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Vapor−Liquid Equilibria of 2-Methyl-1-propanol with Octane

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Isobaric and isothermal vapor−liquid equilibria were measured for the 2-methyl-1-propanol + octane system at a pressure of 101.3 kPa and a temperature of 373.15 K. The measurements were made in an equilibrium still with circulation of both the vapor and liquid phases. The 2-methyl-1-propanol + octane system forms a minimum boiling azeotrope or maximum pressure azeotrope. The azeotropic data are x_1(AZ) = 0.670 and T(AZ) = 376.58 K for the isobaric and x_1(AZ) = 0.654 and P(AZ) = 90.67 kPa for the isothermal system. The activity coefficients of the system were best correlated with the nonrandom two-liquid (NRTL) equation for the isobaric and with the Wilson equation for the isothermal system.

Introduction

Vapor−liquid equilibrium (VLE) data are required for engineering use such as design and operation of separation processes. As a continuation of our studies on the VLE of alkane + alkanol systems (Hiaki et al., 1996a,b, 1997), the isobaric and isothermal VLE of 2-methyl-1-propanol + octane at 101.3 kPa and 373.15 K were measured using a vapor and liquid recirculating still (Hiaki et al., 1992), which had a total capacity of about 100 cm^3. Neither isobaric nor isothermal data for the system have been published previously.

Experimental Section

Materials. 2-Methyl-1-propanol and octane were special-grade reagents, supplied by the Wako Pure Chemical Co. Ltd. Gas-chromatographic analysis materials indicated that each had a purity of at least 99.9 mol %. The measured physical properties of compounds are listed in Table 1 along with the literature values. Normal boiling points were measured by an ebulliometer that has a capacity of about 70 cm^3. Density values were determined using a vibrating tube density meter (Shibayama Kagaku SS-D-200-Exp. Type, Japan). Density was measured with an accuracy of $\pm 1.0 \times 10^{-5}$ (g·cm^{-3}).

Procedure. The isothermal VLE measurement apparatus and associated computer, which were described in our previous work (Hiaki et al., 1994), were used for the measurements. The ebulliometer was used for the determination of the total pressure. The performance of the ebulliometer has been checked with the normal boiling points of several pure components. The platinum resistance thermometers placed in both the equilibrium still and the ebulliometer were linked with a GP-IB bus and enabled temperature measurement and its control and proper adjustment of the system pressure.

The sample was introduced into the VLE still and water into the ebulliometer for the determination of vapor pressure. After a steady state was established in both the sample and water at atmospheric pressure, the sample temperature was maintained at the desired temperature by adjusting the pressure using the computer in conjunction with four solenoid valves and a vacuum pump.

Table 1. Normal Boiling Points, T_b, and Densities, ρ, of the Components

	T_b/K			ρ/g·cm^{-3}		
material	exptl	calc[a]	lit.[b]	exptl	lit.[b]	T/K
2-methyl-1-propanol	381.03	381.042	381.036	0.798 01	0.797 8	298.15
octane	398.84	398.567	398.823	0.698 68	0.698 62	298.15

[a] Calculated value using the Antoine constants with Table 2. [b] Riddick et al. (1986).

For the isobaric system, the pressure P in the still was measured by a Fortin-type mercury barometer. Since the barometric pressure changed slightly, the experimental temperatures were corrected to 101.3 kPa.

The equilibrium temperature T was measured with a calibrated platinum resistance thermometer (Pt 100Ω) with an accuracy of ±0.03 K. A standard resistance thermometer (Chino Co. model R 800-2, Japan), which is based on ITS-90, was used for this calibration. The vapor pressure of the sample was determined by the measurement of the boiling point of water on the basis of vapor pressure data of water (Wagner and Pruss, 1987). From the accuracy of the temperature, the relative error in the values of experimental vapor pressure is estimated to be ±0.03 kPa.

Analysis. The equilibrium composition of the samples was determined using a gas chromatograph (GL Sciences model GC-380, Japan) equipped with a flame ionization detector. The column packing was BX-10 (supplied by the GL Sciences Inc.). The relationship between peak area and composition was determined from analysis of samples of known composition. The accuracy of liquid, x_i, and vapor, y_i, mole fractions is estimated to be 0.003 mole fraction.

