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High-Pressure Phase Equilibrium for Ethane + Ethanol at 311.15 K

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Phase equilibria and saturated densities for ethane + ethanol at high pressures were measured at 311.15 K with a static-circulation apparatus. The 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 vibrating tube density meter, respectively. The precision and uncertainty of the equilibrium compositions appear to be ±0.0001 and ±0.001 in mole fraction, respectively. The uncertainties of density, temperature, and pressure are ±0.1 kg/m^3, ±0.1 K, and ±1 kPa, respectively.

Introduction

Kuenen and Robson (1899) reported an upper critical end point (UCEP) and a lower critical end point (LCEP) on the critical loci for ethane + ethanol. These two end points are connected by a vapor−liquid−liquid (VLL) three-phase line. Brunner (1985) reported the critical phase behaviors of ethane + ethanol system. Lam et al. (1990) investigated VLL phase equilibrium behavior of binary ethane−*n*-alkanol mixtures and reported the UCEP and LCEP for ethane + ethanol. On the basis of a mass balance with an equilibrium view cell, McHugh et al. (1983) determined liquid compositions and their molar volumes along the VLL line for ethane + ethanol, assuming the vapor phase was pure ethane. Suzuki et al. (1990) measured the vapor−liquid equilibria (VLE) for ethane + ethanol with the static apparatus.

A static-circulation apparatus equipped with three density meters for measuring vapor−liquid−liquid equilibria (VLLE) at high pressures was developed previously (Tanaka and Kato, 1995). With this apparatus, the VLE and saturated densities for carbon dioxide + ethanol (Tanaka and Kato, 1995) and carbon dioxide + 1-butanol (Ishihara et al., 1996) at high pressures were measured. The phase-equilibrium properties of ethane + methanol have been measured recently (Ishihara et al., 1998), including VLLE. In the present study, the coexisting phase compositions and their saturated densities for ethane + ethanol at high pressures are measured at 311.15 K including VLE, LLE, and VLLE.

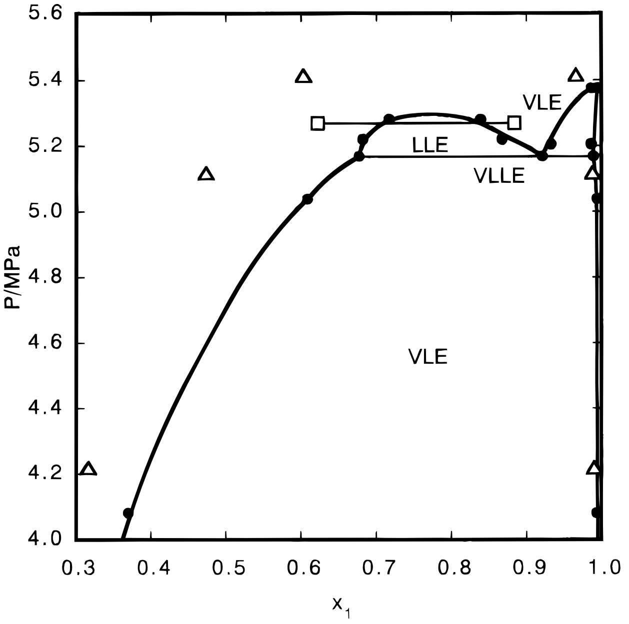

Figure 1. Phase equilibrium for ethane (1) + ethanol (2) at 311.15 K: (−●−) this work; (△) Suzuki et al. (1990), VLE at 313.4 K; (□) McHugh et al. (1983), LLE along VLL loci at 311.25 K.

