this pilot plant, current design plans are now in progress for the construction of a commercial plant capable of producing 500 tons/y of raw lecithin. As pointed out by Coenen et al. (*2*) the economics for the re-refining of used lubricating oils employing supercritical extraction is compatible with current methods of recovery.

The substances selected for the present study are 1-octadecanol [$CH_3(CH_2)_{16}CH_2OH$] and stearic acid [$CH_3(CH_2)_{16}COOH$]. Both compounds are extensively used in the pharmaceutical, cosmetic, and surfactant industries where the need for highly purified components is essential. Hardly any fundamental quantitative studies presently exist on the solubility of these two compounds in supercritical gases. The present study was undertaken to establish the possibility of dissolving these compounds in supercritical carbon dioxide at three different temperatures over a wide range of pressures from roughly 140 to 470 bar. The results obtained from this study can prove to be of industrial value for the manufacture and purification of these aliphatic compounds.

Experimental Section

The 1-octadecanol used in this investigation was of reagent grade (CAS no. 112-92-5), was supplied by the Eastman Kodak Co., and was claimed to be of minimum purity of 95% with a claimed melting point range of 329–331 K. The stearic acid, also supplied by the Eastman Kodak Co., was of reagent grade (CAS no. 57-11-4), with a claimed minimum purity of 97% and a melting point range of 341–343 K.

The equipment and procedure used in the present study have been outlined by Kramer and Thodos (*3*). The experimental uncertainties in this study are estimated to be 0.1 K for temperature and ±1.5 bar.

Results

Experimental Measurements. The experimental measurements for the solubility of 1-octadecanol and stearic acid in supercritical carbon dioxide are presented in Tables I and II. These values are also presented in Figures 1 and 2 to show the relationships between y_2, the mole fraction of the solute in the supercritical fluid versus P, the total pressure of the system. To model the supercritical extraction behavior of these systems, two approaches were applied to the data obtained in this study. In the first approach, y_2 was related to the corresponding density of the pure solvent according to the following dependence:

$$\log y_2 = A + B\rho_{R_1} \qquad (1)$$

where ρ_{R_1} is the reduced density of the pure solvent. Upon plotting y_2 versus ρ_{R_1} on semilogarithmic coordinates, linear relationships resulted for the 328 and 338 K isotherms of the

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Table I. Experimental Data and Calculated Values for the 1-Octadecanol–Carbon Dioxide System

	10^2y_2, mole fraction			abs dev, %				β_{12}	
P, bar	exptl	eq 1	eq 2, 3	eq 1	eq 2, 3	ρ_R	δ	actual	predicted
T = 318 K (45 °C)									
152.0	0.272		0.288		6.13	1.590	6.38	6.81	6.93
202.5	0.352		0.398		13.0	1.745	7.00	4.75	4.99
317.9	0.407		0.518		27.4	1.930	7.74	2.97	3.44
437.9	0.319		0.572		79.2	2.045	8.20	1.76	2.89
					31.4[a]				
T = 328 K (55 °C)									
139.9	0.155	0.162	0.216	4.26	39.6	1.327	5.32	8.22	8.89
153.9	0.224	0.236	0.319	5.16	42.3	1.430	5.74	6.37	7.07
176.9	0.338	0.346	0.463	2.34	37.0	1.535	6.16	4.89	5.52
212.3	0.617	0.508	0.658	17.7	6.58	1.640	6.58	4.13	4.26
280.6	0.875	0.848	1.01	3.12	15.8	1.780	7.14	2.76	3.06
443.2	1.56	1.73	1.73	10.9	10.6	1.975	7.92	2.07	2.28
447.7	1.82	1.79	1.77	1.40	2.80	1.985	7.96	2.32	2.27
				6.41[a]	22.1[a]				
T = 338 K (65 °C)									
145.8	0.104	0.106	0.157	1.97	51.3	1.135	4.55	10.20	11.04
157.7	0.155	0.166	0.221	7.22	42.3	1.250	5.01	7.52	8.24
191.8	0.344	0.356	0.418	3.48	21.5	1.445	5.80	4.15	4.55
237.2	0.657	0.603	0.682	8.19	3.78	1.580	6.34	2.71	2.79
324.0	1.31	1.22	1.39	6.98	5.77	1.760	7.06	1.33	1.45
452.8	2.29	2.37	2.87	3.37	2.52	1.930	7.74	0.77	1.23
				5.20[a]	21.2[a]				

[a] Overall average deviation.