Results and Discussion

The activity coefficients γ_i were calculated from

$$\phi_i P y_i = \gamma_i P_i^\circ x_i \phi_i^\circ \exp[V_i (P - P_i^\circ)/RT] \qquad (1)$$

where ϕ_i and ϕ_i°, the fugacity coefficients of component i in the mixture and pure vapor, respectively, were evaluated by using the second virial coefficients obtained by the Hayden−O'Connell method (1975). The vapor pressures of the pure components, P_i°, were obtained using the

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Table 2. Antoine Constants of the Components^{a,b}

material	A	B	C
2-methyl-1-propanol	6.491 83	1270.273	−97.885
octane	6.043 94	1351.938	−64.030

[a] $\log(P/\mathrm{kPa}) = A - B/[(T/\mathrm{K}) + C]$. [d] Boublik et al. (1984).

Table 3. Corresponding State Parameters^{d}

material	T_c/K	P_c/MPa	RD/nm	DM/D	ZRA
2-methyl-1-propanol	547.73	4.352	0.314	1.64	0.2590
octane	568.83	2.525	0.468	0	0.2567

[a] Prausnitz et al. (1980).

Table 4. Isobaric Vapor−Liquid Equilibrium Data, Temperature, T, Liquid Phase, x_1, and Vapor Phase, y_1, Mole Fractions, and Activity Coefficient, γ_i, for the 2-Methyl-1-propanol (1) + Octane (2) System at 101.3 KPa

T/K	x_1	y_1	γ_1	γ_2
398.84	0.0000	0.0000		
388.75	0.0604	0.3143	4.0568	0.9620
387.52	0.0714	0.3463	3.9363	0.9615
383.06	0.1313	0.4391	3.1499	1.0049
382.27	0.1481	0.4582	2.9936	1.0137
381.01	0.1853	0.4906	2.6747	1.0355
379.86	0.2271	0.5143	2.3811	1.0779
378.97	0.2806	0.5395	2.0848	1.1287
378.15	0.3409	0.5606	1.8354	1.2062
377.76	0.3889	0.5784	1.6820	1.2637
377.37	0.4316	0.5896	1.5668	1.3393
376.80	0.5451	0.6263	1.3435	1.5528
376.77	0.5610	0.6319	1.3186	1.5872
376.69	0.5841	0.6383	1.2829	1.6509
376.67	0.5981	0.6439	1.2644	1.6832
376.60	0.6222	0.6531	1.2356	1.7488
376.58	0.6440	0.6585	1.2043	1.8285
376.58	0.6749	0.6714	1.1714	1.9280
376.60	0.7256	0.6917	1.1210	2.1440
376.73	0.7631	0.7086	1.0864	2.3398
376.95	0.7935	0.7288	1.0657	2.4845
377.13	0.8177	0.7442	1.0488	2.6419
377.33	0.8389	0.7603	1.0364	2.7865
377.45	0.8508	0.7682	1.0280	2.9003
377.65	0.8677	0.7837	1.0206	3.0360
377.86	0.8827	0.7981	1.0140	3.1793
378.73	0.9274	0.8570	1.0038	3.5556
379.96	0.9716	0.9327	0.9973	4.1401
381.03	1.0000	1.0000		

Antoine equation constants (Boublik et al., 1984), which are shown in Table 2. The liquid molar volumes V_i were calculated from the Rackett equation as modified by Spencer and Danner (1972). The corresponding state parameters, which are the critical temperature and pressure, mean radius of gyration, dipole moment, and Rackett parameters, are shown in Table 3.

The experimental VLE data for the 2-methyl-1-propanol (1) + octane (2) system at 101.3 kPa are reported in Table 4 along with the activity coefficients calculated using eq 1. The VLE data for the 2-methyl-1-propanol (1) + octane (2) system at 373.15 K are reported in Table 5. The experimental data are shown graphically in Figures 1−4.

2-Methyl-1-propanol (1) + octane (2) at 101.3 kPa has a minimum boiling azeotrope. The azeotropic point were determined on the basis of the experimental VLE data are $x_1(\mathrm{AZ}) = 0.670$ and $T(\mathrm{AZ}) = 376.58$ K. The 2-Methyl-1-propanol (1) + octane (2) system at 373.15 K forms a maximum pressure azeotrope, yielding $x_1(\mathrm{AZ}) = 0.654$ and $P(\mathrm{AZ}) = 90.67$ kPa.

