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Solubilities of Solid Octacosane and Triacontane in Supercritical Carbon Dioxide

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Solubilities of solid octacosane and triacontane in supercritical carbon dioxide at temperatures between 35 and 45 °C and pressures between 80 and 275 bar have been measured. The results are correlated using the model proposed by Chrastil, and as predicted by this model, a linear relationship between the logarithm of the solubility and the logarithm of the density of carbon dioxide was obtained.

Introduction

Recently attention has been paid to aspects of supercritical fluid extraction (SCFE) because of its potential applications in industrial fields (*1*, *2*). However, information on solubilities in supercritical fluids is required at least on model systems in order to represent the complex systems encountered in industrial applications.

High molecular weight *n*-paraffins can be used as model compounds in petroleum industry applications like the Fischer–Tropsch synthesis. With respect to these applications liquid carbon dioxide solubilities in compounds like eicosane, tetracosane, octacosane, dotriacontane, and hexatriacontane (*3*–*7*) have been reported.

Moreover, C_{25}–C_{35} *n*-paraffins represent the main coextracted compounds (called cuticular waxes) in carbon dioxide SCFE from vegetable matrices like herbs, flowers, and roots. Extraction temperatures between 35 and 50 °C and pressures between 80 and 200 bar are used, and fractionation of the extract is required to separate *n*-paraffins from the odor- and taste-responsible compounds (*8*, *9*).

McHugh et al. (*10*) studied octacosane solubilities in supercritical carbon dioxide at 34.7, 45.4, 50.2, and 52 °C over a range of pressures from 119 to 326.7 bar. Moreover, these researchers demonstrated that between 31.1 and 52.5 °C the octacosane carbon dioxide system exhibits only solid–gas equilibrium whatever the operation pressure. Swaid et al. (*11*) studied supercritical carbon dioxide solubilities of octacosane at 50.5, 70, and 89.3 °C in the range 204–810 bar, i.e., essentially liquid–gas equilibria.

Solubilities of other *n*-paraffins in supercritical ethane have been studied (*12*–*14*).

In this work octacosane and triacontane solubilities in supercritical carbon dioxide are measured in the range from 35 to 45 °C and for pressures between 80 and 275 bar. These compounds have been chosen because they are among the main coextracts during supercritical fluid extraction of essential oils (*8*, *9*).

Experimental Section

A schematic diagram of the experimental single pass flow apparatus is presented in Figure 1. The apparatus is similar to those described by various researchers for supercritical fluid solubilities of several compounds (*15*, *16*).

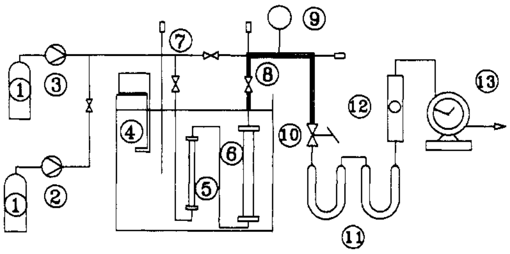

Figure 1. Schematic representation of the flow-type apparatus: (1) gas cylinders; (2) solvent pump; (3) cosolvent pump; (4) thermostated water bath; (5) solvent preheater; (6) saturation column; (7) bypass line; (8) thermostated line; (8) Bourdon gauge; (10) micrometering valve; (11) Pyrex U-tubes; (12) rotameter; (13) wet test meter.

The solvent was sent to the apparatus by a HPLC pump (Gilson 305). The pump head was cooled and adapted to use subcooled liquid carbon dioxide. A dampener (Gilson 805) was inserted in the high-pressure line to damp pressure fluctuations. A second pump was available to add a cosolvent.

All experiments were performed using carbon dioxide flow rates between 0.08 and 0.7 normal L/min (NLPM) (accuracy within 0.5%). In this range, tests performed at the same temperature and pressure demonstrated that measured solubilities were not influenced by the contacting time between the supercritical solvent and the solute.

High-pressure carbon dioxide reached the desired temperature upon flowing through a tubular preheater (L = 200 mm, i.d. = 8 mm) immersed in a thermostated bath (temperature was maintained constant within ±0.1 °C).

The equilibrium pressure was measured by a Bourdon gauge (Salmoiraghi SC3200), accurate to ±0.5 bar.

Then the solvent flowed into a 50 cm^3 column inserted in the same bath. The column was packed with a mixture of solid solute and glass beads to increase contact between supercritical carbon dioxide and the solute and to prevent caking.

