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Solubilities of 1-Nonanol, 1-Undecanol, 1-Tridecanol, and 1-Pentadecanol in Supercritical Carbon Dioxide at $T = 323.15$ K

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By use of a flow-type apparatus, vapor-phase compositions in supercritical carbon dioxide at 323.15 K have been measured for 1-nonanol, 1-undecanol, 1-tridecanol, and 1-pentadecanol over the pressure range from 80 to 250 bar. The measured mole fractions of solute in supercritical carbon dioxide are correlated with the reduced density and reduced pressure of the pure solvent.

Introduction

Supercritical fluid extraction has received wide attention in recent years for potential applications in the chemical industry (Eckert et al., 1996; Brennecke, 1996). Solubility data of low-volatile components in supercritical solvents are of great interest in the process design of the supercritical fluid extraction.

In this work, the solubilities of 1-nonanol, 1-undecanol, 1-tridecanol, and 1-pentadecanol in supercritical carbon dioxide at 323.15 K over the pressure range from 80 to 250 bar have been measured. The higher alcohols are frequently used in surfactant industries where the need for highly purified components is essential.

Limited studies on the solubilities in carbon dioxide of higher alcohols with an even number of carbon atoms on the chain are present in the literature: Katzenski-Ohling and Schneider (1987), Spee and Schneider (1991), and Kordikowski and Schneider (1993) (1-dodecanol); Kramer and Thodos (1988), Iwai et al. (1991), and Yau and Tsai (1992) (1-hexadecanol). No references have been found for higher alcohols with an odd number of carbon atoms on the chain.

The results obtained have been correlated with different equations.

Experimental Section

A flow-type apparatus was used to measure the solubilities of liquid components in supercritical carbon dioxide (Pauchon, 1996).

Carbon dioxide was compressed by a HPLC pump (Waters 590) from a gas cylinder. The phase equilibrium between the supercritical CO_2 and the liquid solute was achieved within an equilibrium cell that was totally submerged in a constant temperature water bath (Julabo SC). To check that thermodynamical equilibrium is reached a study was performed with different products (in particular with naphthalene) for supercritical CO_2 flows between 0.03 mL min^{-1} and 3.5 mL min^{-1}. We have checked that, for those flows, the concentration of the fluid going out of the equilibrium cell is constant in the limit of experimental error. The determinations are performed with a supercritical CO_2 flow of the order of 0.1 mL min^{-1} so as to obtain a great pressure stability. This stability is necessary, particularly between 100 and 150 bar, because of the great variations of solubilities. For this flow, the tests performed at the same pressure range and temperature demostrated that the measured solubilities were not affected by the contact time between supercritical carbon dioxide and solute.

Table 1. Solubility Data, y_1, of Some 1-Alkanols in Carbon Dioxide and Densities, ρ, of Carbon Dioxide Calculated from the Equation of Angus, at $T = 323.15$ K

P/bar	$y_1 \cdot 10^2$	ρ/g·L^{-1}	P/bar	$y_1 \cdot 10^2$	ρ/g·L^{-1}
		1-Nonanol (1) + Carbon Dioxide (2)			
94.5	0.6564	326.19	159.0	3.842	721.22
104.6	0.9435	443.08	173.7	6.000	748.11
104.6	0.9435	443.08	184.7	7.644	764.96
123.6	1.663	607.85	202.8	8.677	788.47
147.3	2.887	694.33	221.7	12.20	809.06
147.3	2.930	694.33			
		1-Undecanol (1) + Carbon Dioxide (2)			
95.1	0.3216	332.18	187.8	4.117	769.32
106.4	0.4114	464.91	202.2	4.986	787.76
114.2	0.6715	544.66	213.1	5.510	800.08
131.4	1.040	643.76	233.3	6.400	820.28
150.2	1.504	701.59	238.5	6.212	824.99
169.6	3.074	741.20			
		1-Tridecanol (1) + Carbon Dioxide (2)			
84.1	0.0145	243.90	172.5	1.177	746.13
95.1	0.0328	332.18	185.2	1.390	765.67
103.7	0.1651	431.95	185.2	1.418	765.67
120.8	0.4960	591.92	195.5	1.466	779.49
135.6	0.7109	659.39	203.3	1.661	789.04
147.3	0.9012	694.33	224.3	2.310	811.66
165.6	1.135	734.07	241.2	2.307	827.37
		1-Pentadecanol (1) + Carbon Dioxide (2)			
90.8	0.0342	292.62	193.5	0.8604	776.93
112.5	0.1538	529.69	201.0	0.9238	786.31
125.8	0.2994	619.12	207.9	1.003	794.36
139.4	0.4454	671.93	212.3	1.005	799.25
153.2	0.5618	708.68	219.9	1.010	807.26
165.9	0.6646	734.60	228.5	1.102	815.75
179.2	0.7626	756.82	236.6	1.200	823.28

