Solubilities of 1-Hexadecanol and 1-Octadecanol in Subcritical and Supercritical Carbon Dioxide

Jun-Shun Yau and Fuan-Nan Tsai*

Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan 70101, ROC

The solubilities of 1-hexadecanol and 1-octadecanol in carbon dioxide have been measured by a phase equilibrium apparatus over the temperature ranges from 308 to 328 K and from 302 to 338 K, respectively, at pressures from 50 to 205 bar. For each isotherm the mole fraction solubilities of 1-hexadecanol and 1-octadecanol in carbon dioxide are correlated with the reduced density and reduced pressure of the pure solvent.

Introduction

Supercritical fluid extraction has received wide attention during the past few years for potential application in the special chemicals, food processing, pharmaceutical, and petroleum industries (*1*). The knowledge of the solubilities of low-volatile components in supercritical solvents is of interest for supercritical fluid extraction. In early papers it was shown that carbon dioxide has a high solvent power for many low-volatile components, and it is one of the most important supercritical solvents for practical application (*2*).

Limited studies on the solubility of heavy-cut detergent-range alcohols have been presented in the literature. Schneider et al. (*2–4*) have measured the solubilities of 1-dodecanol and 1-hexadecanol in supercritical carbon dioxide at 333 and 393 K. Kramer and Thodos (*5*, *6*) measured the solubilities of 1-hexadecanol and 1-octadecanol in dense supercritical carbon dioxide at 318, 328, and 338 K over the pressure range from 140 to 453 bar. Giddings et al. (*7*, *8*) have reported the solubilities of 1-octadecanol in dense supercritical carbon dioxide at 313 K.

Although some solubilities for supercritical carbon dioxide + heavy alcohol have been reported, none have been studied in detail from the subcritical to the supercritical state. In the present work, the solubilities of 1-hexadecanol and 1-octadecanol in carbon dioxide over the temperature ranges from 308 to 328 K and from 302 to 338 K, respectively, at pressures from 50 to 205 bar have been measured, and the results have been correlated by an equation.

Experimental Section

The experimental apparatus is shown schematically in Figure 1. Liquid carbon dioxide is compressed by a positive-displacement liquid pump (Laboratory Data Control minipump, Model 396-31) from a cylinder into a preheating coil inserted in a constant-temperature water bath. To prevent hydrate formation (*9*), traces of water are removed from the carbon dioxide by a gas purifier (Matheson Model 450) placed upstream of the pump. The desired pressure is adjusted by a back-pressure regulator (Tescom Model 26-1723-24). The pressure of the system is measured with a pressure gauge (Heise Model CMM 0-276 bar) to ±0.3 bar. The phase equilibrium between the supercritical carbon dioxide and solid solute was achieved within an equilibrium cell which was totally submerged in a constant temperature water bath. The temperature uniformity across the equilibrium cell was measured to an accuracy of ±0.2 K by a type J thermocouple.

Table I. Solubility Data y_2 of 1-Hexadecanol in Carbon Dioxide and Reduced Densities of Carbon Dioxide $\rho_{r,1}$ as a Function of Temperature and Pressure

T/K	P/bar	$10^2 y_2$	$\rho_{r,1}$
308	50.0	0.025	0.235
	68.8	0.038	0.400
	92.0	0.146	1.480
	113.8	0.210	1.628
	134.0	0.290	1.717
	153.8	0.320	1.759
	165.5	0.370	1.787
	175.0	0.430	1.811
	203.7	0.495	1.847
318	50.0	0.034	0.224
	69.6	0.040	0.373
	85.5	0.106	0.582
	113.4	0.241	1.300
	133.0	0.360	1.475
	153.8	0.465	1.582
	174.8	0.571	1.664
	201.3	0.743	1.727
323	52.7	0.035	0.232
	70.0	0.040	0.355
	85.5	0.041	0.532
	112.7	0.146	1.118
	133.8	0.343	1.400
	154.4	0.460	1.518
	174.8	0.654	1.618
	200.6	0.873	1.691
328	52.2	0.038	0.220
	69.0	0.032	0.327
	86.4	0.035	0.489
	111.7	0.093	0.961
	133.1	0.269	1.259
	154.4	0.393	1.411
	182.4	0.612	1.567
	203.0	0.906	1.631

