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Volumetric Behavior and Saturated Pressure for Carbon Dioxide + Ethyl Acetate at a Temperature of 313.15 K

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Volumetric property was measured for carbon dioxide + ethyl acetate at $T = 313.15$ K and pressures to 10 MPa. Saturated pressure was also measured by the synthetic method. The experimental data obtained were correlated with various equations of state.

Introduction

Fish oil ethyl esters are derived from esterification with ethanol. The separation and fractionation of eicosapentaenoic acid from fish oil with supercritical carbon dioxide have been studied by others.[1,2] The volumetric properties and vapor−liquid equilibria (VLE) for (carbon dioxide + ethyl acetate) are required to design the separation equipment.[3]

For (carbon dioxide + ethyl acetate), VLE were reported by Wagner and Pavliček.,[4] Chrisochoou et al.,[5] and da Silva et al.[6] at $T = 313.15$ K, however, with big differences between them. However, ref 4, 5 and 6 do not report volumetric data. Smith et al.[3] have reported the volumetric behavior of (carbon dioxide + ethyl acetate) at $T = 313.2$ K, using the flow apparatus.

In the present study, the volumetric properties were measured in the homogeneous region for (carbon dioxide + ethyl acetate) at $T = 313.15$ K. The saturated pressure was also measured by the synthetic method.

Experimental Sections

Materials. The carbon dioxide was supplied by Showa Tansan Co. Ltd. with a mole fraction purity stated by them of 0.99999. Ethyl acetate was supplied by Wako Pure Chemicals Co. Ltd. It was used without further purification. Gas chromatograph analysis gave a mole fraction purity > 0.999. The physical properties of ethyl acetate used in this work are listed in Table 1.

Table 1. Physical Properties of Material Used

	T_b/K		ρ(298.15 K)/kg·m^{-3}		n_D/(298.15 K)	
material	exptl	lit[a]	exptl	lit[b]	exptl	lit[a]
ethyl acetate	350.21	350.21	894.4	894.46	1.3702	1.3704

[a] TRC Thermodynamic Table Non-Hydrocarbons.[14] [b] Timmermans.[15]

Apparatus and Procedure. The experimental apparatus is schematically shown in Figure 1. The apparatus is the same as that described previously.[7−10] The maximum operating temperature and pressure of the apparatus are 400 K and 20 MPa, respectively. The main parts of the apparatus are a variable volume cell, A; piston, P; Ruska 2465-752 and Ruska 2470-703 air lubricated dead weight gauge, N; Ruska 2480-700 oil dead weight gauge, O; hand pump syringe, S; Anton Paar DMA 512P density meters, D; circulation pumps, C; gas reservoir, F; and Ruska 2439-702 pressure transducers, T. The apparatus is housed in a constant temperature liquid bath E controlled to a temperature to about ± 0.01 K. Temperatures were measured with the Hewlett-Packard 2804A quartz thermometer. The volume of the lower portion of the cell could be varied between (78 and 134) cm^3 by moving a piston, which gave a volume uncertainty of ± 0.01 cm^3. The accuracy with which the total volume is known is about ± 1 cm^3.

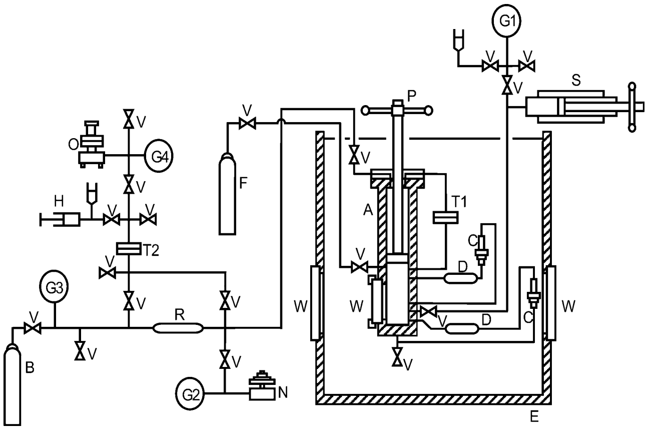

Figure 1. Schematic diagram of experimental apparatus: A, variable volume cell; B, nitrogen reservoir; C, circulation pump; D, density meter; E, constant temperature liquid bath; F, gas reservoir; G, pressure gauge; H, hand pump; N, air dead weight gauge; O, oil dead weight gauge; P, piston; R, reservoir; S, hand syringe pump; T, pressure transducer; V, valve; W, visual glass window.

