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

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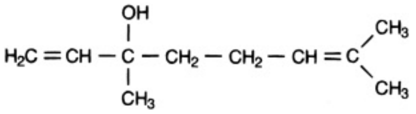
A circulation-type apparatus was constructed to measure high-pressure vapor−liquid equilibria. The vapor−liquid equilibria for carbon dioxide + linalool at 313.2 K from 4.00 to 7.99 MPa, at 323.2 K from 4.00 to 9.78 MPa, and at 333.2 K from 5.00 to 10.96 MPa were measured. The results were correlated by the Peng−Robinson equation of state using conventional mixing rules with two interaction parameters.

Introduction

Citrus oil is widely used as a raw material of flavor. Steam distillation or solvent extraction is usually applied to refine citrus oil. However, the drawbacks of these processes are considered to be low yields, formation of degradation products under a high operating temperature, and solvent residue. Supercritical fluid extraction is found to be an alternative process for refining citrus oil because of its advantages of a low operating temperature and no solvent residue. The high-pressure vapor−liquid equilibria for CO_2 + citrus oil are required for rational equipment design. However, few measurements on that system were available.

The main purpose of this work is to provide comprehensive measurements for the vapor−liquid equilibria of CO_2 + citrus oil. For this purpose, a circulation-type apparatus was designed and constructed. The vapor−liquid equilibria for CO_2 + decane were measured in order to ascertain the reliability of the apparatus and experimental procedure. Then, those for CO_2 + linalool were measured at 313.2, 323.2, and 333.2 K up to the critical region of the mixture. Linalool is one of the most important flavor fractions in citrus oil. The structure of linalool is shown in Figure 1. The results obtained were correlated by the Peng−Robinson equation of state using conventional mixing rules with two interaction parameters.



$$H_2C{=}CH-\underset{CH_3}{\overset{OH}{C}}-CH_2-CH_2-CH{=}C\begin{matrix}CH_3\\CH_3\end{matrix}$$

Figure 1. Structure of linalool (3,7-dimethyl-3-hydroxy-1,6-octadiene) ($C_{10}H_{18}O$, molecular weight 154.3, boiling point 198 °C).

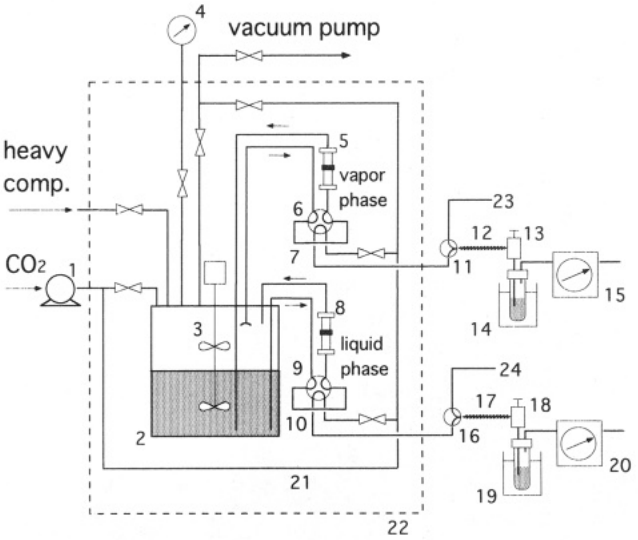


Figure 2. Circulation-type apparatus to measure the high-pressure vapor−liquid equilibria: (1) pump; (2) equilibrium cell; (3) impeller; (4) precision pressure gauge; (5, 8) magnetic pumps; (6, 9) six-way valves; (7, 10) sampling loops; (11, 16) three-way valves; (12, 17) line heaters; (13, 18) expansion valves; (14, 19) cold traps; (15, 20) dry test meters; (21) bypass line; (22) water bath; (23, 24) solvent lines.