The equilibrium cell consisted of a stainless steel pipe (30 cm in length with a 1.93-cm inner diameter) with reducer–adapter couplings at each end. The solute was introduced into the cell in solid form at three evenly spaced points separated by 0.2-cm-diameter stainless steel balls. Approximately 27 g of solute was charged into the equilibrium cell before initiating a run. The temperature of the saturated supercritical carbon dioxide leaving the equilibrium cell was increased to approximately 175 K above the bath temperature to avoid precipitation of the heavy alcohol in the line (*10*). The cold trap was attached directly to the metering valve with a high-pressure connection and was submerged in an ice bath. The trap was packed with cotton in order to catch the small particles of solute. After the flow had passed the equilibrium cell for about 1 h, the sample in the equilibrium cell was withdrawn, reduced in pressure, and collected in a trap. The cold trap was weighed before and after a run to determine the amount of solute. The amount of carbon dioxide was measured volumetrically in a wet test meter (America Meter Model AL17-1). The U tube was filled with water to protect the wet test meter from damage.

Materials. The carbon dioxide had a stated minimum purity of 99.5 mol %. The 1-hexadecanol and 1-octadecanol were

---

* To whom correspondence should be addressed.

0021-9566/92/1737-0285$03.00/0

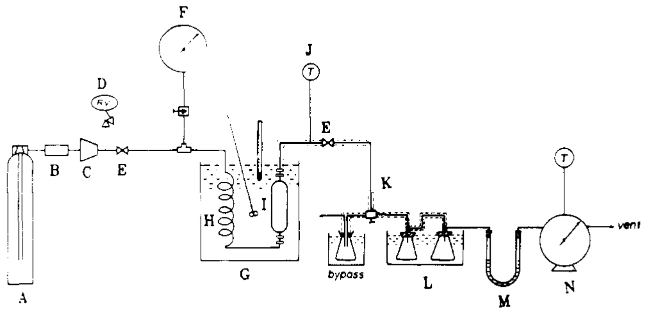

Figure 1. Schematic diagram of the experimental apparatus: A, carbon dioxide cylinder; B, purifier; C, compressor; D, back pressure regulator; E, metering valve; F, pressure gauge; G, constant-temperature bath; H, preheater; I, equilibrium cell; J, thermocouple; K, heating tape; L, cold trap (ice bath); M, filter; N, wet test meter.

Table II. Solubility Data y_2 of 1-Octadecanol in Carbon Dioxide and Reduced Densities of Carbon Dioxide $\rho_{r,1}$ as a Function of Temperature and Pressure

T/K	P/bar	10^2y_2	$\rho_{r,1}$
302	50.7	0.029	0.250
	68.2	0.026	0.700
	102.7	0.052	1.722
	127.6	0.072	1.800
	160.2	0.102	1.860
	177.9	0.106	1.886
	201.7	0.109	1.917
308	50.0	0.042	0.235
	70.0	0.043	0.410
	86.2	0.046	1.400
	111.9	0.066	1.620
	133.8	0.088	1.716
	154.4	0.105	1.762
	175.8	0.140	1.814
	199.6	0.233	1.850
318	49.8	0.038	0.221
	69.6	0.041	0.373
	86.2	0.041	0.600
	111.0	0.100	1.260
	133.1	0.162	1.476
	153.8	0.216	1.582
	174.8	0.280	1.664
	200.3	0.350	1.725
328	48.6	0.054	0.200
	70.3	0.034	0.336
	87.6	0.038	0.505
	110.7	0.054	0.932
	132.4	0.178	1.252
	153.0	0.288	1.405
	175.0	0.391	1.532
	199.3	0.509	1.618
338	50.0	0.035	0.191
	68.8	0.040	0.300
	84.5	0.045	0.409
	111.0	0.048	0.700
	130.7	0.093	0.950
	151.7	0.191	1.175
	170.5	0.302	1.332
	204.4	0.481	1.505

from Sigma and had a stated purity of 99 mol %. No further purifications were made.

