High-Pressure Phase Equilibrium for Ethylene + Methanol at 278.15 K and 283.65 K

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Phase equilibria and saturated density for ethylene + methanol system at high pressures were measured at 278.15 K and 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, liquid−liquid, and vapor−liquid−liquid equilibria. The equilibrium composition and saturated density of each phase were determined by gas chromatograph 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 in 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 hydration of alkenes. With a static-circulation apparatus[1] equipped by use of three density meters, the phase equilibrium properties of ethylene + 1-propanol[1] and ethylene + ethanol[2] have been recently measured, including VLLE.

On the phase equilibrium behavior for ethylene + methanol system, Alwani and Schneider[3] estimated no liquid−liquid or high-pressure gas−gas phase separation with their experience. Ohgaki et al.[4] however observed the strange phase separation behaviors at 298.15 K and 313.15 K. After that, Brunner[5] reported the phase separation behavior at 284.15 K including the VLE data interpolated graphically from the VLE and LLE data concerned. Brunner[5] however did not observe the VLLE separation at 298.15 K. Zeck and Knapp[6] reported the LLE data at 283.60 K.

In the present study, the coexisting phase compositions and their saturated densities for the ethylene + methanol mixture at high pressure were measured at 278.25 K and 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[7] and the pseudocubic equation of state.[8]

Experimental Section

Materials. In the present experiments, ethylene was supplied by Takachiho Chemical Industry Co. Ltd. with the guarantee of 99.9 % in purity. Methanol was a special-grade reagent of Wako Pure Chemical Industries Ltd. and was used without further purification. The purity of methanol was more than 99.8 mol % by gas chromatographic area analysis.

Apparatus and Procedure. The experimental apparatus is schematically shown in Figure 1, almost similarly with the one in the previous study.[1] 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 (D). The density meters (D) were calibrated by dry air and water at experimental temperatures. The apparatus is in a constant-temperature liquid bath (E) controlled with ± 0.005 K by PID regulator. The cell volume is approximately 320 ± 5 cm^3. The coexisting phases are continuously recirculated through the sampling valves (K) and density meters (D) with the three magnetic circulation pumps (C). Temperatures were measured by means of the Hewlett-Packard 2804A quartz thermometer (J), calibrated by the triple point of water in the reference cell with an accuracy of ± 0.001 K. The reliability of the thermometer (J) used was certified by the boiling point of water at 1 atm pressure in the standard ebulliometer within an accuracy of 0.005 K. The accuracy of the experimental temperature seems therefore ± 0.01 K. Pressures were measured by means of the Ruska 2480-700 oil dead weight gauge (O) and the Ruska 2439-702 pressure transducer (T). 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 30 $cm^3 \cdot min^{-1}$. The column temperature was about 363 K. The injector and detector temperatures were about 373 K and 383 K. The current value of a thermal conductivity detector (TCD) was 100 mA.

First, the cell (A) was evacuated by the rotary oil vacuum pump (Q). The samples, ethylene and methanol, were then charged into the cell (A). The fluid in the cell (A) was mixed by means of the magnetic-driven agitator (I). Each phase was circulated through the circulation pump (C). After the steady state was established for 3 h, the agitator (I) and circulation pumps (C) were stopped. After 1 h, the densities and the pressure were measured by means of the density meters (D) and dead weight gauge (O), respectively. The sample of each phase was

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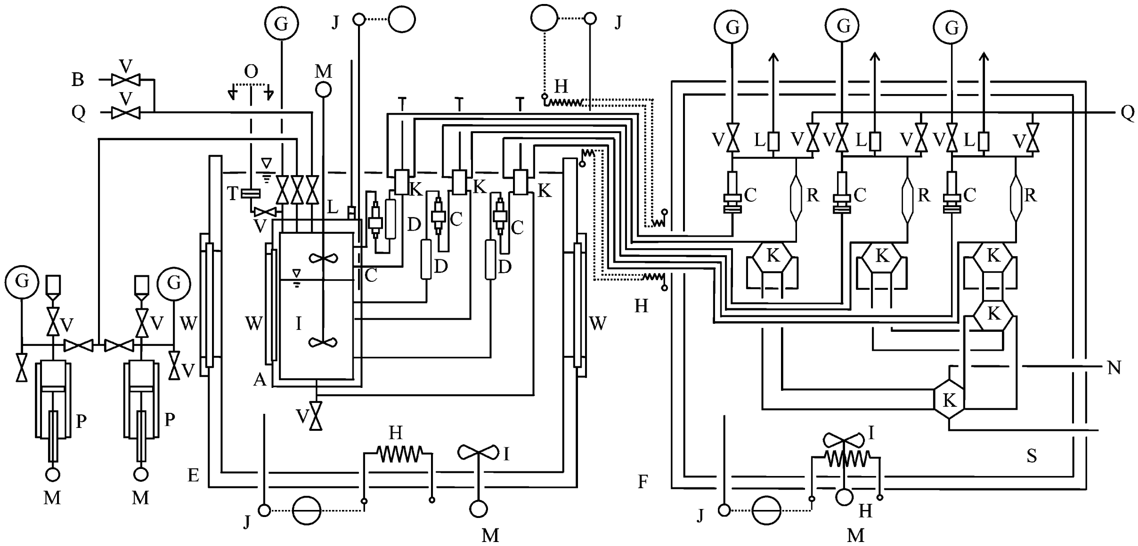

