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High-Pressure Vapor−Liquid Equilibrium for Ethylene + 2-Methyl-1-propanol

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Vapor−liquid equilibria and the saturated density for the ethylene + 2-methyl-1-propanol system at high pressures were measured at the temperatures (278.15, 283.65, and 288.15) 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 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 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 are essential in the design and operation of distillation. Many experimental and theoretical investigations have been performed in chemical engineering problems concerning phase equilibria. High-pressure multiphase behavior is also important in the development, often at cryoscopic temperatures, of new and highly efficient separation techniques in the natural gas, oil, and petrochemical industries.

A static-circulation apparatus[1] equipped with three density meters for measuring vapor−liquid−liquid equilibrium (VLLE) at high pressures was used for various systems. The phase equilibrium properties of ethane + methanol,[2] ethane + ethanol,[3] ethane + 1-propanol,[4] ethane + 1-butanol,[5] ethylene + methanol,[6] ethylene + ethanol,[7] and ethylene + 1-propanol[1] have been measured, including VLLE. The phase equilibrium properties of ethylene + 1-butanol[8] have been recently measured including VLLE, and the saturated points near the critical region were further measured by the conventional indirect method.[9]

There are no data on the phase equilibrium behavior for the ethylene + 2-methyl-1-propanol system. In the present study, the coexisting phase compositions and their saturated densities for ethylene + 2-methyl-1-propanol at high pressures were measured at the temperatures (278.15, 283.65, and 288.15) K with a static-circulation apparatus. The equilibrium composition and saturated density of each phase were determined by using gas chromatography and vibrating-tube density meters, respectively. The experimental data were correlated with a Soave−Redlich−Kwong (SRK) equation of state[10] and the pseudocubic equation of state.[11]

Experimental Section

Materials. In the present experiments, ethylene was supplied by Takachiho Chemical Industry Co., Ltd., with the guarantee of 0.999 mol fraction purity. 2-Methyl-1-propanol was a special-grade reagent of Wako Pure Chemical Industries, Ltd. and was used without further purification. The purity of 2-methyl-1-propanol was more than 0.999 mol fraction by gas chromatographic area analysis. The physical properties of 2-methyl-1-propanol used in this work are listed in Table 1.

Table 1. Physical Properties of Material Used

	T_b/K		ρ(298.15 K)/kg·m^{-3}		n_D/(298.15 K)	
material	exptl	lit.[a]	exptl	lit.[b]	exptl	lit.[b]
2-methyl-1-propanol	380.976	381.040	797.6	797.8	1.3939	1.3939

[a] Timmermans.[13] [b] TRC Thermodynamic Tables Non-Hydrocarbons.[14]

Apparatus and Procedures. The apparatus and experimental procedures are the same as described previously. The apparatus is a static-circulation type,[1] 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 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 40 cm^3·min^{-1}. The column and injector temperatures were about 423 K. The detector temperature was about 433 K. The current value of a thermal conductivity detector (TCD) was 100 mA.

The samples, ethylene and 2-methyl-1-propanol, were charged into the cell after the evacuation of the cell. 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,

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Table 2. Saturation Pressure P, Liquid Mole Fraction x, Vapor Mole Fraction y, Liquid Density ρ_L, and Vapor Density ρ_V for Ethylene (1) + 2-Methyl-1-propanol (2) at (278.15, 283.65, and 288.15) K

P/(MPa)	x_1	y_1	ρ_L/(kg·m^{-3})	ρ_V/(kg·m^{-3})
		T = 278.15 K		
2.236	0.275	0.995	753.2	33.8
3.117	0.400	0.990	717.1	52.6
3.569	0.470	0.991	691.1	65.4
4.058	0.584	0.993	639.8	88.0
4.262	0.668	0.997	604.1	96.7
4.389	0.841	0.998	495.9	105.3
4.425	0.941	0.999	402.3	108.1
4.497	0.988	0.999	340.4	114.6
		T = 283.65 K		
2.107	0.232	0.987	759.0	29.9
3.106	0.363	0.991	725.9	49.6
4.147	0.508	0.996	674.4	81.8
4.694	0.630	0.996	617.8	108.8
4.933	0.809	0.998	512.8	130.3
4.980	0.955	0.999	361.3	137.2
5.047	0.990	0.998	303.3	151.8
		T = 288.15 K		
2.252	0.234	0.996	755.4	32.6
2.822	0.294	0.996	739.3	43.1
3.523	0.377	0.993	715.8	58.9
4.028	0.439	0.989	695.0	72.2
4.703	0.544	0.994	656.2	99.4
5.211	0.654	0.995	602.1	131.5
5.453	0.837	0.996	479.3	173.3
5.474	0.962	0.996	340.7	183.4

and pressure are ± 0.001 mol fraction, ± 0.1 kg·m^{-3}, ± 0.1 K, and ± 1 kPa, respectively.

