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High-Pressure Vapor−Liquid Equilibria for Carbon Dioxide + Limonene + Linalool

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High-pressure vapor−liquid equilibria for the carbon dioxide + limonene + linalool ternary system were measured at (313.2 K and 6.9 MPa), (333.2 K and 6.9 MPa), and (333.2 K and 10.0 MPa). A circulation-type method and a flow-type method were used for liquid-phase sampling and vapor-phase sampling, respectively. The results obtained were correlated by the Peng−Robinson equation of state using conventional mixing rules with two interaction parameters.

Introduction

As noted in previous papers (Iwai et al., 1994; Iwai et al., 1996), citrus oil is widely used as a raw material to extract flavors. Steam distillation or solvent extraction is usually applied to refine citrus oil. However, the drawbacks of these processes are low yields, formation of degradation products under high operating temperatures, and solvent residues. Therefore, supercritical fluid extraction using CO_2 is under consideration as an alternative process for refining citrus oil because of its advantages of low operating temperatures and no solvent residues. Limonene is a principal compound of citrus oil. It makes up approximately 90 wt % of citrus oil but does not contribute much to the flavor or fragrance of citrus oil. Linalool is an important oxygenated compound which makes the characteristic flavor or fragrance of citrus oil. It makes up approximately 1 wt % of citrus oil. The chemical structures of limonene and linalool are shown in previous papers (Iwai et al., 1994; Iwai et al., 1996). Limonene is an unsaturated terpene hydrocarbon which is unstable to heat, light, and oxygen. So, it is common industrial practice to remove limonene and other terpenes to concentrate the oxygenated compounds such as linalool. To apply supercritical fluid extraction with CO_2 to this separation process, vapor−liquid equilibrium data are required for the mixture of CO_2, limonene, and linalool. The binary data of the vapor−liquid equilibria for CO_2 + linalool and for CO_2 + limonene were measured and reported in previous works (Iwai et al., 1994; Iwai et al., 1996). In this work, the vapor−liquid equilibria for the CO_2 + limonene + linalool ternary system were measured at (313.2 K and 6.9 MPa), (333.2 K and 6.9 MPa), and (333.2 K and 10.0 MPa) by using a circulation-type method for liquid-phase sampling and a flow-type method for vapor-phase sampling. The relative volatilities between limonene and linalool can be evaluated from the present ternary vapor−liquid equilibrium data. They are important to consider the possibility for separation of limonene and linalool by extraction using supercritical carbon dioxide. The results obtained were correlated by the Peng−Robinson equation of state using conventional mixing rules with two interaction parameters.

Experimental Section

Materials. High-purity CO_2 (more than 99.9 vol % purity, Sumitomo Seika Co.) was used as received. *R*-(+)-Limonene (supplied by Aldrich Chemical Co., Inc.) and linalool (supplied by Wako Pure Chemical Industries, Ltd.) were used without further purification. Linalool is a mixture of optical isomers. The purities of limonene and linalool were ascertained to be more than 99% by gas chromatographic area analysis.

Apparatus and Procedures. The schematic diagram of the apparatus is shown in Figure 1. A circulation-type method was used to measure the concentrations of the liquid phase. Carbon dioxide, limonene, and linalool were fed into an equilibrium cell *3*. An impeller *4* was used to promote the equilibrium condition. The volume of the cell was 500 cm^3. After equilibrium (about 1 h), stirring by the impeller was stopped and circulation of the liquid phase was started with a magnetic pump *5*. A small amount of liquid phase was introduced into a sampling loop *7*. The volume of the sampling loop was about 3 cm^3. After circulation for about 30 min, the sampling loop was isolated from the equilibrium cell by switching a six-way valve *6*. The sample in the loop was decompressed through an expansion valve *11* and then introduced into a cold trap *12*, in which CO_2, limonene, and linalool were separated. The traps were cooled to under −40 °C and contained hexane to trap limonene and linalool. Hexane had already been saturated with CO_2 by using a bypass line *14* before the sampling operation to avoid dissolution of CO_2 in the sampling loop into hexane. The amount of gaseous CO_2 was measured by a dry test meter *13*. A small amount of limonene and linalool remaining in the tubing and the expansion valve was removed and trapped by using supercritical CO_2 through the bypass line and hexane through a solvent line *16*. The amount of limonene and linalool was determined by means of gas chromatograph. The pressure was measured with a Bourdon gauge, which had an accuracy of ±0.15% full scale. The equilibrium temperature was measured with a chromel−alumel thermocouple within ±0.1 K. In addition, a flow-type method was used to measure the concentrations of the vapor phase. After equilibrium (about 1 h), supercritical carbon dioxide was fed into the equilibrium cell. Then the vapor-phase sample in the cell was introduced into a cold trap *9* through an