Figure 1. Schematic diagram of experimental apparatus: A, equilibrium cell; B, to sample reservoir; C, circulation pump; D, density meter; E, constant temperature liquid bath; F, constant temperature air bath; G, pressure gauge; H, heater; I, agitator; J, thermometer; K, sampling valve; L, safety valve; 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) + Methanol (2)

P/MPa	x_1	y_1	ρ_L/kg·m^{-3}	ρ_V/kg·m^{-3}
		278.15 K		
2.050	0.147^a	0.996^a	742.3^a	30.2^a
2.659	0.189^a	0.992^a	722.2^a	42.2^a
3.613	0.295^a	0.985^a	675.3^a	67.0^a
4.015	0.373^a	0.989^a	644.9^a	83.1^a
4.447	0.525^b, 0.901^b	0.996^b	568.3^b, 362.1^b	109.9^b
4.524	0.989^a	0.997^a	322.0^a	118.9^a
5.404	0.690^c, 0.889^c	517.2^c, 403.6^c		
5.769	0.789^c, 0.865^c	487.6^c, 417.4^c		
		283.65 K		
2.222	0.140^a	0.983^a	741.3^a	32.2^a
3.227	0.221^a	0.983^a	706.0^a	53.2^a
4.227	0.325^a	0.984^a	657.5^a	84.3^a
4.816	0.432^a	0.991^a	610.9^a	119.2^a
4.983	0.475^a	0.991^a	589.1^a	141.0^a
5.003	0.485^b, 0.955^b	0.993^b	585.1^b,320.6^b	145.5^b
5.059	0.984^a	0.993^a	258.5^a	160.8^a
5.390	0.506^c, 0.930^c	575.9^c, 352.8^c		
5.906	0.532^c, 0.894^c	564.0^c, 375.6^c		

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

taken by the sampling valve (K). The sample was introduced into the sampling room (F) to be homogeneous vapor by a circulation of 2.5 h. The vapor obtained was analyzed by gas chromatography. The uncertainties of the experimental equilibrium composition, density, temperature, and pressure are ± 0.001 mole fraction, ± 0.1 kg·m^{-3}, ± 0.01 K, and ± 1 kPa, respectively. The reproducibility of VLLE was within 0.001 mole fraction at the same pressure.

Results and Discussion

Table 1 gives all the experimental results of coexisting phase compositions and their saturated densities for the ethylene + methanol system at 278.15 K and 283.65 K. The VLLE phase separation pressures were 4.447 MPa and 5.003 MPa, respectively, at 278.15 K and 283.65 K, as shown in Table 1. Figures 2 and 3, respectively, give the experimental pressure-composition and their saturated density diagrams at 278.15 K. Figures 4 and 5, respectively, show the expanded phase equilibrium and saturated density diagrams in the vicinity of critical region at 278.15 K. Figures 6 and 7, respectively, give the experimental pressure-composition and their saturated density diagrams at 283.65 K. Figures 8 and 9, respectively, show the expanded phase equilibrium and saturated density diagrams in the vicinity

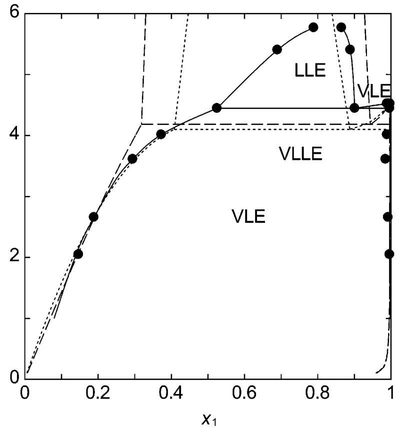

Figure 2. Phase equilibria for ethylene (1) + methanol (2) system at 278.15 K: ●, this work; − −, pseudocubic EOS (k_{12} = 0.0639); - - -, SRK EOS (k_{12} = −0.0417).