First, the cell is evacuated and then filled with carbon dioxide. The pressure difference between the upper and lower spaces is kept close to zero. The temperature and pressure are measured. The volume is determined by the motion of the piston. The amount of carbon dioxide is determined from the volume and density. The volume of ethyl acetate is charged into the cell with the syringe pump S with an uncertainty ± 0.01 cm^3. As the volume of cell A is changed, the volumetric properties of the mixture can be measured at a fixed and known composition. The discontinuity of the pressure as a function of cell volume, as shown in Figure 2, is used as the determinant of the saturation pressure. The saturated densities of the vapor and liquid were

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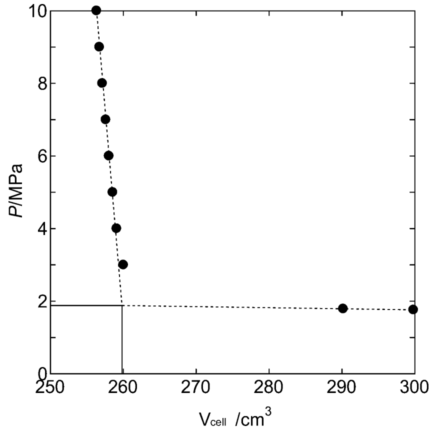

Figure 2. Typical example of experimental results by synthetic method, 0.300 CO_2 mole fraction: ●, experimental.

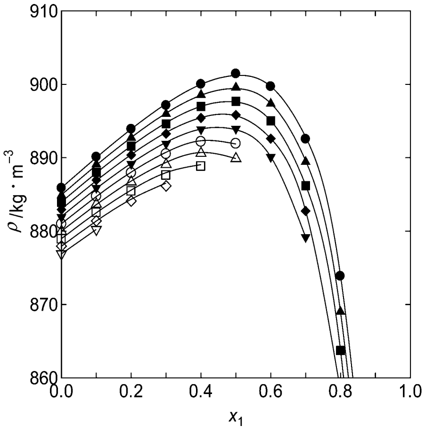

Figure 3. Experimental and correlatd densities for carbon dioxide (1) + ethyl acetate (2) at 313.15 K: ●, 10 MPa; ▲, 9 MPa; ■, 8 MPa; ◆, 7 MPa; ▼, 6 MPa; ○, 5 MPa; △, 4 MPa; □, 3 MPa; ◇, 2 MPa; ▽, 1 MPa; —, eqs 1 to 14.

measured at fixed pressures, while maintaining the VLE separation in the cell.

Results and Discussion

The experimental densities of fixed compositions for (carbon dioxide + ethyl acetate) at $T = 313.15$ K are shown in Table 2, and Figures 3 and 4 show the average difference of 0.1 % between our results and those reported by Smith et al.[3] The experimental saturated pressures and densities are listed in Table 3, and Figure 5 shows the experimental saturated density of vapor and liquid phases at equilibria. Figure 6 shows the pressure−composition diagram for (carbon dioxide + ethyl acetate) at $T = 313.15$ K, including the experimental data and the ones in the literature. As shown in Figure 6, large differences exist between the three set of results from the literature. The data given by Chrisochoou et al.[5] agree well with the present experimental ones as shown in Figure 6, giving the average difference in equilibrium liquid composition mole fraction of 0.012. The previous data reported by Wagner and Pavliček[4] and da Silva et al.[6] are inconsistent with the our experimental results, as shown in Figure 6.

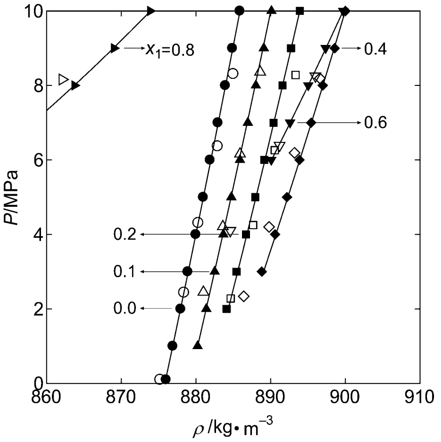

Figure 4. Volumetric property for carbon dioxide (1) + ethyl acetate (2) at 313.15 K: <experimental> this work: ●, $x_1 = 0.0$; ▲, 0.1; ■, 0.2; ◆, 0.4; ▼, 0.6; solid triangle pointing right, 0.8, Smith et al.;[3] ○, $x_1 = 0.0$; △, 0.1; □, 0.2; ◇, 0.4; ▽, 0.6; open triangle pointing right, 0.8, <correlated>; —, eqs 1 to 14.

