High Pressure Phase Equilibrium for Ethane + 1-Propanol at 314.15 K

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Phase equilibria and saturated densities for ethane + 1-propanol at high pressures were measured at 314.15 K with a static-circulation apparatus. The experimental apparatus equipped with three Anton Paar DMA 512S vibrating tube density meters was previously developed for measuring vapor−liquid−liquid phase separation properties 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. For the above system, Suzuki et al. previously reported vapor−liquid equilibria. Lam et al. previously reported only vapor−liquid−liquid locus and their saturated density. There are considerable differences between the results of Suzuki et al. and those of Lam et al. The present experimental results include vapor−liquid equilibria, liquid−liquid equilibria, and vapor−liquid−liquid equilibria. The equilibrium composition and density of each phase were determined by gas chromatography and density measurements, respectively. The experimental data were correlated with various equations of state.

Introduction

Phase equilibrium properties of mixtures at high pressures are required for practical use such as in the design and operation of separation equipment in the petroleum, natural gas, and related industries. Supercritical fluid extraction is now attractive as a separation technology.

Suzuki et al.[1] previously reported vapor−liquid equilibria (VLE) for the ethane + 1-propanol system at high pressures with a conventional circulation apparatus. They, however, reported no density data. Lam et al.[2] previously reported only the vapor−liquid−liquid locus and their saturated density for the ethane + 1-propanol system at high pressures, based on mass balance and the phase rule.

A static-circulation apparatus equipped with three density meters for measuring vapor−liquid−liquid equilibria (VLLE) at high pressures was previously developed.[3] With this apparatus, VLE and their saturated densities were measured for carbon dioxide + ethanol[3] and carbon dioxide + 1-butanol[4] at high pressures. The phase equilibrium properties of ethane + methanol[5] and ethane + ethanol[6] have been recently measured, including VLLE.

In the present study, the coexisting phase compositions and their saturated densities for the ethane + 1-propanol mixture at high pressures were measured at 314.15 K, including in the vicinity of the critical region.

The phase equilibrium relations obtained in the present study are correlated with the Soave−Redlich−Kwong[7] (SRK) and pseudocubic[8] equations of state.

Experimental Section

Materials. Ethane was supplied by Takachiho Chemical Industry Co. Ltd. with the gas guarantee of 99.9% in purity. 1-Propanol was the special-grade reagent of Wako Pure Chemicals Co. Ltd. and was used without further purification. The purity of 1-propanol was determined to be 99.5% from gas chromatography peak areas.

Apparatus and Procedures. The apparatus and experimental procedures[3] are the same as described previously. The apparatus is a static-circulation type, which 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 with the Hewlett-Packard 2804A quartz thermometer. Pressures were measured with the Ruska 2480-700 oil dead weight gauge and the Ruska 2439-702 pressure transducer. The equilibrium phase compositions were determined by using a Shimazu GC-14A gas chromatograph equipped with a 3-m Porapak Q column. Helium was used as a carrier gas at a flow rate of 30 $cm^3\ min^{-1}$. The injection temperature and column temperature were about 373 K and 369 K, respectively. The current value of a thermal conductivity detector (TCD) was 100 mA.

The samples, ethane and 1-propanol, were charged into the cell after the evacuation of the cell. The fluid in the cell was mixed with the magnetic-driven agitator. Each phase was circulated through the circulation pump. After the steady state was established for 2 or 3 h, the agitator and circulation pumps were stopped. After 1 h, the densities and the pressure were measured with the density meters and the dead weight gauge, respectively. The sample of each phase was taken with the sampling valve and analyzed by gas chromatography after a circulation of 2 h in the sampling room.

Results and Discussion

Table 1 gives the experimental results of coexisting phase compositions and their saturated densities for the

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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 Ethane (1) + 1-Propanol (2) at 314.15 K

P/MPa	x_1	y_1	ρ_L/(kg·m^{-3})	ρ_V/(kg·m^{-3})
1.609[a]	0.134[a]	0.991[a]	750.8[a]	21.4[a]
3.317[a]	0.300[a]	0.993[a]	697.5[a]	54.1[a]
4.550[a]	0.457[a]	0.993[a]	639.1[a]	90.3[a]
5.487[a]	0.782[a]	0.975[a]	475.4[a]	184.2[a]
5.489[b]	0.799,[b] 0.903[b]	0.965[b]	450.2,[b] 367.1[b]	187.7[b]
5.507[a]	0.964[a]	0.985[a]	296.6[a]	203.6[a]
5.512[a]	0.982[a]	0.996[a]	275.7[a]	222.7[a]
5.519[c]	0.810,[c] 0.900[c]		451.3,[c] 374.3[c]	
5.537[c]	0.815,[c] 0.898[c]		448.1,[c] 383.5[c]	

[a] Vapor–liquid equilibria. [b] Vapor–liquid–liquid equilibria. [c] Liquid–liquid equilibria.