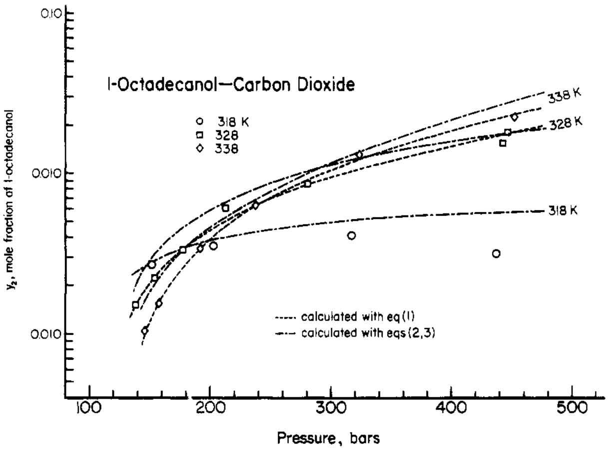

Figure 1. Experimental and calculated solubilities of 1-octadecanol in supercritical carbon dioxide.

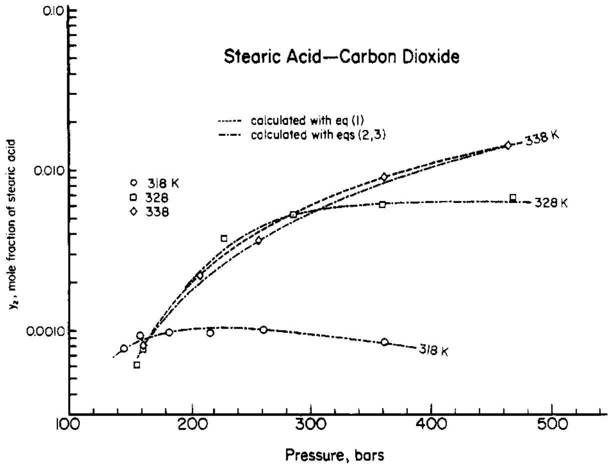

Figure 2. Experimental and calculated solubilities of stearic acid in supercritical carbon dioxide.

1-octadecanol–carbon dioxide system. The reduced densities for carbon dioxide used in the present study were obtained from the work of Kennedy and Thodos (*4*). The data for the 318 K isotherm produced a nonlinear behavior and exhibited a maximum solubility at $\rho_{R_1} \approx 1.90$, and therefore, the treatment of this isotherm could not be properly accommodated with eq 1. The information available for this system at 328 and 338 K yielded the parameters A and B to be as follows:

1-octadecanol–carbon dioxide (328 and 338 K)

$$A = -4.90$$

$$B = 0.01076T - 1.942$$

where T is the temperature of the system in degrees Kelvin. For the system stearic acid–carbon dioxide, the only isotherm at 338 K exhibited a linear behavior. For this system at this temperature, the parameters A and B were found to be as follows:

stearic acid–carbon dioxide (338 K)

$$A = -5.605$$

$$B = 1.965$$

The other two isotherms for this system exhibited a strong nonlinear behavior with the 318 K isotherm producing a maximum solubility at $\rho_{R_1} \approx 1.85$.

By use of eq 1 and the parameters obtained for both systems, values of y_2 were calculated and when compared with corresponding experimental measurements produced the absolute average deviations presented in Tables I and II. The overall average deviation for the 328 and 338 K isotherms of the 1-octadecanol–carbon dioxide system was found to be 5.85% (13 points) while that for the stearic acid–carbon dioxide system at 338 K was 3.39% (5 points). The values resulting from these parameters and eq 1 have been introduced in Figures 1 and 2. The parameters used in these calculations have been established from limited experimental measurements and cannot yet be predicted accurately without additional experimental recourse.

The second approach utilizes the three-dimensional solubility parameter defined by Hansen (*5*) and the Flory–Huggins theory to model all isotherms for both systems. The details associated with the development of this model are presented elsewhere by Kramer and Thodos (*6*). This approach utilizes the concept of treating the dense supercritical fluid as an expanded liquid and the solid solute as a subcooled liquid. Following basic

Table II. Experimental Data and Calculated Values for the Stearic Acid-Carbon Dioxide System

