High-Pressure Phase Equilibrium for Ethylene + 2-Propanol at 283.65 K

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The phase equilibria and saturated density for the ethylene + 2-propanol system at high pressures were measured at 283.65 K with a static-circulation apparatus. The experimental apparatus equipped with three Anton Paar DMA 512S vibrating tube density meters was previously developed to measure vapor−liquid−liquid equilibrium at high pressures. The coexisting phase composition and saturated density of each phase can be measured by means of the apparatus with a maximum temperature and pressure of 400 K and 20 MPa, respectively. The equilibrium composition and saturated density of each phase were determined by gas chromatography and vibrating-tube density meters, respectively. The experimental data were correlated with various equations of state.

Introduction

In an industrial process, alcohol can be produced from the hydration of alkenes. However, phase equilibrium properties at low temperatures are not available in the literature for the ethylene + 2-propanol system.

A static-circulation apparatus[1] equipped with three density meters for measuring vapor−liquid−liquid equilibria (VLLE) at high pressures was previously used for various systems. With this apparatus, vapor−liquid equilibria (VLE) and their saturated densities were reported for the ethylene + 1-propanol[1] and the ethylene + ethanol[2] systems have been recently measured, including VLLE.

In the present study, the coexisting phase compositions and their saturated densities for the ethylene + 2-propanol mixture at high pressure were measured at 283.65 K including the vicinity of the critical region. The phase equilibrium data are correlated with the Soave−Redlich−Kwong (SRK) equation of state (EOS)[3] and pseudocubic equation of state.[4]

Experimental Sections

Materials. In the present experiments, ethylene was supplied by Takachiho Chemical Industry Co. Ltd. with a guarantee of 99.9 % purity. 2-Propanol was a special-grade reagent of Wako Pure Chemical Industries Ltd. and was used without further purification. The purity of 2-propanol was more than 99.9 mol % by gas chromatographic area analysis.

Apparatus and Procedure. The schematic diagram of experimental apparatus[1] is shown in Figure 1. The apparatus is a static-circulation type that can operate to a maximum temperature and pressure of 400 K and 20 MPa, respectively, and has three Anton Paar DMA 512S vibrating-tube density meters. The vibrating-tube density meters have been calibrated by dry air and water. The apparatus is in a constant-temperature liquid bath controlled within ± 0.01 K. The cell volume is approximately 320 cm^3. The coexisting phases are continuously recirculated through the sampling valves and density meters with the three magnetic circulation pumps. Temperatures were measured by means of the Hewlett-Packard 2804A quartz thermometer. Pressures were measured by means of a Ruska 2480-700 oil dead-weight gauge and the Ruska 2439-702 pressure transducer. The equilibrium phase compositions were determined by using a Shimadzu GC-14A gas chromatograph equipped with a 3-m Porapak Q column. Helium was used as a carrier gas at a flow rate of 50 $\text{cm}^3\cdot\text{min}^{-1}$. The column temperature was about 403 K. The injector and detector temperatures were about 423 K. The current value of a thermal conductivity detector (TCD) was 100 mA.

The cell was evacuated and then charged with the samples of ethylene and 2-propanol. The fluid in the cell was mixed by means of the magnetic-driven agitator. Each phase was circulated through the circulation pump. After the steady state was established for 3 h, the agitator and circulation pumps were stopped. After 1 h, the densities and the pressure were measured by means of the density meters and dead-weight gauge, respectively. The sample of each phase was taken by the sampling valve and analyzed by gas chromatography after a circulation of 3 h in the sampling room. The uncertainties of the experimental equilibrium composition, density, temperature, and pressure are ± 0.001 mole fraction, ± 0.1 $\text{kg}\cdot\text{m}^{-3}$, ± 0.1 K, and ± 1 kPa, respectively.

Results and Discussion

Table 1 gives all of the experimental results of coexisting phase compositions and their saturated densities for the ethylene + 2-propanol system at 283.65 K.