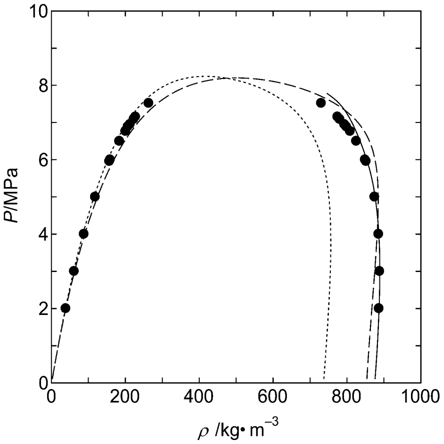

Figure 5. Saturated density behaviors of carbon dioxide (1) + ethyl acetate (2) at 313.15 K: ●, this work; —, eqs 1 to 14; − −, pseudocubic EOS ($k_{ij} = 0.0838$); - - -, SRK EOS ($k_{ij} = -0.0028$).

Table 2. Experimental Density ρ, Mole Fraction x, and Pressure P for Carbon Dioxide (1) + Ethyl Acetate (2) at 313.15 K

	ρ/kg·m^{-3} at P/MPa									
x_1	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10.0
0.000	876.9	878.0	878.9	880.0	881.0	881.9	882.9	883.9	884.9	885.9
0.100	880.2	881.4	882.5	883.7	884.7	885.9	887.0	888.0	889.1	890.1
0.200		884.1	885.4	886.7	887.9	889.2	890.4	891.6	892.7	893.9
0.300		886.2	887.6	889.1	890.5	891.9	893.3	894.6	896.0	897.2
0.400			888.8	890.6	892.2	893.9	895.4	897.0	898.6	900.0
0.500				889.9	891.9	893.9	895.8	897.7	899.6	901.4
0.600						890.1	892.6	895.0	897.4	899.7
0.700						879.2	882.7	886.2	889.4	892.5
0.800							858.2	863.7	869.0	873.9
0.900								800.6	813.0	823.7
0.950									745.6	767.4
1.000	17.8	37.3	58.6	83.4	112.5	148.7	197.5	276.7	482.6	627.3

Table 3. Saturation Pressure P, Liquid Mole Fraction x, Liquid Density ρ_L, and Vapor Density ρ_V for Carbon Dioxide (1) + Ethyl Acetate (2) at 313.15 K

P/MPa	x_1	ρ_L/kg·m^{-3}	ρ_V/kg·m^{-3}
0.629	0.100[a]		
1.226	0.200[a]		
1.881	0.300[a]		
2.000		886.7[b]	38.8[b]
2.551	0.400[a]		
3.000		888.3[b]	61.6[b]
3.338	0.500[a]		
4.000		885.7[b]	88.2[b]
4.146	0.600[a]		
5.000		874.8[b]	118.6[b]
5.038	0.700[a]		
5.959		851.7[b]	156.9[b]
6.000		849.1[b]	159.0[b]
6.031	0.800[a]		
6.500		825.3[b]	184.0[b]
6.766		808.6[b]	200.7[b]
6.888		798.4[b]	206.9[b]
6.953		792.9[b]	212.9[b]
7.089		780.4[b]	223.0[b]
7.153		774.5[b]	227.6[b]
7.220	0.900[a]		
7.520		730.4[b]	263.1[b]
7.788	0.950[a]		

[a] Synthetic method. [b] VLE separation.

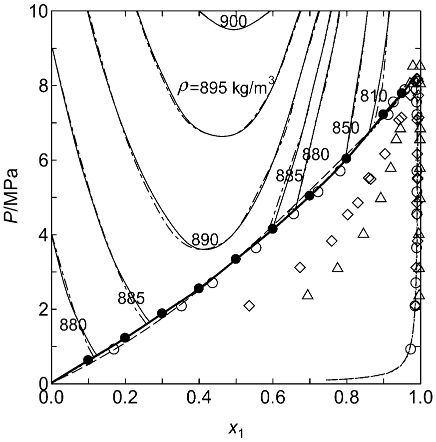

Figure 6. VLE and density curves for carbon dioxide (1) + ethyl acetate (2) at 313.15 K: —●—, —, this work; ◇, Wagner and Pavliček;[4] ○, Chrisochoou et al.;[5] △, da Silva et al.;[6] — • —, eqs 1 to 14; — —, pseudocubic EOS (k_{ij} = 0.0838); - - -, SRK EOS (k_{ij} = −0.0028).

