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

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A circulation-type apparatus was used to measure the high-pressure vapor-liquid equilibria for carbon dioxide + limonene at 313.2 K from (3.93 to 7.87) MPa, at 323.2 K from (3.94 to 9.27) MPa, and at 333.2 K from (4.99 to 10.26) MPa. 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 to extract flavors. Steam distillation or solvent extraction are 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 residue. So, supercritical fluid extraction can be considered as an alternative process for refining citrus oil because of its advantage of low operating temperature and no solvent residue.

Limonene is the principal compound of citrus oil. It makes up approximately 90 wt % of citrul oil but does not contribute much to the flavor or fragrance of citrus oil. Limonene is an unsaturated terpene hydrocarbon which is unstable to heat, light, and oxygen. So, it is common industrial practice to remove some of the limonene and terpenes to concentrate the oxygenated compounds, which makes the characteristic flavor or fragrance of citrus oil, such as linalool in citrus oil. For this purpose, the vapor−liquid equilibria for the mixture of CO_2, limonene, and linalool are required. The vapor−liquid equilibria for CO_2 + linalool were measured and reported in previous work (Iwai et al., 1994). In this work, the vapor−liquid equilibria for CO_2 + limonene were measured at (313.2, 323.2, and 333.2) K up to the critical region of the mixture by using a circulation-type apparatus. The structure of limonene 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.

Experimental Section

Equipment and Procedure. A circulation-type apparatus was used to measure high-pressure vapor−liquid equilibria. A detailed description of the equipment and operating procedures is given in a previous work (Iwai et al., 1994). Carbon dioxide and limonene were fed into an equilibrium cell. An impeller was used to promote the equilibrium condition. The volume of the cell is 500 cm³. After equilibrium (about 1 h), stirring by the impeller was stopped and circulation of the vapor and liquid phases was started by magnetic pumps. A small amount of each phase was introduced into sampling loops. The volume of the vapor sampling loop was about 15 cm³ and that of the liquid sampling loop was 3 cm³. After circulation for about 30 min, the sampling loops were isolated from the equilibrium cell by switching valves. The samples in the loops were decompressed through expansion valves and then intro-
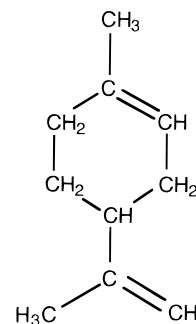
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Figure 1. Structure of limonene (4-isopropenyl-1-methyl-1-cyclohexene), $C_{10}H_{16}$, molecular weight = 136.2, boiling point = 176 °C.

Table 1. Vapor−Liquid Equilibria for CO_2 (1) + Limonene (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
3.94	0.3847		3.94	0.2873	0.9982	4.99	0.3401	0.9973
5.97	0.5805	0.9989	6.02	0.4541	0.9980	6.97	0.4812	0.9975
6.93	0.7004	0.9985	7.97	0.6650	0.9973	8.82	0.6415	0.9962
7.53	0.8025	0.9974	8.94	0.7744	0.9958	9.73	0.7109	0.9944
7.87	0.8871	0.9969	9.27	0.8338	0.9922	10.26	0.7696	0.9922

duced into cold traps, in which CO_2 and limonene were separated. The amount of CO_2 was measured by dry test meters. The amount of limonene was determined by means of gas chromatography. The pressure was measured by a Bourdon gauge, which had an accuracy of ±0.15% full scale. The equilibrium temperature was measured by a chromela-lumel thermocouple within ±0.1 K.

Materials. Limonene (supplied by Aldrich Chemical Co., Inc.) was used without further purification. The purity of limonene is 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.

Results and Discussion

The values listed in Table 1 were obtained from an arithmetic average of several measurements at each pressure. The standard deviations are less than 4.04×10^{-4} in the vapor phase and 8.24×10^{-3} in the liquid phase mole fraction. The values at 323.2 K are in good agreement with literature values (Matos et al., 1989) in the critical region of the mixture, as shown in Figure 2.

Correlation

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

Figure 2. Vapor−liquid equilibria for CO_2 (1) + limonene (2): ($\triangle$, $\diamondsuit$, $\bigcirc$) present data at 313.2, 323.2, and 333.2 K; ($\blacklozenge$) literature data at 323.2 K (Matos et al., 1989); (—) calculated results by Peng−Robinson EOS with $k_{12} = 0.09$, $l_{12} = -0.04$ at 323.2 and 333.2 K, $k_{12} = 0.09$, $l_{12} = -0.02$ at 313.2 K.

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

where p is the equilibrium pressure and x_i and y_i are the mole fractions of the ith component in the liquid phase and vapor phase, respectively. In order to evaluate ϕ_i, the Peng−Robinson equation of state (Peng and Robinson, 1976) 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:

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

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

where k_{ij} and l_{ij} are the 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

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]
limonene	662.6[b]	2.75[b]	0.310[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).

properties of pure components listed in Table 2. The properties of limonene were not available in the literature, so these were estimated by the methods of Lydersen and Edmister (Reid et al., 1977), which were group contribution methods. 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:

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

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 correlation results for CO_2 + limonene are shown in Figure 2. The present data were well correlated by the Peng−Robinson equation of state.

Literature Cited

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