Results

Tables I and II present solubilities of 1-hexadecanol and 1-octadecanol in carbon dioxide over the temperature ranges from 308 to 328 K and from 302 to 338 K, respectively, at pressures from 50 to 205 bar. These results are shown graphically in Figures 2–5. The solubilities of the solutes increase with pressure in the supercritical state, but in the subcritical state, the solubilities decrease with increasing pressure. From the effect of temperature on the solubilities, we find that the retrograde solubility (crossover pressure) behavior (*11–13*)

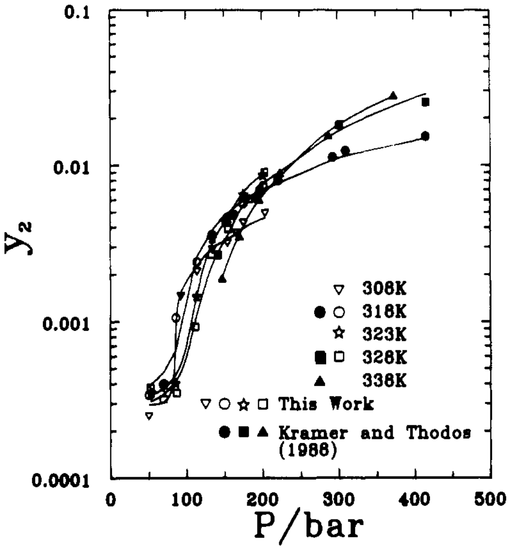

Figure 2. Comparison of calculated solubilities of 1-hexadecanol in carbon dioxide by eq 2 with experimental data.

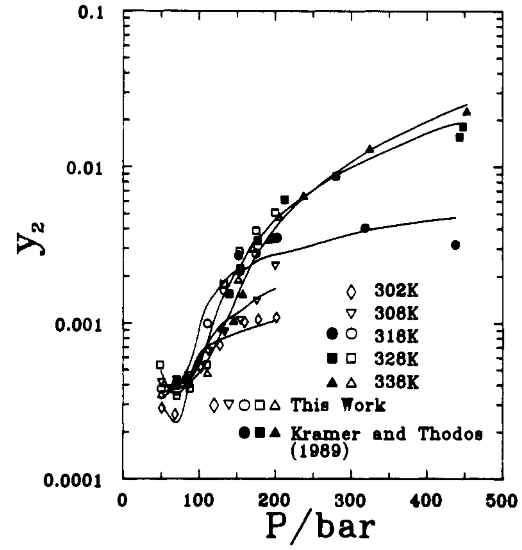

Figure 3. Comparison of calculated solubilities of 1-octadecanol in carbon dioxide by eq 2 with experimental data.

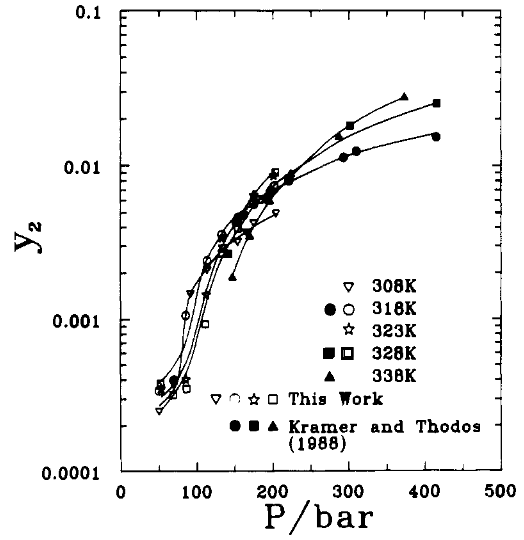

Figure 4. Comparison of calculated solubilities of 1-hexadecanol in carbon dioxide by eq 3 with experimental data.