The temperature of the water bath was determined by a thermocouple. The pressure was measured by a pressure sensor (Validyne model DP 15 TL) and registered by a digital indicator (CD 15). The experimental uncertainties were estimated to be ±0.3 bar for pressure and ±0.025 K for temperature. The equilibrium cell was composed of a

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Table 2. Empirical Correlation of Solubility Data of 1-Alkanols at T = 323.15 K

			eq 2			eq 3				eq 4			
solute	P/bar	N_p	A	B	AAD%	A	B	C	AAD%	A	B	D	AAD%
1-nonanol	82.5−221.7	11	−3.1445	1.1811	10.0	−1.3501	−2.0039	1.2926	4.44	−2.3932	1.8268	9.4435	2.34
1-undecanol	95.1−238.5	11	−3.6669	1.3612	10.0	−1.9449	−1.5823	1.1516	3.90	−2.8860	1.5712	4.4375	4.68
1-tridecanol	84.1−241.2	14	−4.5785	1.6847	7.02	−5.2984	3.1238	−0.6140	4.69	−5.0103	1.6648	0.6774	5.46
1-pentadecanol	90.8−236.6	14	−4.3343	1.3703	0.88	−4.2938	1.2967	0.0298	0.86	−4.7735	1.5835	0.9187	3.62

stainless steel pipe 19 cm long and with an inner diameter of 0.9 cm. The solute was introduced into the cell as a liquid (5 mL) impregnated in an inert solid support (gas chrom RZ 60/80 mesh).

Supercritical carbon dioxide saturated with solute was collected using a HPLC injection valve in a calibrated loop of 551 μL and depressurized through a HPLC chromatographic column (250 mm in length and 2.1 mm inside diameter; package: silica, particle size 5 μm). The component trapped in the HPLC column was quantitatively recovered in 5 cm^3 of eluent (methanol). This solution was analyzed by gas-phase chromatography using a Porapack P column (1 m long, $^1/_8$ in. diameter, particle size 80/100 mesh).

The solubility of naphthalene was measured to test the apparatus. Results were compared with published values (McHugh and Paulaitis, 1980). The measured solubilities of naphthalene agreed with the bibliographic data within 7% for pressures around 100 bar and 4% for pressures above 150 bar.

Materials

The carbon dioxide had a stated minimum purity of 99.5 mol % and was supplied by Air Liquide. 1-Nonanol (+96 mol %) and 1-undecanol (96 mol %) were supplied by Merck, and 1-tridecanol (97 mol %) and 1-pentadecanol (+99 mol %) were from Aldrich. Each material was used without further purification.

Results and Discussion

Table 1 presents solubilities of different 1-alkanols in carbon dioxide at the temperature of 323.15 K for pressures from 80 to 250 bar and reports densities as a function of the pressure. The reproducibility of the data was calculated to be within ±3.1%. Pure CO$_2$ density values have been calculated by the Angus equation (Angus et al., 1976)-where $\omega = \rho/\rho_c$ and $\tau = T_c/T$ with $\rho_c = 0.010\,63$ mol cm^{-3}

$$z = 1 + \omega \sum_{i=0}^{9} \sum_{j=0}^{Ji} b_{ij}(\tau - 1)^j(\omega - 1)^i \qquad (1)$$

and T_c = 304.2 K. The coefficients b_{ij} are given in the IUPAC table (Angus et al., 1976).

