Solubility of Menthol in Supercritical Carbon Dioxide

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The solubility of menthol [$C_{10}H_{20}O$] in supercritical carbon dioxide was measured by using a flow-type apparatus at 35−55 °C and pressures ranging from 6.7 to 11.6 MPa. The results were correlated with the density of pure solvent according to the Adachi−Lu equation. This approach yielded deviations of 4.4%.

Introduction

Supercritical fluid extraction has been given much attention recently as one of the new separation technologies in the industry. Especially the pharmaceutical and food industries are currently examining the application of supercritical separation processes with carbon dioxide as a cheap and safe solvent for nonpolar substances, including essential oils. Peppermint oil, containing L-menthol as the main component, is among the examined natural products. The supercritical carbon dioxide extraction of peppermint and spearmint was studied with promising results (*1*).

The knowledge of solubility data in supercritical fluids is necessary to establish the optimum conditions of the extraction. In this work, the solubility of menthol ($C_{10}H_{20}O$) in supercritical CO_2 was measured at five different temperatures in the range from 35 to 55 °C. The results were correlated with the density of pure solvent by using the Adachi−Lu equation.

Table 1. Solubilities of Menthol in Supercritical CO_2 (y_2) and Densities of Pure CO_2 (d)

P/MPa	$10^3 y_2$	d/(kg·m^{-3})	P/MPa	$10^3 y_2$	d/(kg·m^{-3})	P/MPa	$10^3 y_2$	d/(kg·m^{-3})
	308.15 K			313.15 K				
6.70	0.47	198.3	8.07	1.07	287.5			
7.51	0.96	276.3	8.26	1.33	313.6			
7.74	1.23	319.8	8.77	4.10	423.5			
7.80	1.51	335.9	8.84	5.07	443.3			
8.02	4.80	440.6	8.94	7.92	471.3			
8.11	12.60	502.2	9.07	13.09	504.8			
	318.15 K			323.15 K			328.15 K	
7.14	0.48	190.2	6.40	0.22	149.1	6.52	0.23	146.4
8.03	0.79	243.6	7.27	0.47	183.6	7.56	0.49	184.8
8.47	1.18	279.7	8.32	0.77	237.8	9.22	1.13	269.2
8.66	1.21	298.5	9.26	1.35	307.5	9.51	1.38	288.6
8.74	1.26	307.1	9.58	1.82	338.4	10.33	2.27	353.3
9.20	2.44	367.3	9.75	2.29	356.6	10.74	3.78	391.0
9.60	5.39	433.6	10.15	3.96	403.5	10.98	5.10	413.9
9.72	6.63	454.3	10.32	5.01	424.5	11.36	7.44	450.1
9.91	10.86	485.8	10.54	7.49	451.6	11.56	9.13	468.5
			10.69	9.11	469.6			

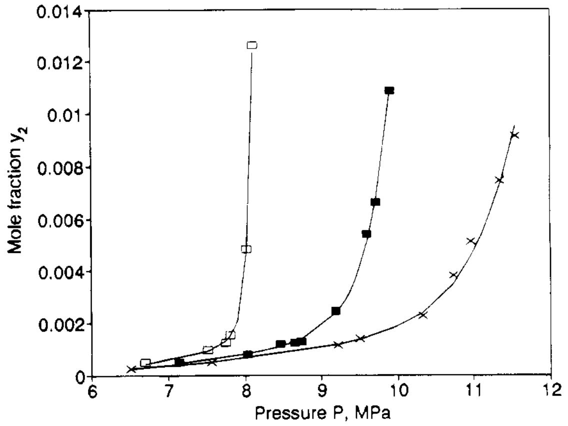

Figure 1. Solubilities of menthol in CO_2. Experimental data: (□) 308.15 K; (■) 318.15 K; (×) 328.15 K. Lines are calculated by the Adachi−Lu equation with the parameters of Table 2.

Experimental Section

Materials. Menthol (mixture of isomers) supplied by Fluka had a purity better than 98 mass %. No further purification was done. High-purity CO_2 (more than 99.9 mass %, Chemické závody Litvínov) was used as the solvent.

Equipment and Procedures. A flow-type apparatus was used to measure the solubilities of liquid menthol in dense CO_2 above its critical temperature. A detailed description of the equipment and operating procedures is given in a previous work (*2*). Carbon dioxide supplied from a gas cylinder was pumped into the system by a diaphragm compressor. A back-pressure regulator was used to maintain a constant pressure within the saturator, a high-pressure column of 12 cm^3 volume filled with menthol and glass beads and submerged in a water bath with temperature controlled within ±0.1 °C. The equilibrium pressure was measured with an accuracy of ±0.01 MPa, and its changes during a run ranged from 0.02 to 0.08 MPa, dependent on the amount of solvent consumed during the run. The mean pressure value was used in the evaluation of the run.