	$10^2 y_2$, mole fraction			abs dev, %				β_{12}	
P, bar	exptl	eq 1	eq 2, 3	eq 1	eq 2, 3	ρ_R	δ	actual	predicted
				T = 318 K (45 °C)					
145.4	0.0791		0.0781		1.23	1.565	6.28	7.67	7.65
159.4	0.0935		0.0892		4.60	1.625	6.52	6.95	6.87
183.3	0.0979		0.0994		1.48	1.700	6.82	5.90	5.94
217.7	0.0963		0.104		7.72	1.775	7.12	4.91	5.06
261.6	0.101		0.102		5.28	1.850	7.42	4.22	4.23
361.5	0.087		0.085		2.52	1.975	7.92	3.02	2.98
					3.81[a]				
				T = 328 K (55 °C)					
154.8	0.0621		0.0603		2.86	1.430	5.74	6.57	6.52
160.3	0.0774		0.0813		5.00	1.465	5.88	6.25	6.35
228.0	0.386		0.329		14.8	1.680	6.74	5.62	5.31
285.2	0.538		0.512		4.90	1.795	7.20	4.85	4.76
359.5	0.629		0.627		0.34	1.890	7.58	4.30	4.30
467.5	0.702		0.653		7.02	2.020	8.10	3.81	3.68
					5.82[a]				
				T = 338 K (65 °C)					
161.5	0.0813	0.0812	0.0836	0.00	2.81	1.280	5.13	7.06	7.13
207.8	0.226	0.230	0.197	1.77	13.0	1.510	6.06	3.92	3.65
256.1	0.372	0.424	0.356	14.0	4.39	1.645	6.60	2.64	2.56
360.5	0.924	0.935	0.846	1.19	8.47	1.820	7.30	2.36	2.19
463.8	1.47	1.47	1.46	0.00	0.90	1.920	7.70	2.52	-2.51
				3.39[a]	5.91[a]				

[a] Overall average deviation.

Table III. Solubility Parameters at Different Temperatures for 1-Octadecanol and Stearic Acid[a]

	1-octadecanol (T_m = 331.04 K)				stearic acid (T_m = 342.49 K)			
	298 K	318 K	328 K	338 K	298 K	318 K	328 K	338 K
ΔH^{vap}, kcal/mol	29.62	28.17	27.56	26.86	29.56	28.11	27.50	26.80
v_2, cm^3/mol	322.90	328.55	331.49	334.44	326.0	331.65	334.59	337.54
δ_{t_2}, (cal/cm^3)$^{1/2}$	9.482	9.154	9.010	8.848	9.427	9.102	8.958	8.798
δ_{d_2}, (cal/cm^3)$^{1/2}$	8.238	8.056	7.967	7.878	8.044	7.866	7.779	7.693
τ, (cal/cm^3)$^{1/2}$	4.691	4.347	4.209	4.028	4.916	4.579	4.442	4.270
$f^\circ{}_2{}^s/f^\circ{}_2{}^l$		0.3691	0.8052	1.000		0.1933	0.3911	0.7590

[a] ΔH^{vap} and v_2 were obtained from the extrapolation of values given by Smith (*10*) and Barton (*11*). For ΔH^{fus} needed for the calculation of $f^\circ{}_2{}^s/f^\circ{}_2{}^l$, values were obtained from Mosselman et al. (*12*) and Shaake et al. (*13*). For 1-octadecanol, T_m = 331.04 K, obtained from Smith (*10*). For stearic acid, T_m = 342.49 K, obtained from Shaake et al. (*13*).

thermodynamic arguments, it can be shown that the mole fraction of the heavy component in the fluid phase becomes

$$y_2 = \frac{1}{\gamma_2^\infty} \frac{f^\circ{}_2{}^s}{f^\circ{}_2{}^l} \tag{2}$$

where γ_2^∞ is the activity coefficient for the heavy component at infinite dilution and $f^\circ{}_2{}^s/f^\circ{}_2{}^l$ is the ratio for the solid and liquid fugacities of the pure component. This ratio becomes unity when the solute is in the liquid state. Following the development presented elsewhere (*6*), it can be shown that the activity coefficient can be expressed as

$$\ln \gamma_2^\infty = \frac{v_2}{RT}[(\delta_{d_1} - \delta_{d_2})^2 + \tau_2^2 - \beta_{12}] + 1 + \frac{v_2}{v_1} + \ln \frac{v_2}{v_1} \tag{3}$$

where β_{12} = binary molecular interaction coefficient between solute and solvent; v_1 = molar volume of solvent; v_2 = molar volume of the solute in its extrapolated liquid state; δ_{d_1}, δ_{d_2} = dispersion part of the solubility parameter for the solvent and solute, respectively; and $\tau = (\delta_p^2 + \delta_h^2)^{1/2}$, the combination of the polar and hydrogen-bonding contribution to the total solubility parameter, defined as $\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$.

Assuming as a first order of approximation that $\delta_{t_1} \approx \delta_{d_1}$, for the solvent, Giddings et al. (*7*) show that

$$\delta_{d_1} = 1.25P_c \frac{\rho_{R_1}}{\rho_{Rl_1}} \tag{4}$$

where P_c is the critical pressure of the solvent, ρ_{R_1} is the reduced density of this solvent, and ρ_{Rl_1} is the reduced density of its liquid state, commonly taken as 2.66.

The solubility parameters needed for eq 3 were calculated in accordance with the procedure outlined by Kramer (*8*). The final results for 1-octadecanol and stearic acid are summarized in Table III. In this table are also included values for 298 K, since the dispersion contribution for 1-octadecanol and stearic acid, δ_{d_2}, was established from the molar attraction group contribution technique outlined by Koenhen and Smolders (*9*) at this temperature.

