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High-Pressure Phase Equilibrium for Ethylene + Ethanol at 283.65 K

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The phase equilibria and saturated density for the ethylene + ethanol 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 equilibria 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 present experimental results include vapor−liquid, liquid−liquid, and vapor−liquid−liquid equilibria. 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

Phase equilibria such as vapor−liquid equilibria (VLE), liquid−liquid equilibria (LLE), and vapor−liquid−liquid equilibria (VLLE) are essential to the design and operation of distillation equipment.

High-pressure multiphase behavior is also important in the development of new and highly efficient separation techniques in the natural gas, oil, and petrochemical industries. In the industrial process, alcohol is produced from the hydration of alkenes. With a static-circulation apparatus equipped with three density meters, the phase-equilibrium properties of ethylene + 1-propanol[1] have been recently measured, including VLLE. The saturated points near the critical region are further measured by the conventional indirect method.

For the ethylene + ethanol system, Ellis et al.[2] reported VLE at 348 K. Tsiklis and Kofman[3] gave VLE and saturated densities between 423 and 493 K in thick-walled glass tubes. Narasimhan et al.[4] measured solubilities at 293 and 298 K. Gupta et al.[5] measured the saturated vapor behavior at 298, 323, and 348 K. However, no data for the ethylene + ethanol system are available at temperatures lower than 293 K.

In the present study, the coexisting phase compositions and their saturated densities for the ethylene + ethanol mixture at high pressure were measured at 283.65 K including the vicinity of the critical region. The experimental data obtained were correlated with the Soave−Redlich−Kwong (SRK) equation of state[6] and the pseudocubic equation of state.[7]

Experimental Section

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

Apparatus and Procedures. The apparatus and experimental procedures are the same as described previously. The apparatus is a static-circulation type[5] 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 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 the 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 the thermal conductivity detector (TCD) was 100 mA.

The cell was evacuated and then charged with the samples, ethylene and ethanol. 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. The uncertainty represents the difference between the experimental value and the absolute real value. The reproducibility of VLLE was within 0.001 mole fraction at the same pressure.

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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) + Ethanol (2) at 283.65 K

P/MPa	x_1	y_1	ρ_L/kg·m^{-3}	ρ_V/kg·m^{-3}
1.243^a	0.101^a	0.991^a	767.8^a	17.5^a
2.173^a	0.178^a	0.991^a	741.9^a	31.2^a
3.071^a	0.268^a	0.991^a	708.7^a	49.0^a
4.099^a	0.408^a	0.990^a	661.3^a	78.8^a
4.668^a	0.512^a	0.995^a	614.1^a	106.8^a
4.919^a	0.614^a	0.995^a	564.2^a	130.6^a
4.956^b	0.667^b, 0.938^b	0.997^b	543.4^b, 377.6^b	134.4^b
4.973^a	0.940^a	0.992^a	347.3^a	138.6^a
5.040^a	0.989^a	0.996^a	295.1^a	154.9^a
5.082^c	0.685^c, 0.892^c		529.3^c, 385.6^c	
5.267^c	0.712^c, 0.862^c		503.5^c, 410.0^c	

^{a} Vapor–liquid equilibria. ^{b} Vapor–liquid–liquid equilibria. ^{c} Liquid–liquid equilibria.

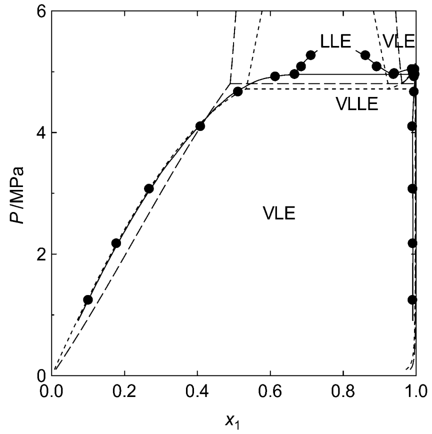

Figure 1. Phase equilibria for the ethylene (1) + ethanol (2) system at 283.65 K: –●–, this work; – – –, pseudocubic EOS (k_{ij} = 0.0499); - - -, SRK EOS (k_{ij} = −0.0057).