The solubilities of the alkanols studied here decrease as the carbon number increase and fit in with the solubilities found in the literature for alcohols with similar chain length and an even number of carbon atoms. The results exhibit trends that are typical of the solubility of nonvolatile organic molecules in supercritical CO$_2$.

The solubilities of the different alkanols have been correlated with three methods. The fittings of experimental data have been made using a regression tool based on an optimization method, the simplex method, that minimizes the sum of the differences between the experimental data and the calculated ones. In the first method, the mole fraction of alkanol, y_1, was related to the reduced density of pure solvent, ρ_r, by a linear relation (Kramer and Thodos, 1988):

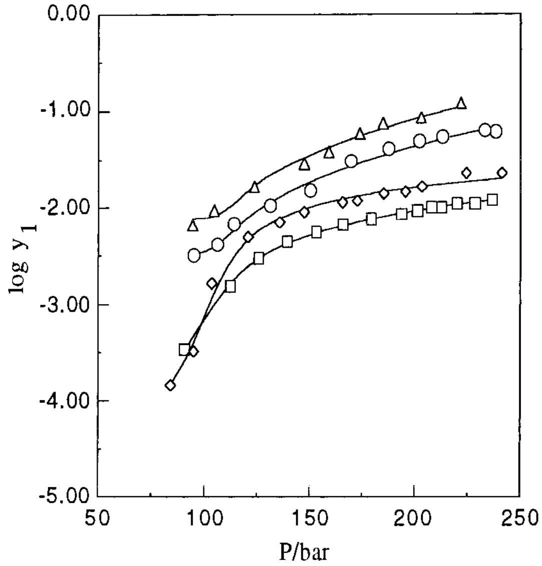

Figure 1. Comparison of calculated solubilities of [△, 1-nonanol; ○, 1-undecanol; or ◇, 1-tridecanol; □, 1-pentadecanol + CO$_2$ by eq 3 with experimental data.

$$\log y_1 = A + B\rho_r \qquad (2)$$

The optimum values of A and B for each isotherm are listed in Table 2. It can be seen that the average absolute deviations (AAD) in y_1 are 10% for carbon dioxide + 1-nonanol and carbon dioxide + 1-undecanol, and 7% for 1-tridecanol. For the system carbon dioxide + 1-pentadecanol an abnormally low average absolute deviation is obtained.

The second method is similar but now the relation is polynomial:

$$\log y_1 = A + B\rho_r + C\rho_r^2 \qquad (3)$$

The optimum values of A, B, and C for each system are listed in Table 2. The average absolute deviations are between 4% and 5% for all the systems studied here except for carbon dioxide + 1-pentadecanol, which shows again an abnormally low AAD value. The results obtained with this equation mean a clear improvement with respect to those obtained using eq 2.

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

$$\log y_1 = A + B\rho_r/D^{1/P_r} \qquad (4)$$

where P_r is the reduced pressure of carbon dioxide. The optimum values for A, B, and D for each isotherm are given in Table 2. The average absolute deviations range from 2.34% for carbon dioxide + 1-nonanol to 5.46% for carbon dioxide + 1-tridecanol. For carbon dioxide + 1-pentadecanol, an AAD value of 3.62% is obtained using this equation, which is a more reasonable value than those obtained using eqs 2 and 3. In any case the results obtained with eq 4 are similar to those using eq 3; therefore, it seems adequate to use an equation fitting y_1 against the reduced density of pure solvent, and the introduction of reduced pressures in the fitting equation does not seem necessary.

Figure 1 is a comparison of results calculated using eq 3 with the experimental values.

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