The saturated solution, flowing through a thermostated line, passed to a temperature-controlled micrometering valve (Hoke 1315G4Y) in which the solution expanded to atmospheric pressure, releasing the dissolved solute. The valve temperature was measured by an Fe–constantan thermocouple and the temperature adjusted through a variable resistance heating cable (Watlow 62H36A5X) wrapped around the valve body.

After the expansion valve, the gaseous carbon dioxide was allowed to flow through a calibrated rotameter (Matheson

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Table I. Experimental Solubilities for Naphthalene and Octacosane in Supercritical Carbon Dioxide

Naphthalene					
p/bar	10^2x	$S/(\mathrm{g \cdot L^{-1}})^a$	p/bar	10^2x	$S/(\mathrm{g \cdot L^{-1}})^a$
t = 35 °C					
90	0.930	18.50	180	1.62	41.10
140	1.39	33.78	230	1.81	48.15
Octacosane					
p/bar	10^4x	$S/(\mathrm{g \cdot L^{-1}})^a$	p/bar	10^4x	$S/(\mathrm{g \cdot L^{-1}})^a$
t = 35 °C					
80	0.123	0.055	150	0.683	0.500
90	0.345	0.209	180	0.813	0.625
100	0.517	0.340	200	0.936	0.725
110	0.546	0.374	220	0.990	0.790
120	0.591	0.420			
t = 40 °C					
90	0.187	0.081	140	0.962	0.666
95	0.280	0.142	150	1.025	0.731
100	0.484	0.269	180	1.304	0.972
110	0.600	0.363	225	1.672	1.289
130	0.905	0.611	275	1.710	1.365
t = 45 °C					
105	0.396	0.187	175	2.754	1.949
110	0.760	0.407	200	3.195	2.336
125	1.278	0.771	225	3.900	2.933
135	1.790	1.130	250	3.893	2.974
150	2.371	1.587			

[a] Solvent density evaluated at operating conditions (*18*).

304) and a wet test meter (Sim Brunt A-B1) to determine flow rate stability and to measure the total volume of solvent used in each run.

The solute was collected in two Pyrex U-tubes arranged in series and partly packed with glass wool, immersed in a cooled bath (Neslab RTE-220) maintained at approximately −20 °C. The solid collected in the tubes was weighted by an analytical balance (Gibertini E42, accuracy ±0.1 mg). Part of the solute tended to deposit within the valve; then, after each run, the valve was flushed with octane. The contribution of the solute recovered by this technique was added to that obtained from the mass in the glass tubes.

Source and Purity of the Materials. Octacosane and triacontane were obtained from Sigma, and each had a stated purity of 99%. They were used without further purification.

Carbon dioxide was furnished by SON (Società Ossigeno Napoli, Italy) with a purity of 99.99%.

Results

The reliability of the apparatus was preliminarily tested by measuring the solubilities of naphthalene in supercritical carbon dioxide at 35 °C. The measurements were performed at several carbon dioxide flow rates within the range indicated in the Experimental Section. The solubilities obtained resulted independent from the carbon dioxide flow rate and in good agreement with those of Tsakhanskaya et al. (*17*) and McHugh and Paulaitis (*16*). The data are shown in the first part of Table I.

The solubilities of octacosane in carbon dioxide at 35, 40, and 45 °C are shown in Figure 2 in terms of the molar fraction of solute against pressure. For comparison purposes octacosane solubilities measured by McHugh et al. (*10*) at 45.4 °C are also shown.

Full comparison between the two studies is not possible because the temperatures at which solubilities have been measured are slightly different. In fact, solubilities measured at 45.4 °C by McHugh et al. (*10*) are systematically higher than those measured in the present work at 45 °C. The difference between the two data sets (average deviation 13%) can be partly attributed to the difference in temperatures: at pressures higher than the crossover point, solubility increases with temperature.

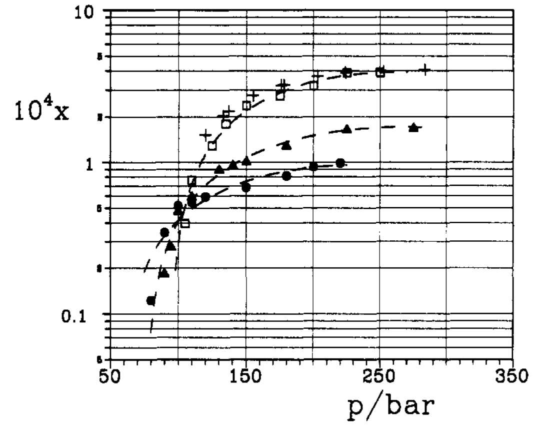

Figure 2. Octacosane mole fraction x in supercritical carbon dioxide, as a function of pressure: (●) 35 °C (▲) 40 °C, (□) 45 °C, (+) 45.4 °C (McHugh et al. (*10*)). Dashed lines were obtained by the polynomial best fit of the data sets.