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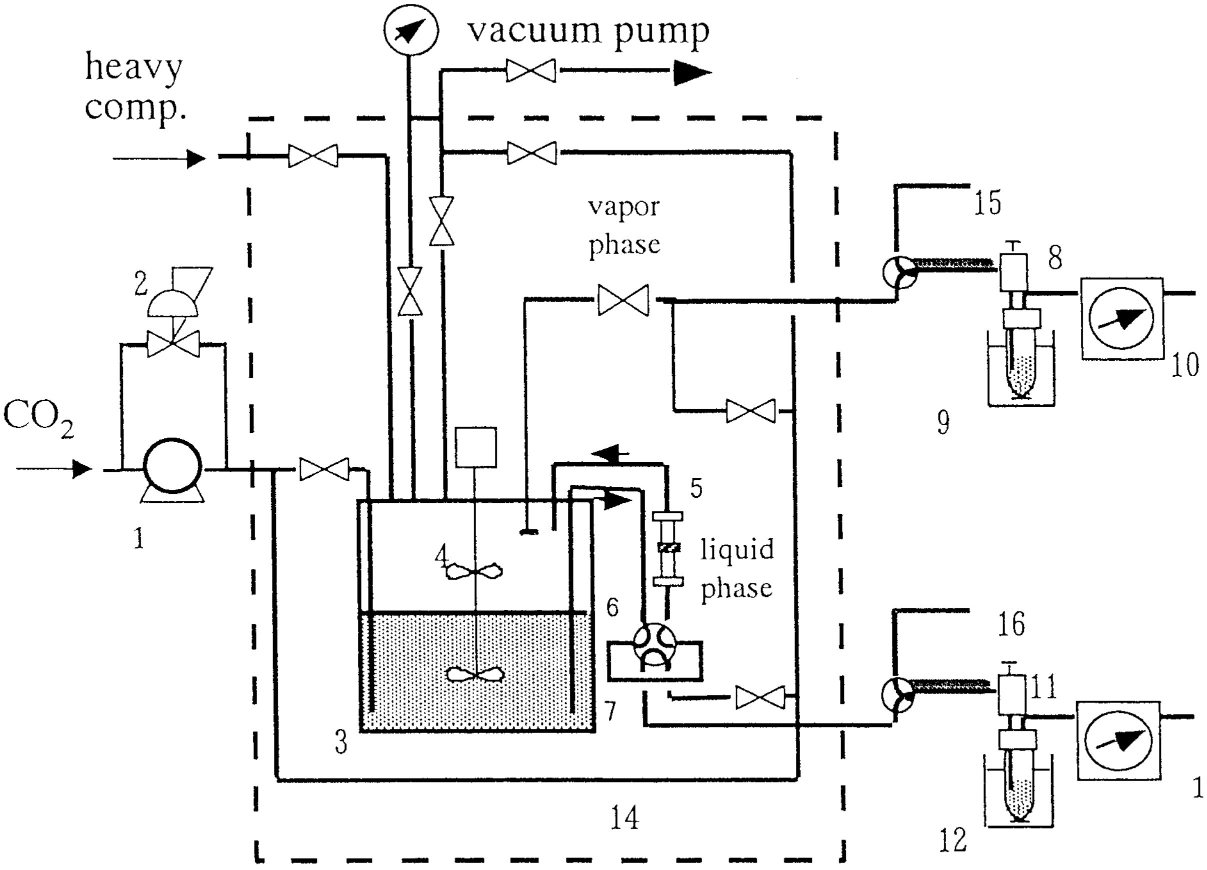

Figure 1. Experimental apparatus to measure high-pressure vapor−liquid equilibria: (*1*) pump; (*2*) back-pressure valve; (*3*) equilibrium cell; (*4*) impeller; (*5*) magnetic pump; (*6*) six-way valve; (*7*) sampling loop; (*8, 11*) expansion valves; (*9, 12*) cold traps; (*10, 13*) dry test meters; (*14*) bypass line; (*15, 16*) solvent lines.

expansion valve *8*. The equilibrium pressure in the cell was maintained with a back-pressure valve *2*. About 100 L (at atmospheric pressure) of CO_2 was supplied. The amounts of CO_2, limonene, and linalool were determined by the same procedure for the liquid sample. A flow-type sampling method was found to be more suitable than a circulation-type sampling method to obtain reliable data because the vapor-phase concentrations of limonene and linalool were extremely small.