Correlation

The experimental volumetric data were correlated with the Tait equation as follows:

$$\rho = \rho^{\text{ref}}\left\{1 - c\ln\frac{\beta + P}{\beta + P^{\text{ref}}}\right\}^{-1} \tag{1}$$

where ρ^{ref} and P^{ref} are the reference density and pressure and c and β are fitting parameters. In the present study, the reference state was given at P = 10 MPa:

$$P^{\text{ref}} = 10 \times 10^6\,\text{Pa} \tag{2}$$

The reference densities ρ^{ref} at P = 10 MPa in Table 2 were correlated as follows:

$$\rho^{\text{ref}} = \rho_0^{\text{ref}} + mx_1\frac{1 + \kappa_1 x_1 + \kappa_2 x_1^{\,2}}{1 + \tau_1 x_1 + \tau_2 x_1^{\,2}} \tag{3}$$

where x_1 is the mole fraction of carbon dioxide:

$$\rho_0^{\text{ref}} = 885.9\ \text{kg/m}^3 \tag{4}$$

$$m = 41.85 \tag{5}$$

$$\kappa_1 = -1.528 \tag{6}$$

$$\kappa_2 = 0.256 \tag{7}$$

$$\tau_1 = -1.404 \tag{8}$$

$$\tau_2 = 0.448 \tag{9}$$

The parameters c and β were correlated by

$$c = 0.0885 \tag{10}$$

$$\ln\beta = A + \frac{B}{x_1 + C} \tag{11}$$

where

$$A = 5.104 \tag{12}$$

$$B = 0.8801 \tag{13}$$

$$C = -1.066 \tag{14}$$

The calculation results with eqs 1 to 14 were shown in Figures 3 to 6, giving an average difference of 0.01 % for our experimental density data in the composition mole fraction of carbon dioxide range between 0.0 and 0.8

The experimental saturated data obtained were correlated with the conventional SRK equation of state[11] and pseudocubic equation of state. The pseudocubic equation of state[12] is expressed as follows:

$$P = \frac{RT}{v^* - b} - \frac{a}{v^{*2}} \tag{15}$$

$$v^* = \frac{(v - \epsilon b)(v + \sigma b)}{v} \tag{16}$$

$$\epsilon = (1 - \theta)(\xi - 2) \tag{17}$$

$$\sigma = (1 - \theta)(\xi + 2) \tag{18}$$

$$\xi = \sqrt{\frac{4 - \theta}{1 - \theta}} \tag{19}$$

$$\theta = \frac{8Z_c}{3} \tag{20}$$

$$Z_c = \frac{P_c v_c}{RT_c} \tag{21}$$

$$a = K_a a_c \tag{22}$$

$$b = \frac{RT_c}{8P_c} \tag{23}$$

$$a_c = \frac{27(RT_c)^2}{64P_c} \tag{24}$$

$$\ln K_a = S(1 - \sqrt{T_r}) \tag{25}$$

and

$$S = 1.1746 + 3.4539\omega \tag{26}$$

where P, R, T, v, Z, and ω, respectively, denote the pressure, gas constant, temperature, molar volume, compressibility factor, and acentric factor. K_a, S, a, b, ϵ, θ, σ, and ξ represent the parameters. The subscripts c and r denote the critical properties and reduced properties, respectively. The asterisk indicates the apparent value.

The following mixing rules were used, introducing binary interaction parameter k_{ij}:

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad b = \sum_i \sum_j x_i x_j b_{ij} \quad \theta = \sum_i x_i \theta_i \qquad (27)$$

$$a_{ij} = (1 - k_{ij})\sqrt{a_i a_j} \quad \text{and} \quad b_{ij} = \frac{b_i + b_j}{2} \qquad (28)$$

where x is the mole fraction. The subscripts i and j denote the components.

The binary interaction parameter k_{ij} was found to be 0.0838 from our experimental bubble point-pressure data in the lower pressure regions. In this correlation, the critical properties and acentric factors for carbon dioxide and ethyl acetate were obtained from ref 13.

The values obtained from the equations of state are shown in Figures 5 and 6. In Figures 5, the solid, dotted, and broken lines, respectively, denote the values obtained from the Tait equation, the values obtained from the SRK equation, and those from the pseudocubic equation. The solid line in Figure 5 was calculated by eqs 1 to 14, giving the experimental saturated pressure and composition in Table 3. The solid line shows the excellent agreement with the experimental saturated liquid densities at pressures lower than 6 MPa. At pressures higher than 6 MPa in Figure 5, the solid line deviates from the experimental ones, as the saturated composition mole fraction of carbon dioxide is greater than 0.8. The Tait equation (eq 1) is useful for liquid but cannot be applied for gas. At the composition mole fraction of carbon dioxide greater than 0.8, the fluid is far from liquid. Figure 6 shows the VLE and density curves.

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