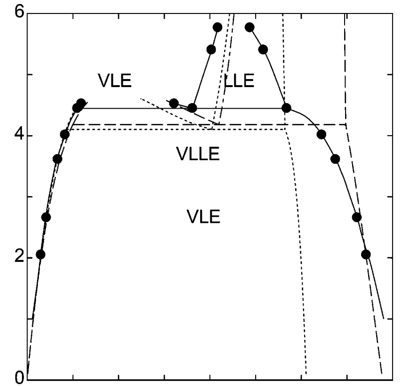

Figure 3. Saturated densities for ethylene (1) + methanol (2) system at 278.15 K: ●, this work; − −, pseudocubic EOS (k_{12} = 0.0639); - - -, SRK EOS (k_{12} = −0.0417).

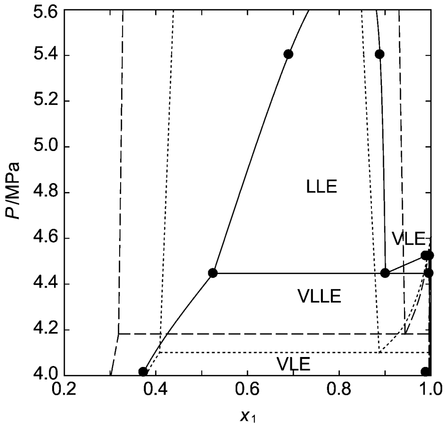

Figure 4. Expanded phase equilibrium diagram for ethylene (1) + methanol (2) system at 278.15 K: ●, this work; — —, pseudocubic EOS (k_{12} = 0.0639); - - -, SRK EOS (k_{12} = −0.0417).

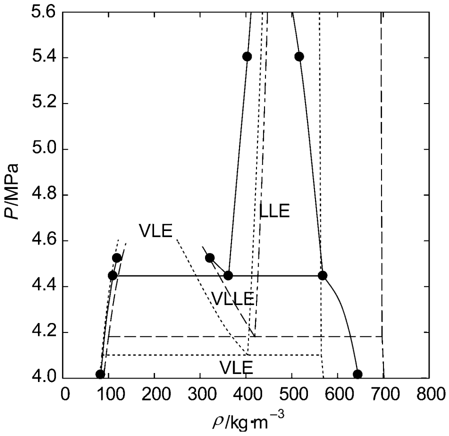

Figure 5. Expanded saturated densities for ethylene (1) + methanol (2) system at 278.15 K: ●, this work; — —, pseudocubic EOS (k_{12} = 0.0639); - - -, SRK EOS (k_{12} = −0.0417).

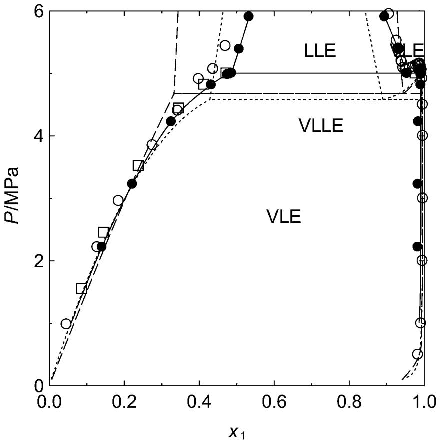

Figure 6. Phase equilibria for ethylene (1) + methanol (2) system at 283.65 K: ●, this work; ○, Brunner[5] at 284.15 K; □, Zeck and Knapp[6] at 283.60 K; — —, pseudocubic EOS (k_{12} = 0.0672); - - -, SRK EOS (k_{12} = −0.0406).

of critical region at 283.65 K. In Figures 2 to 9, the solid lines were smoothly drawn for the present experimental data obtained. As shown in Figures 6 to 9, the data of Brunner[5] agreed fairly well with the present experimental results at 284.15 K. The VLLE data given by Brunner[5] are however the graphically interpolated ones, combining the VLE and LLE data. The saturated liquid data given by Zeck and Knapp[6] at 283.60 K seem reasonable, comparing well with the present experimental data as shown in Figures 6 and 8. At 278.15 K, the previous

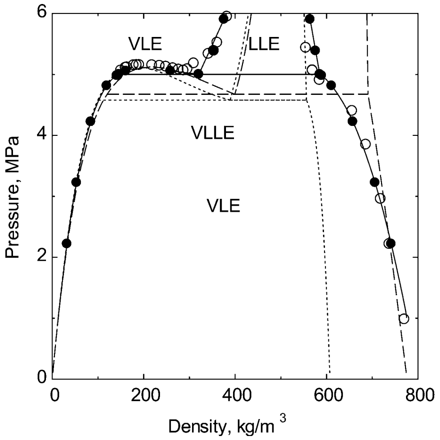

Figure 7. Saturated densities for ethylene (1) + methanol (2) system at 283.65 K: ●, this work; ○, Brunner[5] at 284.15 K; — —, pseudocubic EOS (k_{12} = 0.0672); - - -, SRK EOS (k_{12} = −0.0406).