Supercritical fluid saturated with menthol was depressurized through a heated expansion valve and introduced into a U-shaped glass tube cooled in a mixture of ethanol and dry ice. The solid menthol trapped in the tube was determined by mass. The flow rate of CO_2 was adjusted to be 1−2 L/h. (With the flow rate increased to 10 L/h in several preliminary experiments, the amounts of menthol precipitated in the separator remained unchanged. Saturation of the solvent was proved in this way for the range of the applied flow rates.) The volume of CO_2 flowing out of the separator was measured by a calibrated glass vessel. Its consumption per run, which ranged from 0.25 to 3 L, was adjusted to obtain at least 0.015 g of menthol in the

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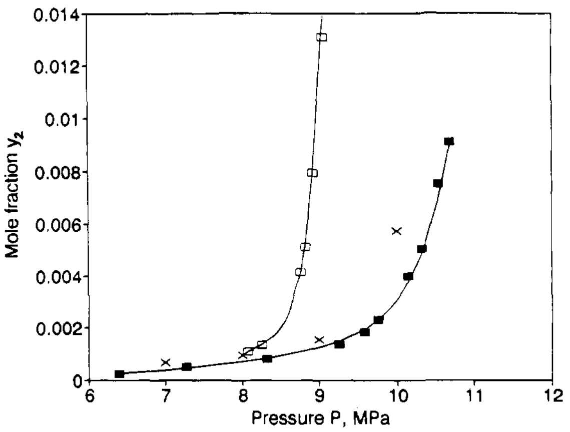

Figure 2. Solubilities of menthol in CO_2 compared with the data of Maier and Stephan (*3*). Experimental data: (□) 313.15 K, this work; (■) 323.15 K, this work; (×) 323.15 K (*3*). Lines are calculated by the Adachi–Lu equation with the parmeters of Table 2.

separator, except for the measurements of solubilities below 10^{-3} mol/mol, where the yields of menthol were proportionally lower.

Results and Discussion

The reproducibility of the solubility measurements was within 11%, the main source of errors being a small and varying amount of solute precipitated inside the expansion valve. The estimated accuracy of the values listed in Table 1, which were obtained as an arithmetic average of 3–6 measurements at each pressure, is ±6%. The solubilities are also presented in Figures 1 and 2 to show the relationship between y_2, the mole fraction of menthol in carbon dioxide, and P, the total pressure of the system, for the individual isotherms.

Figure 2 shows also a comparison of our data at 50 °C with the solubilities of L-menthol in CO_2 measured by Maier and Stephan (*3*) using an equilibrium cell. Though the data (*3*) were published in a small graph and could not be read with a comparable accuracy, they are obviously systematically higher. It is not clear whether the difference is due to the different techniques of measurement or due to the differences in the menthol purity (not indicated by Maier and Stephan).

Table 2. Solubility Coefficients for Eq 2 for Menthol in the Range of CO_2 Densities from 146 to 505 $kg \cdot m^{-3}$

a	b	e_0	e_1	e_2
−1513	−33.7	8.03	-6.295×10^{-3}	7.29×10^{-6}

Correlation

Modifying the Chrastil equation, Adachi and Lu (*4*) developed the following equation for relating solubility and density:

$$c/(\mathrm{kg \cdot m^{-3}}) = \{d/(\mathrm{kg \cdot m^{-3}})\}^k \exp\{a/(T/\mathrm{K}) + b\} \qquad (1)$$

$$k = e_0 + e_1\{d/(\mathrm{kg \cdot m^{-3}})\} + e_2\{d/(\mathrm{kg \cdot m^{-3}})\}^2$$

where c is the concentration of a solute in dense gas, d is the density of the gas, T is the absolute temperature, and a, b, e_0, e_1, and e_2 are solubility coefficients. Using the relation

$$y_2 = c/[c + (M_2/M_1)\{d/(\mathrm{kg \cdot m^{-3}})\}] \qquad (2)$$

where M_1 and M_2 are the molecular weights of CO_2 and menthol, respectively, the experimental results from Table 1 were correlated by eq 1. The densities used were calculated from Altunin and Gadetskii's equation of state given in the IUPAC tables (*5*), and they are listed in Table 1. The solubility coefficients from Table 2 yield a mean absolute deviation of eq 1 from the experimental solubilities of 4.4%. The course of the calculated isotherms is depicted in Figures 1 and 2. As the coefficients e_0, e_1, and e_2 are sensitive to the density, the correlation should not be extrapolated outside the range of CO_2 density between 146 and 505 $kg \cdot m^{-3}$.

Literature Cited

(1) Barton, P.; Hughes, R. E., Jr.; Hussein, M. M. *J. Supercrit. Fluids* **1992**, *5*, 157.
(2) Richter, M.; Sovová, H. *Fluid Phase Equilib.* **1993**, *85*, 285.
(3) Maier, M.; Stephan, K. *Chem.-Ing.-Tech.* **1984**, *56*, 222.
(4) Adachi, Y.; Lu, B. C.-Y. *Fluid Phase Equilib.* **1983**, *14*, 147.
(5) Angus, S.; Armstrong, B.; de Reuck, K. M. *International thermodynamic tables of fluid state, Carbon dioxide*; Pergamon Press: Oxford, 1976.

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