Table III. Correlation of Solubility Data with Three Equations

				eq 1			eq 2				eq 3			
solute	T/K	P range/bar	pts	A	B	AAD[a]/ %	A	B	C	AAD[a]/ %	A	B	D	AAD[a]/ %
1-hexadecanol	308	50.0–203.7	9	−3.7690	0.7296	14.69	−3.5115	−0.1781	0.4371	8.00	−3.6511	0.9027	1.8810	4.15
	318[b]	50.0–415.1	15	−3.6670	0.8766	13.49	−3.5407	0.5279	0.1586	9.49	−3.5300	0.9252	1.5250	6.99
	323	52.7–200.6	8	−3.7854	0.9642	16.94	−3.5029	0.0594	0.4712	4.37	−3.5841	1.3202	2.7950	8.01
	328[b]	52.7–415.9	13	−3.8981	1.0981	22.67	−3.5707	0.1900	0.4322	10.75	−3.7147	1.1902	1.7340	12.44
	338[b]	147.1–373.0	6	−4.5621	1.6125	5.28	−3.7937	0.5513	0.3567	2.95	−4.0133	1.4618	1.6320	2.77
	overall	50.0–415.9	51			15.62				7.98				7.54
1-octadecanol	302	50.7–201.7	7	−3.7253	0.3551	22.90	−3.3555	−0.7461	0.4913	10.92	−3.5887	0.7091	7.0550	7.78
	308	50.0–199.6	8	−3.5249	0.3162	30.11	−3.0103	−1.4422	0.8472	15.20	−3.3774	2.0124	97.0801	4.78
	318[b]	49.8–437.9	12	−3.6488	0.6314	19.48	−3.5939	0.4797	0.0691	18.21	−3.5683	0.6546	1.3760	18.29
	328[b]	48.6–447.7	15	−3.8309	0.9410	30.55	−3.3767	−0.2369	0.5427	14.89	−3.5880	1.0564	2.4010	17.72
	338[b]	50.0–452.8	14	−3.8568	1.0177	31.42	−3.4410	−0.1012	0.5469	10.71	−3.4795	1.3397	6.0470	14.43
	overall	48.6–452.8	56			27.38				14.10				13.93

[a] AAD = average absolute deviation. [b] Includes the results of Kramer and Thodos (*5*, *6*) in analysis.

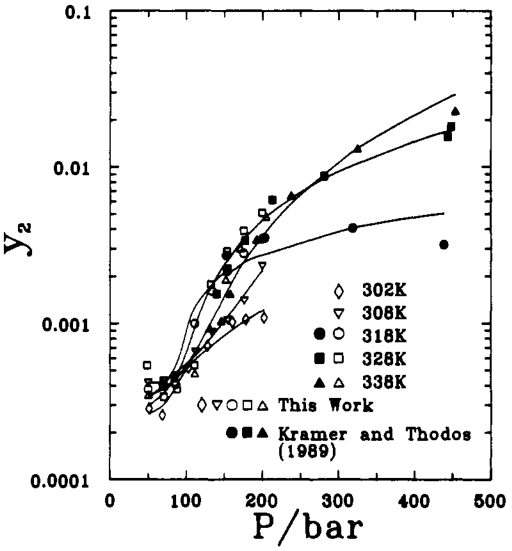

Figure 5. Comparison of calculated solubilities of 1-octadecanol in carbon dioxide by eq 3 with experimental data.

exists in carbon dioxide + 1-hexadecanol and carbon dioxide + 1-octadecanol. Figures 2–5 compare our results with those reported by Kramer and Thodos (*5*, *6*).