Table II. Experimental Solubilities for Triacontane in Supercritical Carbon Dioxide

p/bar	10^4x	$S/(\mathrm{g \cdot L^{-1}})^a$	p/bar	10^4x	$S/(\mathrm{g \cdot L^{-1}})^a$
t = 35 °C					
90	0.051	0.033	160	0.382	0.319
100	0.100	0.075	180	0.420	0.360
110	0.165	0.122	200	0.503	0.432
120	0.200	0.159	250	0.536	0.482
140	0.351	0.288			
t = 45 °C					
105	0.135	0.071	160	2.089	1.526
110	0.283	0.161	180	2.588	1.967
115	0.479	0.292	200	2.601	2.038
120	0.721	0.459	250	3.013	2.477
140	1.163	0.801			

[a] Solvent density evaluated at operating conditions (*18*).

Mole fractions of octacosane around 1 × 10^{-4} are probably the lower limit of solubilities appreciable with their apparatus. This limit could affect their measurements at 45.4 °C and at lower pressures and the whole set of data at 34.7 °C (*18*).

Octacosane solubilities measured by Swaid et al. (*11*) at 50.5 °C showed an average deviation of about 17% with respect to those measured by McHugh et al. (*10*) at 50.2 °C.

The extension of solubility measurements down to pressures lower than those explored by the other researchers (*10, 11*) allowed the localization of a solubility crossover point at about 110 bar for both compounds studied (see figure 2 for octacosane).

Comparison with octacosane and triacontane solubilities measured by Moradinia and Teja (*12*) in supercritical ethane at 35, 40, and 46 °C confirms that these compounds are much less soluble in supercritical carbon dioxide: the difference in solubilities is about 2 orders of magnitude for both compounds.

Tables I and II report solubilities of octacosane and triacontane, respectively, expressed either in terms of the mole fraction of solute or as grams per liter of solvent. Solvent densities were obtained from experimental data reported in the literature (*19*). The reproducibility of the solubilities was within 5%; the less accurate measurements were obtained at the lower pressures.

The solubility data were correlated using the model proposed by Chrastil (*20*). This model is based on the hypothesis that the association between solvent and solute molecules produces a solvato complex. The model gives a

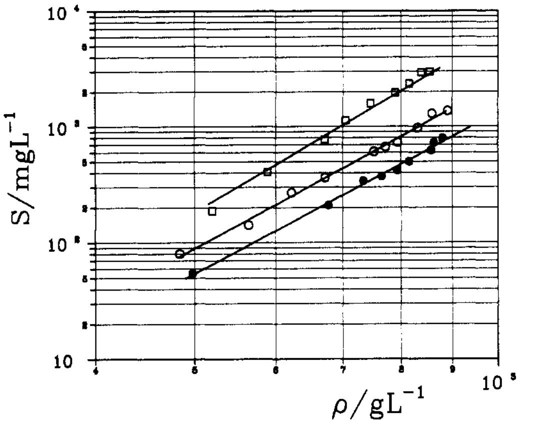

Figure 3. Octacosane solubility S in supercritical carbon dioxide: (●) 35 °C, (○) 40 °C, (□) 45 °C. (Experimental data are plotted in a log–log form; straight lines represent the best fit of eq 1 to the data.

linear relationship between the logarithm of the solubility and the logarithm of the density of the pure solvent. Chrastil's relationship can be expressed as

$$\ln(S/(\mathrm{g{\cdot}L^{-1}})) = k\ln(\rho/(\mathrm{g{\cdot}L^{-1}})) + (a/(T/\mathrm{K}) + b) \quad (1)$$

where S is the solubility, ρ is the solvent density, and T is the temperature. The constant k is the slope of the linear correlation and represents the average number of solvent molecules in the solvato complex. The constant a is dependent on the heat of solvation ($\Delta H_{\mathrm{solv}}/R$), and b depends on the molecular weights and melting points of the two compounds.

The data obtained in this study exhibit the expected linear relationship predicted by the model, as shown in Figures 3 and 4 for octacosane and triacontane, respectively. The straight lines reported in these figures are the best fit of eq 1 to the data. The slopes of the solubility isotherms are with a good approximation equal. Only octacosane solubilities at 45 °C correlate with a slight different slope with respect to the others at 35 and 40 °C. This fact could be explained by an increase of the average number of molecules involved in the solvato complex formation, as the operating temperature rises (*21*), approaching the upper solid–liquid–gas equilibrium line (UCEP) (*10*).