Figures 2 and 3 give the experimental pressure composition and their saturated density diagrams, respectively. In Figures 2 and 3, the solid lines were smoothly drawn for the present experimental data obtained. As shown in Figure 2, the experimental saturated liquid line gave S-shape behavior near the $x = 1$ region. However, the

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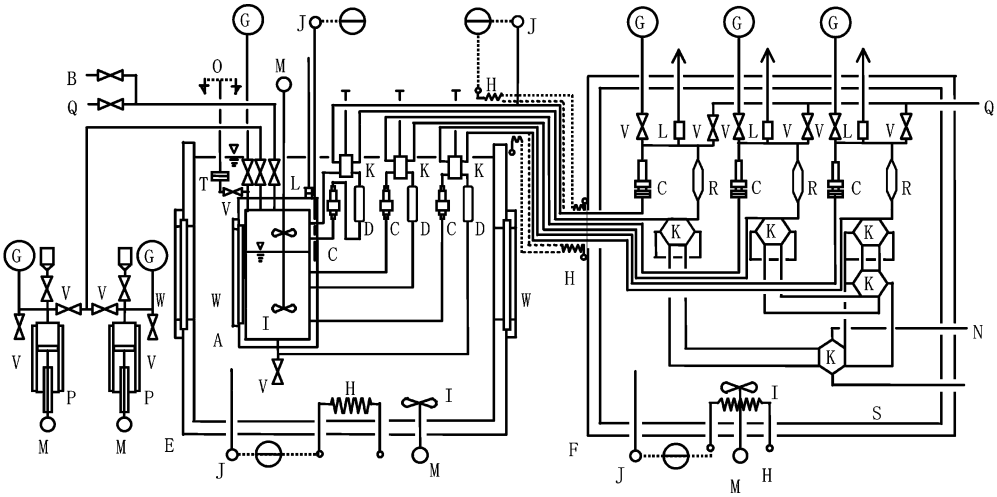

Figure 1. Schematic diagram of experimental apparatus: A, equilibrium cell; B, to sample reservoir; C, circulation pump; D, density meter; E, constant temperature liquid bath; F, constant temperature air bath; G, pressure gauge; H, heater; I, agitator; J, thermometer; K, sampling valve; L, safety valve; M, motor; N, to gas chromatograph; O, to oil dead weight gauge; P, sample charging pump; Q, to vacuum pump; R, surge tank; S, sampling system; T, pressure transducer; V, valve; W, visual glass window.

Table 1. Saturation Pressure (*P*), Liquid Mole Fraction (*x*), Vapor Mole Fraction (*y*), Liquid Density (ρ_L), and Vapor Density (ρ_V) for Ethylene (1) + 2-Propanol (2) at 283.65 K

P/MPa	x_1	y_1	ρ_L/(kg·m^{-3})	ρ_V/(kg·m^{-3})
2.227	0.215	0.996	736.8	32.5
3.047	0.308	0.989	706.7	49.1
3.578	0.382	0.991	680.7	62.7
4.115	0.476	0.992	643.5	80.6
4.699	0.707	0.997	531.5	109.1
4.938	0.956	0.996	347.0	133.9
5.029	0.986	0.997	302.6	152.6

possibility of vapor−liquid−liquid separation was not estimated by our experience for the present system, observing the present experimental results given by Figures 2 and 3 at 283.65 K.

Correlation

The experimental data obtained were correlated with the conventional SRK equation of state[3] and the pseudocubic equation of state.[4]

The pseudocubic equation of state[4] is expressed as follows:

$$P = \frac{RT}{v^* - b} - \frac{a}{v^{*2}} \qquad v^* = \frac{(v - \epsilon b)(v + \sigma b)}{v} \tag{1}$$