Experimental Section

Equipment and Procedure. A circulation-type apparatus was constructed to measure high-pressure vapor−liquid equilibria. The schematic diagram of the apparatus is shown in Figure 2. The equilibrium cell 2 was evacuated. Carbon dioxide was supplied from a gas cylinder, liquefied through a cooling unit, compressed, and directed to the equilibrium cell. The heavy component (decane or linalool) was fed into the equilibrium cell by a charging pump. An impeller 3 was used to promote the equilibrium condition. The equilibrium cell had a dual glass window, and the vapor−liquid interface was controlled to be at the center of the window. The inner diameter and volume of the cell are 69 mm and 500 cm^3, respectively. In order to maintain the desired temperature, the cell and its immediate auxiliaries were placed in a constant-temperature water bath which was controlled within ±0.1 K. After equilibrium (about 1 h after), stirring by the impeller was stopped and circulation of the vapor and liquid phases was started by magnetic pumps 5 and 8. A small amount of each phase was introduced into sampling loops 7 and 10, respectively. The volume of the vapor sampling loop 7 was about 15 cm^3 and that of the liquid sampling loop 10 was 3 cm^3. After circulation for 30 min, the six-way valves 6 and 9 were switched in order to isolate the sampling loops from the equilibrium cell. The samples in the loops were decompressed through expansion valves 13 and 18, and then introduced into glass tubes 14 and 19, in which CO_2 and the heavy component were separated. The glass tubes were cooled under −40 °C, and the tubes contained ethanol or hexane to trap the heavy component. Ethanol and hexane were used to trap decane and linalool, respectively, and had already been saturated with CO_2 by using a bypass line 21 before the sampling operation to avoid dissolution of CO_2 in the sampling loops into ethanol or hexane. The amount of CO_2 was measured by dry test meters 15 and 20. A small amount of heavy component remaining in the tubing and the expansion valve was removed and trapped by using supercritical CO_2 through the bypass line and

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Table 1. Vapor–Liquid Equilibria for CO_2 + Decane and for CO_2 + Linalool

CO_2 (1) + Decane (2)

T = 311.0 K			T = 344.3 K		
p/MPa	x_1	y_1	p/MPa	x_1	y_1
4.55	0.4461	0.9994	5.51	0.3834	0.9975
6.86	0.7466	0.9988	8.55	0.5936	0.9968
			11.85	0.8058	0.9877

CO_2 (1) + Linalool (2)

T = 313.2 K			T = 323.2 K			T = 333.2 K		
p/MPa	x_1	y_1	p/MPa	x_1	y_1	p/MPa	x_1	y_1
4.00	0.3965		4.00	0.3449	0.9997	5.00	0.3864	0.9995
6.00	0.5933	0.9997	6.00	0.5167	0.9996	6.99	0.5351	0.9993
6.99	0.7122	0.9995	7.99	0.6906	0.9991	9.00	0.6799	0.9987
7.49	0.7852	0.9992	9.00	0.8062	0.9980	9.99	0.7431	0.9974
7.99	0.9103	0.9985	9.78	0.9420	0.9921	10.96	0.8294	0.9932

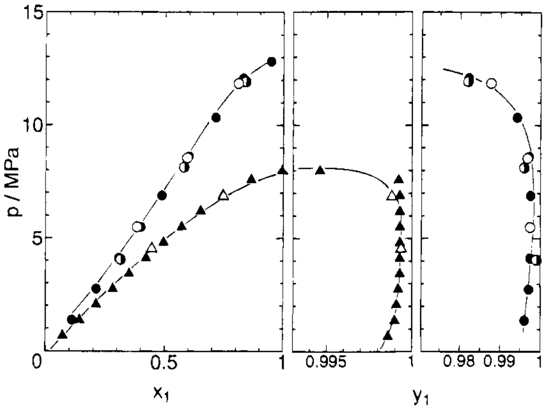

Figure 3. Vapor–liquid equilibria for CO_2 (1) + decane (2): (△, ○) present data at 311.0 and 344.3 K; (▲, ●) data of Reamer and Sage (*1*) at 311.0 and 344.3 K; (◑) data of Chou et al. (*2*) at 344.3 K; (—) smoothed line.

ethanol or hexane through lines 23 and 24. The amount of heavy component was determined by means of a gas chromatograph. The pressure was measured by a Bourdon gauge 4, of which the accuracy was ±0.15% in full scale. The equilibrium temperature was measured by a chromel–alumel thermocouple within ±0.1 K.

Materials. Decane (supplied by Tokyo Kasei Kogyo Co. Ltd.) and linalool (Wako Pure Chemical Industries, Ltd.) were used without further purification. The purities of decane and linalool are more than 99% by gas chromatographic area analysis. High-purity CO_2 (more than 99.9 vol % purity, Sumitomo Seika Co.) was used as received.