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) + Ethanol (2) at 311.15 K

P/MPa	x_1	y_1	ρ_L/(kg·m^{-3})	ρ_V/(kg·m^{-3})
4.081[a]	0.370[a]	0.994[a]	645.4[a]	76.8[a]
5.039[a]	0.609[a]	0.995[a]	554.3[a]	131.2[a]
5.169[b]	0.677,[b] 0.921[b]	0.990[b]	491.3,[b] 355.1[b]	155.8[b]
5.206[a]	0.933[a]	0.987[a]	329.6[a]	169.8[a]
5.221[c]	0.682,[c] 0.868[c]		482.9,[c] 373.1[c]	
5.281[c]	0.717,[c] 0.839[c]		467.3,[c] 393.2[c]	
5.375[a]	0.987[a]	0.995[a]	275.6[a]	212.1[a]

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

Experimental Section

The apparatus and experimental procedures are the same as described previously (Tanaka and Kato, 1995; Ishihara et al., 1998). The apparatus is a static-circulation type with a maximum temperature of 400 K and maximum pressure of 20 MPa. It has three Anton Paar DMA 512S 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 three magnetic circulation pumps. Temperatures were measured with a Hewlett-Packard 2804A quartz thermometer. Pressures were measured with a Ruska 2480-700 oil dead weight gauge and a 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

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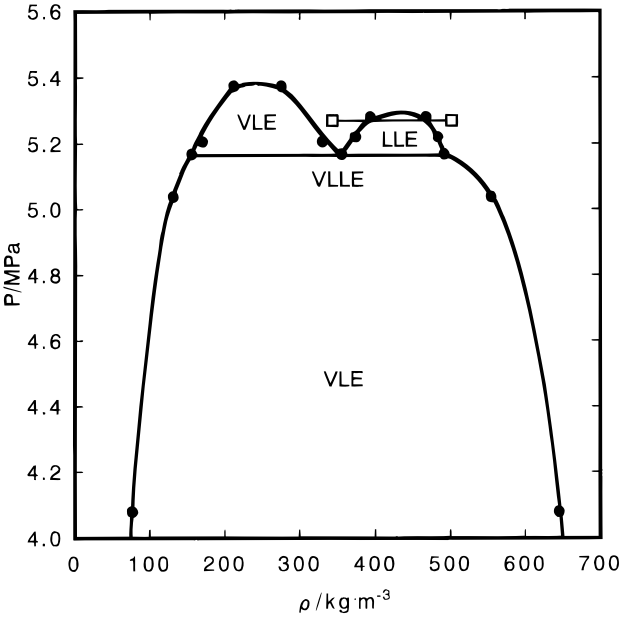

Figure 2. Saturated density behaviors for ethane (1) + ethanol (2) at 311.15 K: (–●–) this work; (□) McHugh et al. (1983), LLE along VLL loci at 311.25 K.

was used as a carrier gas at a flow rate of 30 cm^3/min. The injection temperature and column temperature were about 373 K and 363 K, respectively. The current as measured by a thermal conductivity detector (TCD) was 100 mA.

The samples of ethane and ethanol were charged into the cell after the cell was evacuated. The fluid in the cell was mixed with the magnetic-driven fan. Each phase was circulated through the circulation pump. After a steady state was established for 2 or 3 h, the fan and circulation pumps were stopped. After 1 h, the densities and the pressure were measured. A sample of each phase was obtained with the sampling valve and analyzed by gas chromatography after circulation for 2 h in the sampling room.

Ethane was supplied by Takachiho Chemical Industry Co. Ltd. with a guaranteed 99.9% purity. Special grade reagent ethanol was supplied by Wako Pure Chemicals Co. Ltd. and was used without further purification. The purity of ethanol was determined to be 99.9% from gas chromatograph peak areas.

Results

Table 1 gives the experimental results of coexisting phase compositions and their saturated densities for ethane + ethanol at 311.15 K. The VLLE phase separation was observed at 5.169 MPa, as shown in Table 1. The precision and uncertainty of the equilibrium compositions appear to be ±0.0001 and ±0.001 in mole fraction, respectively. The uncertainties of density, temperature, and pressure are ±0.1 kg/m^3, ±0.1 K, and ±1 kPa, respectively.

Figure 1 gives the experimental pressure–composition diagram, including the VLE data at 313.4 K reported by Suzuki et al. (1990) and LLE data of McHugh et al. (1983) at 311.25 K along the VLL line. Figure 2 shows the saturated density behaviors, including the saturated liquid density data of McHugh et al. (1983) along VLL loci.

Acknowledgment

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