Results and Discussion

The experimental results are shown in Table 1 and Figure 2. The values listed in Table 1 were obtained from an arithmetic average of several measurements at each condition. The standard deviations are less than 1.60×10^{-4} in the vapor phase and 1.63×10^{-2} in the liquid-phase mole fraction, respectively. The relative volatilities defined by eq 1 are also shown in Table 1.

$$\alpha_{23} = (y_2/x_2)/(y_3/x_3) \tag{1}$$

The values of α_{23} show that it is easy to remove limonene from linalool because the values of α_{23} are larger than unity when mixtures are linalool-rich. On the other hand, it is difficult to separate the mixtures in the limonene-rich region because the values of α_{23} are close to unity.

Correlation

The following equation can be used to calculate the vapor−liquid equilibrium:

$$[\phi_i^{V} p y_i = \phi_i^{L} p x_i]_T \tag{2}$$

Table 1. Experimental Vapor−Liquid Equilibria for CO_2 (1) + Limonene (2) + Linalool (3)[a]

T/K	p/MPa	x_1	x_2	x_3	y_1	y_2	y_3	α_{23}
313.2	6.9	0.7122	0	0.2878	0.9995	0	0.0005	
		0.7018	0.0329	0.2653	0.9993	0.0002	0.0005	3.6
		0.7043	0.0800	0.2157	0.9990	0.0005	0.0005	3.0
		0.7028	0.1781	0.1191	0.9989	0.0009	0.0002	2.4
		0.7107	0.2334	0.0559	0.9987	0.0011	0.0002	1.4
		0.7004	0.2996	0	0.9985	0.0015	0	
333.2	6.9	0.5351	0	0.4649	0.9993	0	0.0007	
		0.5510	0.0565	0.3925	0.9989	0.0004	0.0007	3.5
		0.5398	0.1805	0.2797	0.9986	0.0009	0.0005	3.0
		0.5403	0.2312	0.2285	0.9985	0.0011	0.0004	2.7
		0.5134	0.2833	0.2033	0.9983	0.0013	0.0004	2.2
		0.5228	0.4030	0.0742	0.9982	0.0016	0.0002	1.5
		0.4812	0.5188	0	0.9975	0.0025	0	
333.2	10.0	0.7431	0	0.2569	0.9974	0	0.0026	
		0.7483	0.0297	0.2220	0.9968	0.0007	0.0025	2.1
		0.7567	0.1168	0.1265	0.9955	0.0028	0.0017	1.8
		0.7506	0.2111	0.0383	0.9942	0.0050	0.0008	1.2
		0.740	0.260	0	0.9935	0.0065	0	

[a] The data of binary systems are cited from previous papers (Iwai et al., 1994; Iwai et al., 1996). The data of CO_2 + limonene at 333.2 K and 10.0 MPa are obtained by interpolation.

where p is the equilibrium pressure and x_i and y_i are the mole fractions of component i in the liquid phase and the vapor phase, respectively. To evaluate the fugacity coefficient ϕ_i, the Peng−Robinson equation of state (Peng and Robinson, 1976)

