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

Phase equilibria and saturated density for 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 for measuring vapor-liquid-liquid equilibrium at high pressures. 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 equilibria (VLE), liquid-liquid equilibria (LLE), and vapor-liquid-liquid equilibria (VLLE). The reproducibility of VLLE was within 0.001 mole fraction at the same pressure. 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 equilibrium composition and saturated density of each phase were determined by using gas chromatograph and vibrating tube density meters, respectively. The experimental data were correlated with the conventional SRK equation of state and the pseudocubic equation of state. The pseudocubic equation of state gave better calculation results for saturated liquid density behaviors, comparing with the conventional SRK equation of state. For saturated vapor density behavior, the SRK equation of state however gave the better calculation results than the ones of the pseudocubic equation of state.

KEYWORDS
vapor-liquid equilibrium, liquid-liquid equilibrium, vapor-liquid-liquid equilibrium, density

INTRODUCTION

Phase equilibria, such as vapor-liquid equilibria (VLE), liquid-liquid equilibria (LLE), and vapor-liquid-liquid equilibria (VLLE) are essential in the design and operation of distillation. Chemical engineering processes of primary importance are those of mixing, conversion, and separation involving gases, liquids, and solids. Many experimental and theoretical investigations have been performed in chemical engineering problems concerning with phase equilibria.

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 hydration of alkenes. However, phase equilibrium properties at low temperatures are not available in literatures for ethylene + ethanol system.

A static-circulation apparatus (Tanaka and Kato, 1995) equipped with three density meters for measuring VLLE at high pressures was used for various systems. With this apparatus, VLE and their saturated densities were reported for carbon dioxide + ethanol (Tanaka and Kato, 1995), carbon dioxide + 1-butanol (Ishihara et al., 1996), and ethane + 2-propanol (Kodama et al., 2002) at high pressures. The phase equilibrium properties of ethane + methanol (Ishihara et al., 1998), ethane + ethanol (Kato et al., 1999), ethane + 1-propanol (Kodama et al., 2001), ethane + 1-butanol (Kodama et al., 2001), and ethylene + 1-propanol (Kodama et al., 2004) have been recently measured, including VLLE.
In the present study, the coexisting phase compositions and their saturated densities for ethylene + ethanol mixture at high pressure were measured at 283.65 K including the vicinity of the critical region.

MATERIALS AND EXPERIMENTAL METHODS

In the present experiments, ethylene was supplied by Takachiho Chemical Industry Co. Ltd. with the guarantee of 99.9% in purity. Ethanol was the special-grade reagent of Wako Pure Chemical Industries Ltd. and was used without further purification. The purity of ethanol was determined to be 99.9 mol% from gas chromatograph peak areas.

The apparatus and experimental procedures are the same as described previously. The schematic diagram of experimental apparatus is shown in Figure 1. The apparatus is a static circulation type (Tanaka and Kato, 1995), 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 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 cm$^3$·min$^{-1}$. The column temperature was about 403 K. The current value of a thermal conductivity detector (TCD) was 100 mA.

The samples, ethylene and ethanol, 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 3 h, the agitator and circulation pumps were stopped. After 1 h, the densities and the pressure were measured with 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.

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
RESULTS AND DISCUSSION

Figures 2 and 3 give the experimental pressure-composition and their saturated density diagrams. Figure 4 shows the expanded phase equilibrium diagram in the vicinity of critical region. Figure 5 shows the expanded saturated density diagram. In Figures 2 to 5, the solid lines were smoothly drawn for the present experimental data obtained, considering the present experimental uncertainties. The reproducibility of VLLE was within 0.001 mole fraction at the same pressure. 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.

Correlation

The experimental data obtained were correlated with the conventional SRK (Soave, 1972) equation of state and the pseudocubic (Kato and Tanaka, 1986) equation of state.