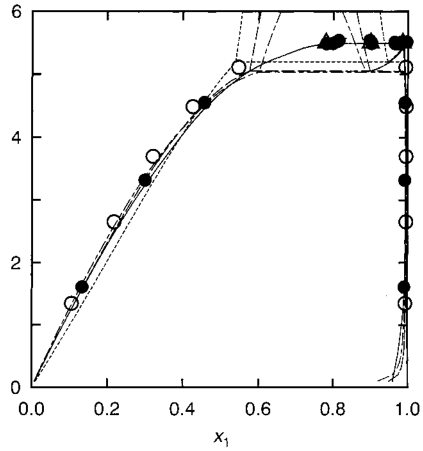

Figure 1. Phase equilibria for the ethane + 1-propanol system at 314.15 K: ●, this work; ○, literature data (Suzuki et al., 1990); △, literature data (Lam et al., 1990); — — —, pseudocubic EOS with two parameters ($k_{112} = -0.0146$, $k_{122} = -0.0475$); - - -, pseudocubic EOS with one parameter ($k_{12} = 0.0907$); — · —, SRK EOS ($k_{12} = 0.0425$).

ethane + 1-propanol system at 314.15 K. The VLLE phase separation was observed at 5.489 MPa, as shown in Table 1. The uncertainties of the experimental equilibrium composition, density, temperature, and pressure are ±0.001 mole fraction, ±0.1 kg/m^3, ±0.1 K, and ±1 kPa, respectively. The uncertainty represents the difference between the experimental value and the absolute real one.

Figure 1 gives the experimental pressure–composition diagram, including the values reported by Suzuki et al.[1] and Lam et al.[2] As shown in Figure 1, the liquid data reported by Suzuki et al.[1] certainly deviated from the present data with increasing pressures. The data reported by Suzuki et al.[1] have no information near the VLLE region at high pressures. Lam et al.[2] reported only VLLE, as shown in Figure 1. Figure 2 gives the experimental saturated density, including the saturated VLLE density data of Lam et al.[2]

Figure 3 shows the expanded phase equilibrium diagram in the vicinity of critical region. When the present experimental VLLE data and the ones given by Lam et al.[2] are compared, the differences of vapor, light liquid, and heavy liquid are 0.0192, 0.0034, and 0.0200 mole fraction, respectively. The VLLE pressure difference between the present study and that of Lam et al.[2] is only 0.012 MPa, as shown in Figure 3. The saturated vapor and liquid density data in the present study deviated from the ones reported by Lam et al.,[2] as shown in Figure 4. When the present experimental VLLE data and the ones reported by Lam et al.[2] are compared, the density differences of vapor, light liquid, and heavy liquid are 36.59, 25.13, and 43.5 kg/m^3, respectively. In Figures 1–4, the solid lines were smoothly drawn for the present experimental data obtained, considering the present experimental uncertainties.

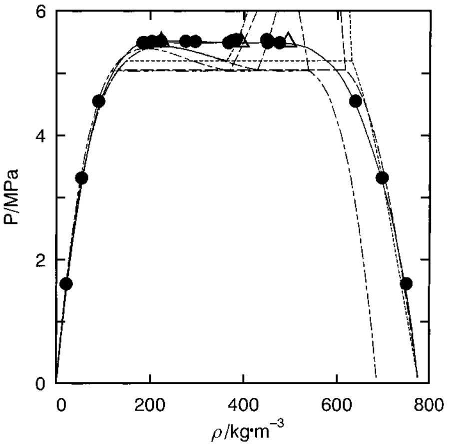

Figure 2. Saturated densities for the ethane + 1-propanol system at 314.15 K: ●, this work; △, literature data (Lam et al., 1990); — — —, pseudocubic EOS with two parameters ($k_{112} = -0.0146$, $k_{122} = -0.0475$); - - -, pseudocubic EOS with one parameter ($k_{12} = 0.0907$); — · —, SRK EOS ($k_{12} = 0.0425$).