$$p = \frac{RT}{v - b} - \frac{a}{v(v + b) + b(v - b)} \tag{3}$$

was used and the conventional mixing rules of eqs 4 and 5

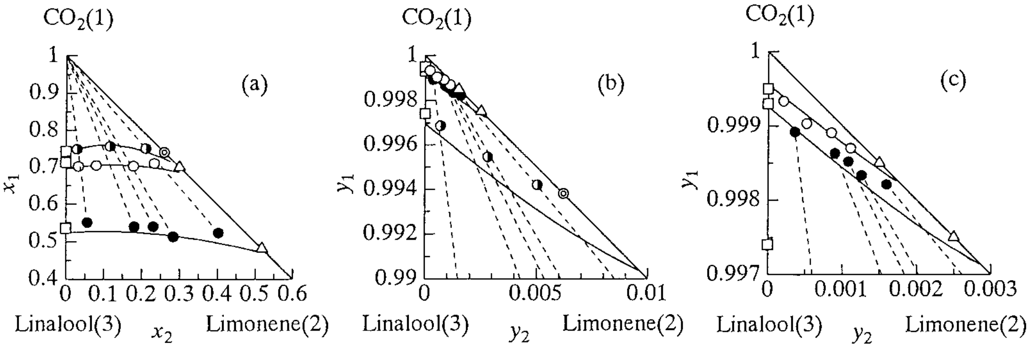

Figure 2. Vapor−liquid equilibria for CO_2 (1) + limonene (2) + linalool (3): (a) liquid phase; (b and c) magnification of vapor phase; (○, ●, ◑) present data at (313.2 K and 6.9 MPa), (333.2 K and 6.9 MPa), and (333.2 K and 10.0 MPa); (□) literature data (Iwai et al., 1994); (△) literature data (Iwai et al., 1996); (◎) interpolated value using literature data (Iwai et al., 1996); (- - -) experimental tie-lines at 333.2 K and 6.9 MPa; (—) calculated results.

Table 2. Critical Constants and Acentric Factors

substance	T_c/K	p_c/MPa	ω
CO_2	304.2[a]	7.37[a]	0.225[a]
limonene	662.6[b]	2.75[b]	0.310[c]
linalool	630.5[b]	2.42[b]	0.748[c]

[a] Reid et al. (1977). [b] Estimated by the Lydersen method (Reid et al., 1977). [c] Estimated by the Edmister method (Reid et al., 1977).

$$a = \sum_i \sum_j x_i x_j a_{ij}, \quad a_{ij} = (1 - k_{ij})\sqrt{a_i a_j} \tag{4}$$

$$b = \sum_i \sum_j x_i x_j b_{ij}, \quad b_{ij} = (1 - l_{ij})\frac{b_i + b_j}{2} \tag{5}$$

were used where k_{ij} and l_{ij} are the interaction parameters between unlike molecules i and j. When eqs 3−5 are used, the fugacity coefficient ϕ_i can be derived thermodynamically. The vapor−liquid equilibria were calculated by using the properties of pure components listed in Table 2, which were estimated by the group contribution methods of Lydersen and Edmister (Reid et al., 1977) because experimental critical properties of citrus oil components are scarce in the literature. Only the T_c data of limonene are available in the literature (Smith et al., 1990). The T_c reported is 653 ± 2 K and is close to the value shown in Table 2. The interaction parameters k_{ij} and l_{ij} were treated as fitting parameters. The values for k_{12}, k_{13}, l_{12}, and l_{13} were determined in previous works (Iwai et al., 1994; Iwai et al., 1996) using the binary data. The values for k_{23} and l_{23} were determined by using the present ternary data because the binary vapor−liquid equilibrium data for limonene + linalool are not available in the literature. The parameter estimation was performed at each temperature by minimizing the following objective function OF:

Table 3. Interaction Parameters k_{ij} and l_{ij} for CO_2 (1) + Limonene (2) + Linalool (3)

T/K	k_{12}[a]	l_{12}[a]	k_{13}[b]	l_{13}[b]	k_{23}	l_{23}
313.2	0.090	−0.020	0.053	−0.035	0.015	0.000
333.2	0.090	−0.040	0.051	−0.027	0.028	0.000

[a] Iwai et al. (1996). [b] Iwai et al. (1994).

$$\mathrm{OF} = \frac{1}{N}\sum_{1}^{N}\sum_{i}^{3}|x_{i,\mathrm{calc}} - x_{i,\mathrm{exp}}| + \frac{1}{N}\sum_{1}^{N}\sum_{i}^{3}|y_{i,\mathrm{calc}} - y_{i,\mathrm{exp}}| \tag{6}$$

where calc and exp denote the calculated and experimental results, respectively. N is the number of data. The values of the interaction parameters are listed in Table 3. The correlation results are shown in Figure 2. The present data are well correlated by the Peng−Robinson equation of state.

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