The pseudocubic (Kato and Tanaka, 1986) equation of state is expressed as follows:

\[ P = \frac{RT}{v^* - b} - \frac{a}{v^*^2} \]  
(1)

where,

\[ v^* = \frac{(v - \xi b)(v + \sigma b)}{v} \]  
(2)

in which,

\[ \xi = (1 - \theta)(1 - 2) \]  
(3)

\[ \sigma = (1 - \theta)(1 + 2) \]  
(4)

\[ \xi = \sqrt[4]{\frac{4 - \theta}{1 - \theta}} \]  
(5)

\[ \theta = \frac{8Z_c}{3} \]  
(6)

\[ Z_c = \frac{P_cv_c}{RT_c} \]  
(7)

and

\[ a = K_a a_c \]  
(8)

\[ b = \frac{RT_c}{8P_c} \]  
(9)

where,

\[ a_c = \frac{27(RT_c)^2}{64P_c} \]  
(10)
Figure 2. Phase equilibria for ethylene + ethanol system at 283.65 K. (—) This work; (—) Pseudocubic EOS ($k_{ij}=0.0499$); (—) SRK EOS ($k_{ij}=-0.0057$)

Figure 3. Saturated densities for ethylene + ethanol system at 283.65 K. (—) This work; (—) Pseudocubic EOS ($k_{ij}=0.0499$); (—) SRK EOS ($k_{ij}=-0.0057$)

Figure 4. Expanded phase equilibrium diagram in the vicinity of the critical point. (—) This work; (—) Pseudocubic EOS ($k_{ij}=0.0499$); (—) SRK EOS ($k_{ij}=-0.0057$)

Figure 5. Expanded saturated densities in the vicinity of the critical point. (—) This work; (—) Pseudocubic EOS ($k_{ij}=0.0499$); (—) SRK EOS ($k_{ij}=-0.0057$)
\[
\ln K_a = S \left(1 - \sqrt{T_c}\right) \\
S = 1.1746 + 3.4539\omega
\]

where \(P, R, T, v, Z,\) and \(\omega,\) respectively, denote the pressure, gas constant, temperature, molar volume, compressibility factor, and acentric factor. \(K_a, S, a, b, \epsilon, \theta, \sigma,\) and \(\xi\) represent the parameters. The subscripts \(c\) and \(r\) denote the critical properties and reduced properties, respectively. The asterisk indicates the apparent value.

The pseudocubic equation of state strictly satisfies the critical point requirements. The conventional SRK equation of state cannot satisfy the critical compressibility factors of the materials. The compressibility factor given by the SRK is fixed as 0.333. For example, the actual values of \(Z_c\) are between 0.26 and 0.28 for hydrocarbons.

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

\[
a = \sum_i \sum_j x_i x_j a_{ij}
\]

\[
b = \sum_i \sum_j x_i x_j b_{ij}
\]

\[
\theta = \sum_i x_i \theta_i
\]

in which,

\[
a_{ij} = \left(1 - k_{ij}\right) \sqrt{a_i a_j}
\]

\[
b_{ij} = \frac{b_i + b_j}{2}
\]

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

The binary interaction parameter \(k_{ij}\) was evaluated as 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 the work (Poling et al., 2000).

Calculation results with the equations of state are shown in Figures 2 to 5. In Figures 2 to 5, the solid, dotted, and broken lines, respectively, denote the experimental smoothed data, the calculation results by the SRK equation of state, and the ones by the pseudocubic equation of state. In Figures 2 to 5, the horizontal lines denote the VLLE separation ranges calculated with equations of state. As shown in Figures 3 and 5, the pseudocubic equation of state gave better calculation results for saturated liquid density behaviors, comparing with the conventional SRK equation of state. For saturated vapor density behavior, the SRK equation of state however gave the better calculation results than the ones of the pseudocubic equation of state, as shown in Figures 3 and 5. The conventional SRK equation of state was more reasonable in the calculation of the second virial coefficients, comparing with the pseudocubic equation of state in the previous work (Kato and Tanaka, 1986). As shown in Figures 2 and 4, the SRK equation of state gave the better calculation results for equilibrium liquid locus on pressure-composition diagrams, comparing the ones of the pseudocubic equation of state.
CONCLUSIONS

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

For the purification of ethanol from biomass alcohols, the supercritical carbon dioxide has a limitation, considering the similar shapes of the pressure-composition diagrams for different alcohols. Ethylene seems to have the possibility as the effective supercritical fluid for the purification of ethanol from the biomass solution. The present study therefore seems useful in the design and operation of the industrial alcohol synthesis process.

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