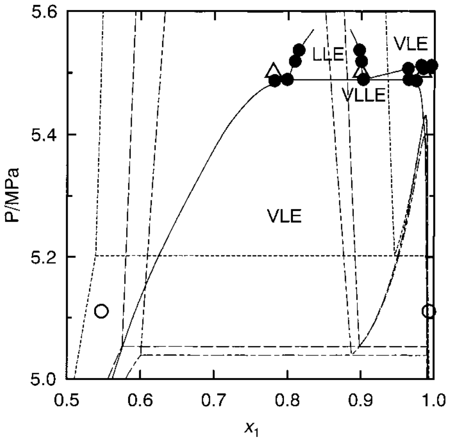

Figure 3. Expanded phase equilibrium diagram in the vicinity of the critical point: ●, this work; ○, literature data (Suzuki et al., 1990); △, literature data (Lam et al., 1990); — — —, pseudocubic EOS with two parameters ($k_{112} = -0.0146$, $k_{122} = -0.0475$); - - -, pseudocubic EOS with one parameter ($k_{12} = 0.0907$); — · —, SRK EOS ($k_{12} = 0.0425$).

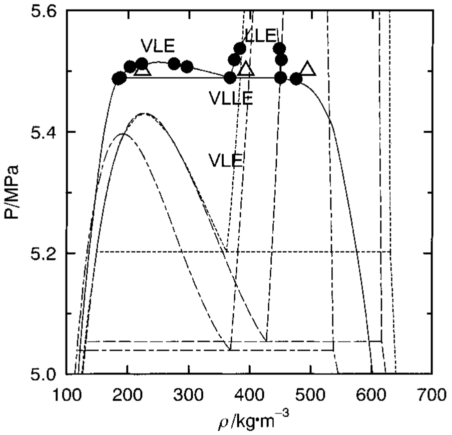

Figure 4. Expanded saturated densities in the vicinity of the critical point: ●, this work; △, literature data (Lam et al., 1990); — — —, pseudocubic EOS with two parameters ($k_{112} = -0.0146$, $k_{122} = -0.0475$); - - -, pseudocubic EOS with one parameter ($k_{12} = 0.0907$); — · —, SR K EOS ($k_{12} = 0.0425$).

When the reliabilities of the experimental apparatus and the meters for measuring the density, temperature, pressure, and compositions are considered, the present experimental data seem the most reliable.

Correlations

The experimental data obtained were correlated with the conventional SRK[7] equation of state and the pseudocubic[8] equation of state.

The pseudocubic[8] equation of state is expressed as follows:

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

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

$$\xi = \sqrt{\frac{4 - \theta}{1 - \theta}}, \quad \theta = \frac{8Z_c}{3}, \quad Z_c = \frac{P_c V_c}{RT_c} \tag{3}$$

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

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

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 first used, introducing the binary interaction parameter k_{ij}:

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

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

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

The binary interaction parameter k_{12} was evaluated as 0.0907 from the present experimental bubble point–pressure data in the lower pressure regions.

The following mixing rules[9] were further used in the present calculations, introducing two binary interaction parameters, k_{112} and k_{122}, almost similar to that of Hattori et al.[10]

$$a = \sum_i \sum_j \sum_k x_i x_j x_k a_{ijk}, \quad b = \sum_i \sum_j x_i x_j b_{ij}, \quad b_{ij} = \frac{b_i + b_j}{2} \tag{8}$$

$$a_{112} = (1 - k_{112}) a_1^{2/3} a_2^{1/3}, \quad a_{122} = (1 - k_{122}) a_1^{1/3} a_2^{2/3} \tag{9}$$

where the subscripts 1, 2, and k denote the components.

The binary interaction parameters, k_{112} and k_{122}, were evaluated as −0.0146 and −0.0475 from the present experimental bubble point–pressure data in the lower pressure regions, respectively.

In the correlations, the critical values and acentric factors of ethane and 1-propanol were obtained from the work of Reid et al.[11]

Calculation results with the equations of state are shown in Figures 1–4. Some difficulties were in the correlations with the equations of state, by reason of the complex phase equilibrium diagrams shown in Figures 1–4. The equation of state is generally applied for the VLE correlation, mainly for the pressure–composition behavior not for the saturated vapor and liquid density behavior. The equation of state is surely an excellent tool for correlation of the VLE composition behavior but a poor one for VLE density behavior. The present experimental data contain the VLE, VLLE, and LLE compositions and further their saturated densities. The perfect correlation of the present complex data with the equation of state is terribly troublesome. The authors are awaiting a new excellent equation of state and its mixing rules for the correlation of the present data with the satisfactory accuracies.

Conclusions

Phase equilibria and saturated densities for ethane + 1-propanol at high pressures were measured at 314.15 K with the static-circulation apparatus, including the VLLE. The experimental data obtained were correlated by the equations of state with some difficulties in the accuracy, by reason of the complex phase separation behaviors.

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