Result and Discussion

In order to ascertain the reliability of the apparatus and procedure, the vapor–liquid equilibria for CO_2 + decane at 311.0 and 344.3 K were measured. The experimental data are shown in Table 1. The values listed in Table 1 were obtained from an arithmetic average of several measurements at each pressure. The standard deviation is less than 8.2×10^{-5}. The values are in good agreement with those of Reamer and Sage (*1*) and those of Chou et al. (*2*) as shown in Figure 3.

The high-pressure vapor–liquid equilibria for CO_2 + linalool at 313.2, 323.2, and 333.2 K were measured. The results are listed in Table 1. The values in the vapor phase are in good agreement with those of Suzuki et al. (*3*) as shown in Figure 4.

Correlation

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

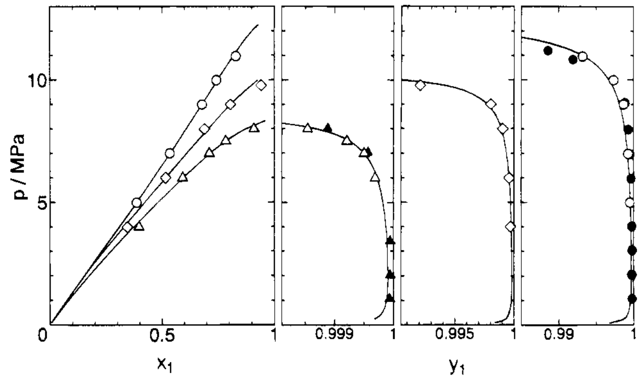

Figure 4. Vapor–liquid equilibria for CO_2 (1) + linalool (2): (△, ◇, ○) present data at 313.2, 323.2, and 333.2 K; (▲, ●) data of Suzuki et al. (*3*) at 313.2 and 333.2 K; (—) calculated results by the Peng–Robinson equation of state.

$$\phi_i^{V} p y_i = \phi_i^{L} p x_i \tag{1}$$

where p is the equilibrium pressure and x_i and y_i are the mole fractions of component i in the liquid phase and vapor phase, respectively. In order to evaluate ϕ_i, the Peng–Robinson equation of state (*4*) was used

$$p = \frac{RT}{v - b} - \frac{a}{v(v + b) + b(v - b)} \tag{2}$$

and conventional mixing rules for the constants a and b were used

$$a_m = \sum_i \sum_j y_i y_j a_{ij}, \quad a_{ij} = (1 - k_{ij})\sqrt{a_i a_j} \tag{3}$$

$$b_m = \sum_i \sum_j y_i y_j b_{ij}, \quad b_{ij} = (1 - l_{ij})\frac{b_i + b_j}{2} \tag{4}$$

where k_{ij} and l_{ij} are interaction parameters between unlike molecules i and j. When eqs 2–4 are used, the fugacity coefficient ϕ_i can be thermodynamically derived. The vapor–liquid equilibria were calculated by using the properties of pure components listed in Table 2. The properties of linalool were not available in the literature, so these were estimated by the method of Lydersen and Edmister (*5*), which is group contribution method. The interaction parameters k_{ij} and l_{ij} are treated as fitting parameters. The parameter estimation was performed at each temperature by minimizing the following objective function:

Table 2. Critical Constants and Acentric Factor

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

[a] Reference 5. [b] Estimated by the Lydersen method (*5*). [c] Estimated by the Edmister method (*5*).

Table 3. Interaction Parameters for CO_2 (1) + Linalool (2)

T/K	k_{ij}	l_{ij}	AAD(x)[a]	AAD(y)[b]
313.2	0.053	−0.035	0.0131	0.0001
323.2	0.046	−0.038	0.0151	0.0005
333.2	0.051	−0.027	0.0039	0.0006

[a] $\mathrm{AAD}(x) = (1/N_x)\sum|x_1(\mathrm{calc}) - x_1|$, where N_x is the number of data for the liquid phase. [b] $\mathrm{AAD}(y) = (1/N_y)\sum|y_1(\mathrm{calc}) - y_1|$, where N_y is the number of data for the vapor phase.

$$\mathrm{OF} = \frac{\sum^{N_x}|x_1(calc) - x_1|}{N_x} + \frac{\sum^{N_y}|y_1(calc) - y_1|}{N_y} \qquad (5)$$

where calc means calculated results and N_x and N_y are the number of data for the liquid phase and vapor phase, respectively. The calculated interaction parameters are listed in Table 3. The correlation results for CO_2 + linalool are shown in Figure 4. The present data were well correlated with the Peng–Robinson equation of state.

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