The slopes were determined to be 4.66 and 8.51 for octacosane and triacontane, respectively.

The constants a and b in eq 1 were determined to be −13 516 and 12.63 for octacosane and −24 584 and 21.09 for triacontane.

Registry Numbers Supplied by Author. carbon dioxide, 124-38-9; octacosane, 630-02-4; triacontane, 638-68-6.

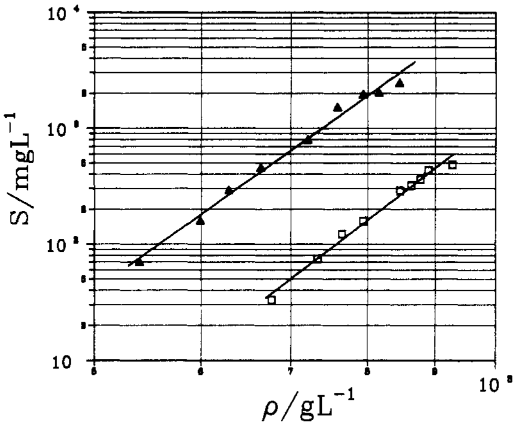

Figure 4. Triacontane solubility S in supercritical carbon dioxide: (□) 35 °C, (▲) 45 °C. Experimental data are plotted in a log–log form; straight lines represent the best fit of eq 1 to the data.

Literature Cited

(1) McHugh, M. A.; Krukonis, V. J. *Supercritical Fluid Extraction Principles and Practice*; Butterworths: Boston 1986.
(2) Bruno, T. J.; Ely, J. F. *Supercritical Fluid Technology: Reviews in Modern Theory and Applications*; CRC Press: Boca Raton, FL, 1991.
(3) Huang, S. H.; Lin, H.-M.; Chao, K.-C. *J. Chem. Eng. Data* **1988**, *33*, 145.
(4) Tsai, F.-N.; Yan, J.-S. *J. Chem. Eng. Data* **1990**, *35*, 43.
(5) Huang, S. H.; Lin, H.-M.; Chao, K.-C. *J. Chem. Eng. Data* **1988**, *33*, 143.
(6) Gasem, K. A. M.; Robinson, R. L. Jr. *J. Chem. Eng. Data* **1985**, *30*, 53.
(7) Tsai, F.-N.; Huang, S.-H.; Lin, H.-M.; Chao, K.-C. *J. Chem. Eng. Data* **1987**, *32*, 467.
(8) Reverchon, E.; Senatore, F. *J. Flavour Fragr.* **1992**, *7*, 227.
(9) Reverchon, E. *J. Supercrit. Fluids* **1992**, *5*, 256.
(10) McHugh, M. A.; Seckner, A. J.; Yogan, T. J. *Ind. Eng. Chem. Fundam.* **1984**, *23*, 493.
(11) Swaid, I.; Nickel, D.; Schneider, G. M. *Fluid Phase Equilib.* **1985**, *21*, 95.
(12) Moradinia, I.; Teja, A. S. *Fluid Phase Equilib.* **1986**, *28*, 199.
(13) Moradinia, I.; Teja, A. S. *ACS Symp. Ser.* **1987**, *329*, 130.
(14) Moradinia, I.; Teja, A. S. *J. Chem. Eng. Data* **1988**, *33*, 240.
(15) Van Leer, R. A.; Paulaitis, M. E. *J. Chem. Eng. Data* **1980**, *25*, 257.
(16) McHugh, M. A.; Paulaitis, M. E. *J. Chem. Eng. Data* **1980**, *25*, 326.
(17) Tsekhanskaya, Y. V.; Iomtev, M. B.; Muskina, E. V. *Russ. J. Phys. Chem. (Engl. Transl.)* **1964**, *38*, 1173.
(18) Bartle, K. D.; Clifford, A. A.; Jafar S. A.; Shilstone G. F. *J. Phys. Chem. Ref. Data* **1991**, *20*, 713.
(19) Angus, S.; Armstrong, B.; de Reuck, K. M.; *International Thermodynamic Tables of the Fluid State, Carbon Dioxide*; Pergamon Press: Oxford, U. K., 1976; Vol. III.
(20) Chrastil, J. *J. Phys. Chem.* **1982**, *86*, 3016.
(21) Wells, P. A.; Chaplin, R. P.; Foster, N. R. *J. Supercrit. Fluids* **1990**, *3*, 8.

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