Results and Discussion

Table 2 gives all the experimental results of coexisting phase compositions and their saturated densities for the ethylene + 2-methyl-1-propanol system at the temperatures (278.15, 283.65, and 288.15) K. Figures 1 and 2 give the experimental pressure−composition and their saturated density diagrams, respectively. As shown in Figures 1 and 2, vapor−liquid equilibria (VLE) were observed, but VLLE were not found for the present system because the experimental temperatures are not between lower critical end point and upper critical end point.

Correlation

The experimental data obtained were correlated with the conventional SRK equation of state[10] and the pseudocubic equation of state.[11]

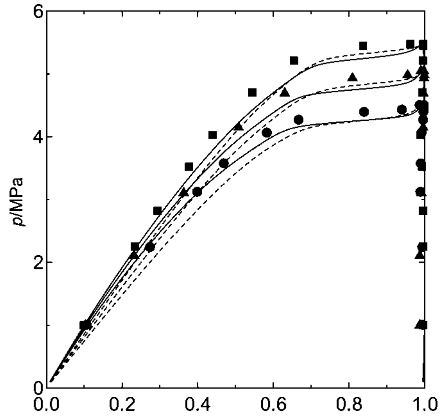

Figure 1. Phase equilibria for the ethylene (1) + 2-methyl-1-propanol (2) system. ●, 278.15 K; ▲, 283.65 K; ■, 288.15 K; —, Pseudocubic EOS (k_{ij} = 0.043, l_{ij} = −0.050); ----, SRK EOS (k_{ij} = 0.017).

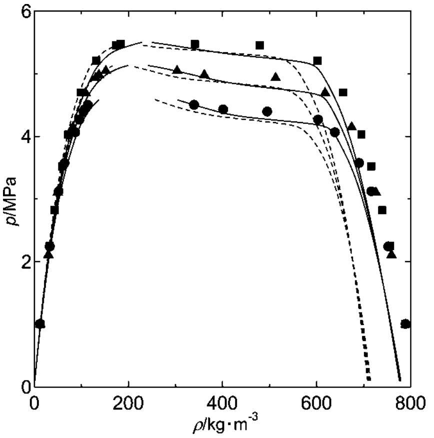

Figure 2. Saturated densities for the ethylene (1) + 2-methyl-1-propanol (2) system: ●, 278.15 K; ▲, 283.65 K; ■, 288.15 K; —, Pseudocubic EOS (k_{ij} = 0.043, l_{ij} = −0.050); ----, SRK EOS (k_{ij} = 0.017).

The pseudocubic equation of state[11] is expressed as follows

$$P = \frac{RT}{v^* - b} - \frac{a}{v^{*2}} \qquad v^* = \frac{(v - \varepsilon b)(v + \sigma b)}{v} \tag{1}$$

$$\varepsilon = (1 - \theta)(\xi - 2) \qquad \sigma = (1 - \theta)(\xi + 2) \tag{2}$$

$$\xi = \sqrt{\frac{4 - \theta}{1 - \theta}} \qquad \theta = \frac{8Z_c}{3} \qquad Z_c = \frac{P_c v_c}{RT_c} \tag{3}$$

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

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

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 parameters k_{ij} and l_{ij}

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

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

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

The binary interaction parameters k_{ij} and l_{ij} were first evaluated to minimize the sum of squares of the differences of liquid compositions. The calculation results with the equation of state however gave the VLLE separation at a high-pressure region. The numerical value of the binary interaction parameters were therefore changed a little to avoid the appearance of VLLE. Consequently, the binary interaction parameters k_{ij} and l_{ij} were obtained as 0.043 and −0.050, respectively. The binary interaction parameters k_{ij} and l_{ij} were used at the same value at the all experimental temperatures because the ones range is close. In the correlations, the critical values and acentric factors of ethylene and ethanol were obtained from the literature.[12]

Calculation results with the equations of state are shown in Figures 1 and 2. In Figures 1 and 2, the solid and short dashed lines, respectively, denote the calculation results by the pseudocubic equation and the ones by the SRK equation. As shown in

Figures 1 and 2, the pseudocubic equation of state gave good results especially for liquid composition and density compared with the SRK equation.

Conclusions

Vapor−liquid equilibria (VLE) and saturated densities for ethylene + 2-methyl-1-propanol at high pressures were measured at the temperatures (278.15, 283.65, and 288.15) K with a static-circulation apparatus.[1] The experimental data obtained were correlated by the equations of state.

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