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

$$\xi = \sqrt{\frac{4 - \theta}{1 - \theta}} \qquad \theta = \frac{8Z_c}{3} \qquad Z_c = \frac{P_c v_c}{RT_c} \tag{3}$$

$$a = K_a a_c \qquad b = \frac{RT_c}{8P_c} \qquad a_c = \frac{27(RT_c)^2}{64P_c} \tag{4}$$

$$\ln K_a = S(1 - \sqrt{T_r}) \qquad S = 1.1746 + 3.4539\omega \tag{5}$$

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

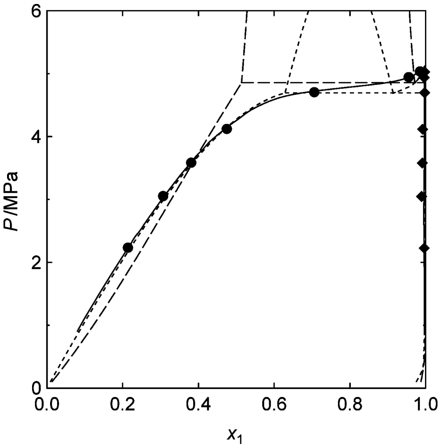

Figure 2. Phase equilibria for the ethylene (1) + 2-propanol (2) system at 283.65 K: −◆−, vapor; −●−, liquid; − −, pseudocubic EOS (k_{ij} = 0.0983); - - -, SRK EOS (k_{ij} = 0.0379).

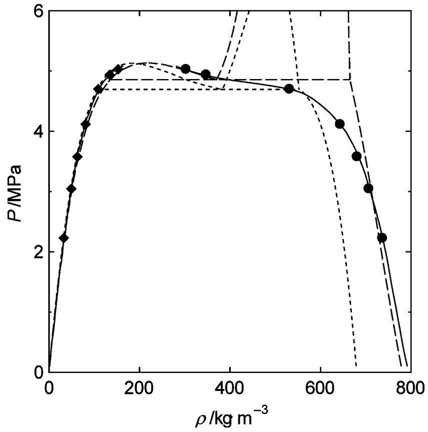

Figure 3. Saturated densities for the ethylene (1) + 2-propanol (2) system at 283.65 K: −◆−, vapor; −●−, liquid; − −, pseudocubic EOS (k_{ij} = 0.0983); - - -, SRK EOS (k_{ij} = 0.0379).

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

$$a = \sum_i \sum_j x_i x_j a_{ij} \qquad b = \sum_i \sum_j x_i x_j b_{ij} \qquad \theta = \sum_i x_i \theta_i \tag{6}$$

$$a_{ij} = (1 - k_{ij})\sqrt{a_i a_j} \quad b_{ij} = \frac{b_i + b_j}{2} \tag{7}$$

where x represents the mole fraction, and subscripts i and j denote the components.

The binary interaction parameter k_{ij} was evaluated to be 0.0983 from the present experimental bubble point-pressure data in the lower pressure regions. In the correlations, the critical values and acentric factors of ethylene and 2-propanol were obtained from ref 5.

Calculation results with the equations of state are shown in Figures 2 and 3. In Figures 2 and 3, the solid, dotted, and broken lines denote the smoothed experimental data, the calculation results by the SRK equation, and the calculation results by the pseudocubic equation, respectively. In Figures 2 and 3, the horizontal lines denote the VLLE separation ranges calculated with equations of state. The correlation results with equations of state were not satisfactory as shown in Figures 2 and 3.

Conclusions

Phase equilibria and saturated densities for ethylene + 2-propanol at high pressures were measured at 283.65 K with a static-circulation apparatus.[1] The experimental data obtained were correlated by the equations of state.

Literature Cited

(1) Kodama, D.; Miyazaki, J.; Kato, M.; Sako, T. High-pressure phase equilibrium for ethylene + 1-propanol system at 283.65 K. *Fluid Phase Equilib.* **2004**, *219*, 19−23.

(2) Kodama, D.; Sato, R.; Haneda, A.; Kato, M. High-pressure phase equilibrium for ethylene + ethanol at 283.65 K. *J. Chem. Eng. Data* **2005**, *50*, 122−124.

(3) Soave, G. Equilibrium constants from a modified Redlich−Kwong equation of state. *Chem. Eng. Sci.* **1972**, *27*, 1197−1203.

(4) Kato, M.; Tanaka, H. A new three-parameter pseudo-cubic equation of state. *Adv. Cryog. Eng.* **1986**, *31*, 1169−1179.

(5) Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P. *The Properties of Gases and Liquids*, 5th ed.; McGraw-Hill: New York, 2001.

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