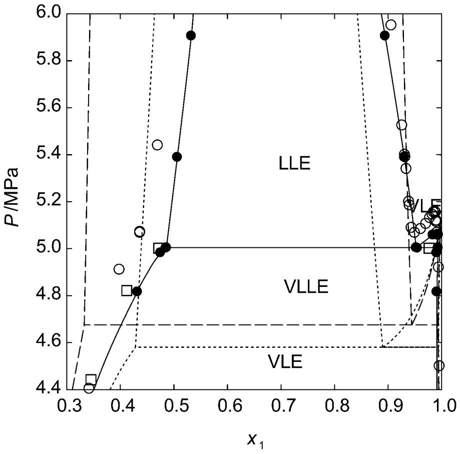

Figure 8. Expanded phase equilibrium diagram for ethylene (1) + ethanol (2) system at 283.65 K: ●, this work; ○, Brunner[5] at 284.15 K; □, Zeck and Knapp[6] at 283.60 K; — —, pseudocubic EOS (k_{12} = 0.0672); - - -, SRK EOS (k_{12} = −0.0406).

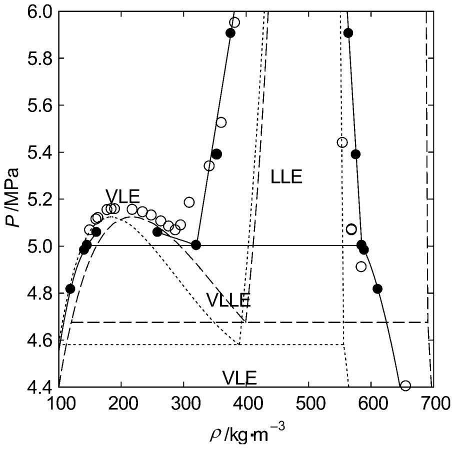

Figure 9. Expanded saturated densities for ethylene (1) + ethanol (2) system at 283.65 K: ●, this work; ○, Brunner[5] at 284.15 K; — —, pseudocubic EOS (k_{12} = 0.0672); - - -, SRK EOS (k_{12} = −0.0406).

equilibrium data for ethylene + methanol are not available in the literature.

Correlation

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

The pseudocubic equation of state[8] 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, 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 used, introducing binary interaction parameter k_{ij}:

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

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

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

The binary interaction parameter k_{ij} was evaluated as 0.0639 and 0.0672, respectively, from the present experimental bubble point-pressure data in the lower pressure regions at 278.15 K and 283.65 K. In the correlations, the critical values and acentric factors of ethylene and methanol were obtained from ref 9.

Calculation results with the equations of state are shown in Figures 2 to 9. In Figures 2 to 9, the solid, dotted, and broken lines, respectively, denote the smoothed experimental data, the calculation results by the SRK equation, and the ones by the pseudocubic equation. In Figures 2 to 9, the horizontal lines denote the VLLE separation ranges calculated with equations of state. As shown in Figures 2 to 9, the VLLE separations in the narrow composition ranges.

Conclusions

Phase equilibria and saturated densities for ethylene + methanol at high pressures were measured at 278.15 K and 283.65 K with a static-circulation apparatus including the VLLE and the vicinity of the critical region. 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 system at 283.65 K. *J. Chem. Eng. Data* **2005**, *50*, 122−124.
(3) Alwani, Z.; Schneider, G, M. Fluid mixtures at high pressure. Phase separation and critical phenomena in binary mixtures of a polar component with supercritical carbon dioxside, ethane, and ethene up to 1000 bar. *Ber. Bunsen-Ges. Phys. Chem.* **1976**, *80*, 1310−1315.
(4) Ohgaki, K.; Nishii, H.; Saito, T.; Katayama, T. High-pressure phase equilibria for the methanol−ethylene system at 25 °C and 40 °C. *J. Chem. Eng. Jpn.* **1983**, *16*, 263−267.
(5) Brunner, E. Fluid mixtures at high pressures. III. Isothermal phase equilibria of (ethane + methanol) at 284.15 K and 298.15 K. *J. Chem. Thermodyn.* **1985**, *17*, 985−994.
(6) Zeck, S.; Knapp, H. Vapor−liquid and vapor−liquid−liquid phase equilibria of binary and ternary systems of nitrogen, ethene and methanol: experiment and data evaluation. *Fluid Phase Equilib.* **1986**, *26*, 37−58.
(7) Soave, G. Equilibrium constants from a modified Redlich−Kwong equation of state. *Chem. Eng. Sci.* **1972**, *27*, 1197−1203.
(8) Kato, M.; Tanaka, H. A new three-parameter pseudo-cubic equation of state. *Adv. Cryog. Eng.* **1986**, *31*, 1169−1179.
(9) 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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