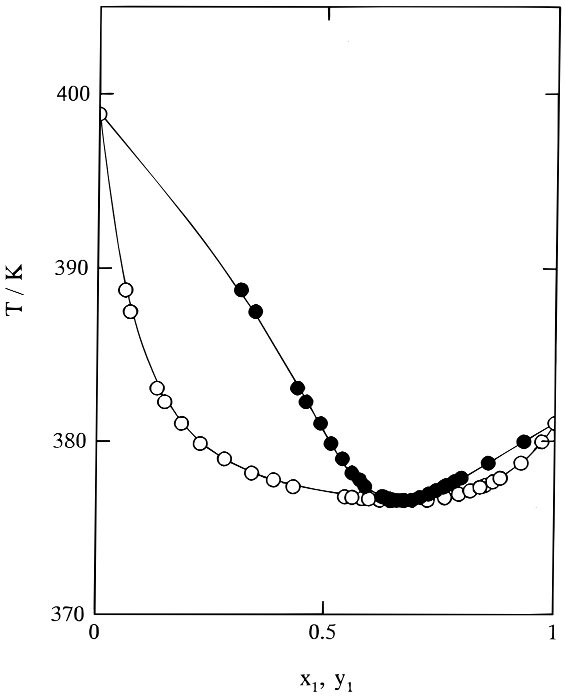

Figure 1. Temperature-composition diagram for 2-methyl-1-propanol (1)+ octane (2) at 101.3 kPa: ○, x_1; ●, y_1; −, NRTL equation.

Table 5. Isothermal Vapor−Liquid Equilibrium Data, Pressure, P, Liquid Phase, x_1, and Vapor Phase, y_1, Mole Fractions, and Activity Coefficient, γ_i, for the 2-Methyl-1-propanol (1) + Octane (2) System at 373.15 K

P/kPa	x_1	y_1	γ_1	γ_2
46.99	0.0000	0.0000		
61.68	0.0437	0.2722	5.1967	0.9939
67.37	0.0724	0.3500	4.3872	0.9970
73.60	0.1150	0.4240	3.6402	1.0093
79.56	0.1813	0.4803	2.8170	1.0619
83.35	0.2537	0.5218	2.2852	1.1218
86.55	0.3469	0.5565	1.8468	1.2339
87.31	0.3682	0.5646	1.7799	1.2630
89.17	0.4539	0.5899	1.5385	1.4056
89.95	0.5346	0.6156	1.3736	1.5606
90.28	0.5668	0.6248	1.3194	1.6430
90.53	0.6178	0.6415	1.2456	1.7853
90.62	0.6358	0.6496	1.2265	1.8337
90.67	0.6447	0.6522	1.2149	1.8668
90.83	0.6559	0.6572	1.2053	1.9036
90.70	0.6620	0.6579	1.1937	1.9314
90.79	0.6812	0.6737	1.1887	1.9566
90.56	0.7120	0.6798	1.1445	2.1208
90.37	0.7295	0.6887	1.1292	2.1919
90.44	0.7318	0.6883	1.1258	2.2150
89.68	0.7681	0.7067	1.0919	2.3935
89.69	0.7713	0.7087	1.0906	2.4111
89.25	0.7998	0.7242	1.0692	2.5975
88.45	0.8310	0.7466	1.0513	2.8063
87.55	0.8528	0.7640	1.0377	2.9743
86.94	0.8701	0.7813	1.0328	3.1052
86.10	0.8855	0.7970	1.0253	3.2426
82.89	0.9371	0.8650	1.0128	3.7990
82.20	0.9445	0.8782	1.0118	3.8562
81.07	0.9569	0.9001	1.0100	4.0241
79.95	0.9686	0.9224	1.0086	4.2384
79.63	0.9725	0.9311	1.0102	4.2828
75.99	1.0000	1.0000		

The results were tested for thermodynamic consistency by using the point test of Fredenslund et al. (1977) and of Van Ness et al. (1973) and the area test of Herington (1951) and of Redlich and Kister (1948) as described by Gmehling and Onken (1977). The results from the two consistency tests indicate that the VLE data for both isobaric and isothermal systems are thermodynamically consistent.

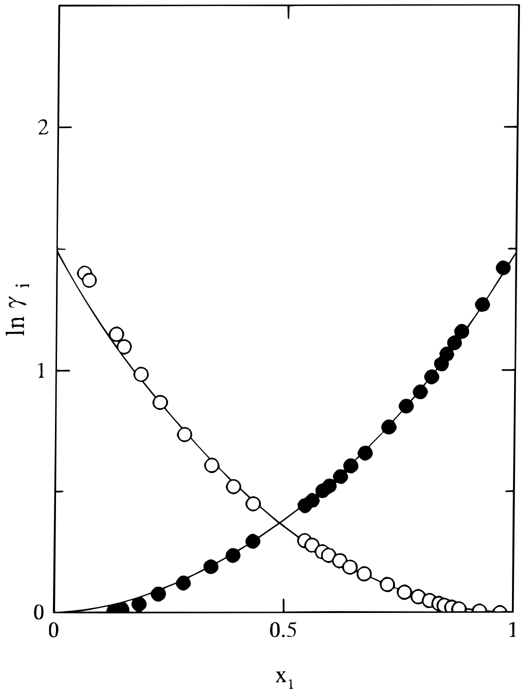

Figure 2. Activity coefficient-liquid composition diagram for 2-methyl-1-propanol (1)+ octane (2) at 101.3 kPa: ○, ln γ_1; ●, ln γ_2; —, NRTL equation.