Correlation

The solubilities of 1-hexadecanol and 1-octadecanol in carbon dioxide have been correlated by three methods. In the first method the mole fraction of alcohol y_2 was related to the reduced density of carbon dioxide $\rho_{r,1}$ by (*5*–*7*)

$$\log y_2 = A + B\rho_{r,1} \tag{1}$$

The reduced densities for carbon dioxide used were obtained from the work of Kennedy and Thodos (*14*) and are given in Tables I and II. The optimum values of A and B for each isotherm are given in Table III. The average absolute deviations in y_2 are 15.62% (51 points) and 27.38% (56 points) for carbon dioxide + 1-hexadecanol and carbon dioxide + 1-octadecanol, respectively. The calculated deviations were too large, so we considered alternative methods.

The second method is similar to the first, with the addition of an $\rho_{r,1}^2$ term:

$$\log y_2 = A + B\rho_{r,1} + C\rho_{r,1}^2 \tag{2}$$

The optimum values of A, B, and C for each isotherm are listed in Table III. The average absolute deviation of 7.98% (51 points) for carbon dioxide + 1-hexadecanol and 14.1% (56 points) for carbon dioxide + 1-octadecanol indicates a considerable improvement over eq 1. These calculated results are shown in Figures 2 and 3.

The third method introduces the total pressure to give the following expression:

$$\log y_2 = A + B\rho_{r,1}/D^{1/P_{r,1}} \tag{3}$$

The optimum values of A, B, and D for each isotherm are also given in Table III. The overall average absolute deviation for carbon dioxide + 1-hexadecanol was found to be 7.54% (51 points) while that for carbon dioxide + 1-octadecanol was 13.93% (56 points). These calculated results are shown in Figures 4 and 5. It can be seen that the calculated results by using eqs 2 and 3 for carbon dioxide + 1-hexadecanol and carbon dioxide + 1-octadecanol give a satisfactory agreement with experimental valves.

Literature Cited

(1) Paulaitis, M. E.; Krukonis, V. J.; Kurnik, R. T.; Reid, R. C. *Rev. Chem. Eng.* **1983**, *1*, 179.
(2) Katzenski-Ohling, G.; Schneider, G. M. *Fluid Phase Equilib.* **1987**, *34*, 273.
(3) Hölscher, I. F.; Spee, M.; Schneider, G. M. *Fluid Phase Equilib.* **1989**, *49*, 103.
(4) Spee, M.; Schneider, G. M. *Fluid Phase Equilib.* **1991**, *65*, 263.
(5) Kramer, A.; Thodos, G. *J. Chem. Eng. Data* **1988**, *33*, 230.
(6) Kramer, A.; Thodos, G. *J. Chem. Eng. Data* **1989**, *34*, 184.
(7) Giddings, J. C.; Myers, M. N.; King, J. W. *J. Chromatogr. Sci.* **1969**, *7*, 276.
(8) Czybryt, J. J.; Myers, M. N.; Giddings, J. C. *J. Phys. Chem.* **1970**, *74*, 4260.
(9) Anderson, F. E.; Prausnitz, J. M. *AIChE J.* **1986**, *32*, 1321.
(10) Dimitrelis, D.; Prausnitz, J. M. *J. Chem. Eng. Data* **1989**, *34*, 286.
(11) Chimowitz, E. H.; Pennisi, K. J. *AIChE J.* **1986**, *32*, 1665.
(12) Chimowitz, E. H.; Kelley, F. D.; Munoz, F. M. *Fluid Phase Equilib.* **1988**, *44*, 23.
(13) Debenedetti, P. G.; Kumar, S. K. *AIChE J.* **1988**, *34*, 645.
(14) Kennedy, J. T., Jr.; Thodos, G. *J. Chem. Eng. Data* **1960**, *5*, 293.

Received for review December 12, 1991. Revised April 2, 1992. Accepted April 20, 1992. Acknowledgment is made to the National Science Council of the Republic of China (Grant NSC 80-0402-E006-25) for financial support of this work.