Values of parameter β_{12}, needed to apply in eq 3 for modeling supercritical solubilities, were calculated from the experimental data in conjunction with eq 2. These calculated values are presented in Tables I and II and show a strong dependence on δ_{d_1}, the solubility parameter of the pure solute. These values exhibit a slight temperature dependence. Using an empirical approach, these values of β_{12} have been correlated to produce the combined temperature and solvent solubility parameter expressions

1-octadecanol–carbon dioxide

$$\beta = (4082.2605 - 1113.748\delta + 75.798\delta^2) - (24.71262 - 6.8795\delta + 0.4745\delta^2)T + (0.03794 - 0.01075\delta + 0.00075\delta^2)T^2 \tag{5}$$

stearic acid–carbon dioxide

$$\beta = (41264.648 - 11616.008\delta + 792.12\delta^2) - (252.702 - 71.327\delta + 4.875\delta^2)T + (0.3870 - 0.1095\delta + 0.0075\delta^2)T^2 \tag{6}$$

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Equations 5 and 6 were used to calculate the solubilities of 1-octadecanol and stearic acid in supercritical carbon dioxide. The values of β_{12}, together with the calculated fluid-phase compositions, are presented in Tables I and II. A comparison between these calculated compositions and the corresponding experimental measurements produced an overall average deviation of 24.0% (17 points) for 1-octadecanol and 5.14% (17 points) for stearic acid. These average deviations are comparable to those obtained from an earlier experimental study (*8*) for the 1-hexadecanol-carbon dioxide and palmitic acid-carbon dioxide systems in which the overall average deviations were 11.4% (18 points) and 20.2% (19 points), respectively.

It should be noted that the solutes investigated in the present study contain up to 5% impurities that may affect the measured solubilities in spite of the fact that the experimental procedure was designed to minimize these effects by discarding the initial samples of each experimental run. The fact that impurities exist makes the meltings point of the pure solutes uncertain, since their presence lowers these melting points and indirectly influences the proper value of the ratio, $f^{\circ}{}_2^{s}/f^{\circ}{}_2^{l}$, to be used with eq 2.

Conclusions. Solubility measurements for 1-octadecanol and stearic acid in supercritical carbon dioxide were made, and the results obtained have been modeled by using two different approaches. One approach utilizes the involvement of only density and two adjustable parameters while the other employs three-dimensional solubility parameters and a single adjustable interaction parameter. Both models predict the composition of the solute present in the supercritical fluid phase. Both systems exhibited an interesting experimental behavior for the 45 °C isotherm for which a maximum solubility is encountered at pressures around 280-300 bar.

Glossary

A, B	parameters, eq 1
f	fugacity, bar
ΔH	molar heat, kcal/mol
P	pressure, bar
R	gas constant, 1.9872 cal/(mol·K)
T	temperature, K
v	molar volume, cm^3/mol
y	mole fraction of solute in vapor phase

Greek Letters

β	interaction parameter
γ	activity coefficient
δ	solubility parameter, $(cal/cm^3)^{1/2}$
ρ	density, g/cm^3
τ	$(\delta_p{}^2 + \delta_h{}^2)^{1/2}$

Subscripts

1	solvent
2	solute
c	critical
d	dispersion
h	hydrogen bonding
l	liquid phase
m	melting point
P	polar
R	reduced
t	total

Superscripts

fus	fusion
l	liquid
o	pure component
s	solid
vap	vaporization
∞	infinite

Registry No. $CH_3(CH_2)_{16}CH_2OH$, 112-92-5; $CH_3(CH_2)_{16}COOH$, 57-11-4; CO_2, 124-38-9.

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Solubilities of Ethane in Heavy Normal Paraffins at Pressures to 7.8 MPa and Temperatures from 348 to 423 K

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Solubility data have been obtained for ethane in the heavy normal paraffin solvents *n*-eicosane, *n*-octacosane, *n*-hexatriacontane, and *n*-tetratetracontane. Measurements were made over the temperature range from 348 to 423 K (167-302 °F) at pressures up to 7.8 MPa (1127 psia). The data can be described with average deviations of less than 0.003 mole fraction by the Soave-Redlich-Kwong or Peng-Robinson equation when two interaction parameters per isotherm are used in the equation.

Introduction

This work is a continuation of our studies of binary vapor-liquid phase behavior for selected solute gases (e.g. CO_2, ethane) in a series of heavy hydrocarbon solvents of interest in the processing of petroleum products, production of coal liquids, and enhanced oil recovery operations. Previously, we have reported data on the solubility of CO_2 in a number of paraffinic (*1*), naphthenic (*2*), and aromatic (*3*, *4*) solvents. Correlations describing the behavior of the CO_2 + *n*-paraffin systems have also been presented (*5*).

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