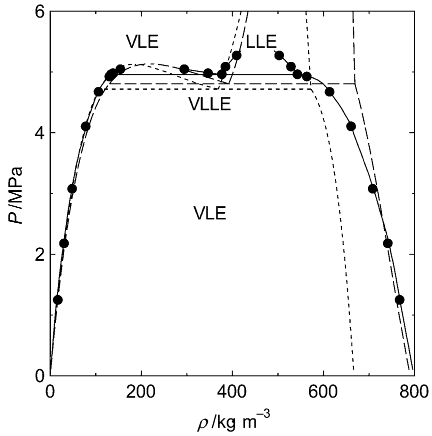

Figure 2. Saturated densities for the ethylene (1) + ethanol (2) system at 283.65 K: –●–, this work; – – –, pseudocubic EOS (k_{ij} = 0.0499); - - -, SRK EOS (k_{ij} = −0.0057).

Results and Discussion

Table 1 gives all of the experimental results of coexisting phase compositions and their saturated densities by the direct method for the ethylene + ethanol system at 283.65 K. The VLLE phase separation was observed at 4.956 MPa, as shown in Table 1.

Figures 1 and 2 give the experimental pressure–composition and their saturated density diagrams. Figure 3 shows the expanded phase-equilibrium diagram in the vicinity of the critical region. Figure 4 shows the expanded saturated-density diagram. In Figures 1 to 4, the solid lines were smoothly drawn for the present experimental data obtained.

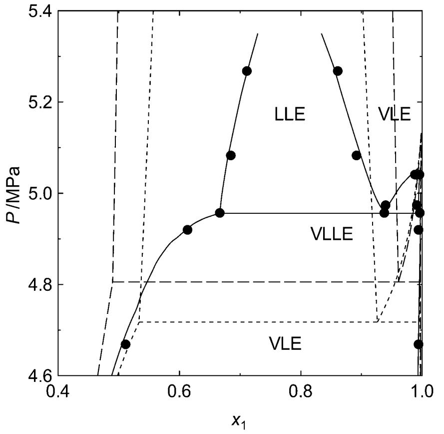

Figure 3. Expanded phase-equilibrium diagram for the ethylene (1) + ethanol (2) system at 283.65 K: –●–, this work; – – –, pseudocubic EOS (k_{ij} = 0.0499); - - -, SRK EOS (k_{ij} = −0.0057).

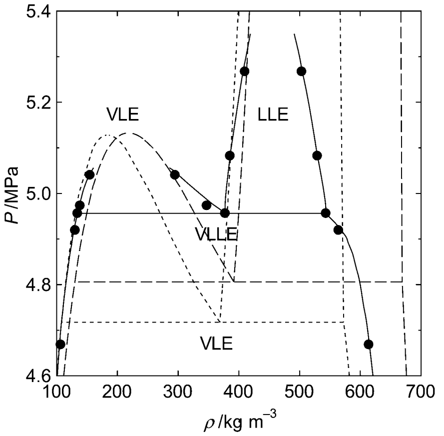

Figure 4. Expanded saturated densities for the ethylene (1) + ethanol (2) system at 283.65 K: –●–, this work; – – –, pseudocubic EOS (k_{ij} = 0.0499); - - -, SRK EOS (k_{ij} = −0.0057).

Correlation

The experimental data obtained were correlated with the conventional SRK equation of state[6] and the pseudocubic equation of state.[7]

The pseudocubic equation of state[7] 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.

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

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

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

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

The binary interaction parameter k_{ij} was evaluated to be 0.0499 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 ethanol were obtained from ref 8.

Calculation results with the equations of state are shown in Figures 1 to 4. In Figures 1 to 4, 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 1 to 4, the horizontal lines denote the VLLE separation ranges calculated with equations of state. As shown in Figures 1 to 4, the VLLE separations in the narrow composition ranges were calculated by the equations of state. The equation of state is generally applied to the VLE correlation, mainly for the pressure−composition behaviorrather than the saturated vapor and liquid density behavior.

Conclusions

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

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