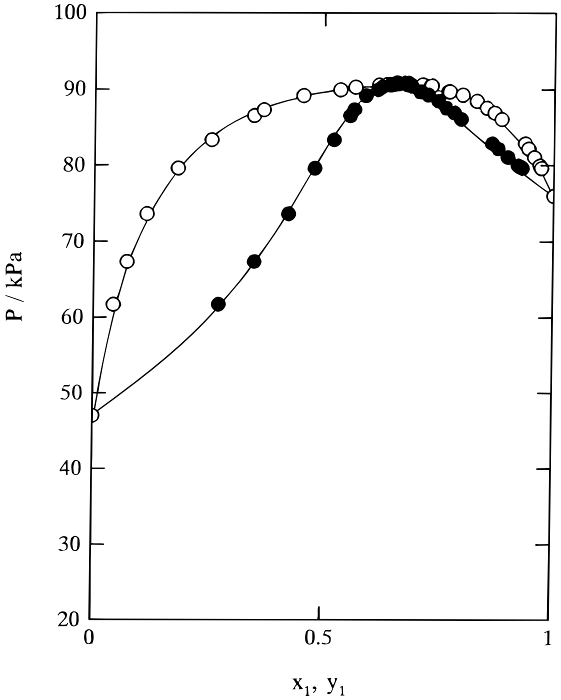

Figure 3. Pressure-composition diagram for 2-methyl-1-propanol (1) + octane (2) at 373.15 K: ○, x_1; ●, y_1; —, Wilson equation.

The activity coefficients were correlated with the Wilson (Wilson, 1964), modified Wilson (Tsuboka and Katayama, 1975), nonrandom two-liquid (NRTL) (Renon and Prausnitz, 1968), and UNIQUAC (Abrams and Prausnitz, 1975) equations. The parameters in each of these equations are obtained by using the Marquardt method (Marquardt, 1963). The sum of the squares of relative of deviations of activity coefficients was minimized during optimization of the parameters.

For the experimental isobaric system of 2-methyl-1-propanol (1) + octane (2), the NRTL equation yielded the lowest mean deviations between the experimental and calculated vapor composition, 0.006 mole fraction, and temperature, 0.05 K, for the average absolute deviations. The maximum absolute deviations are 0.032 mole fraction and 0.163 K. The NRTL parameters for this system were found to be

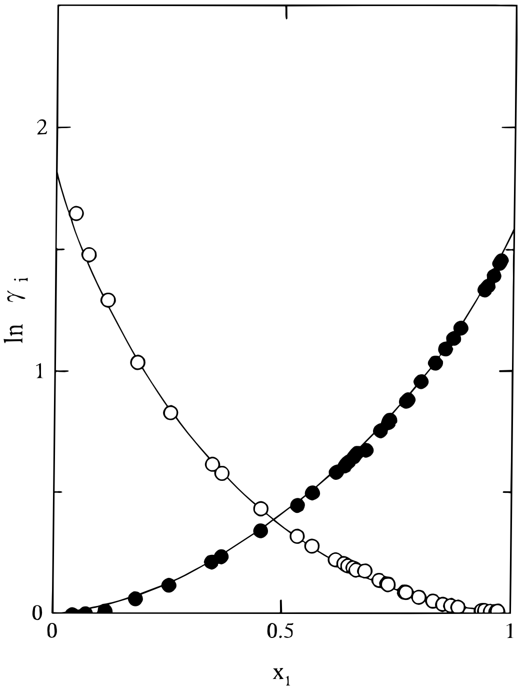

Figure 4. Activity coefficient-liquid composition diagram for 2-methyl-1-propanol (1)+ octane (2) at 373.15 K: ○, ln γ_1; ●, ln γ_2; —, Wilson equation.

$$g_{12} - g_{11} = 1.1436 \text{ kJ·mol}^{-1}$$

$$g_{12} - g_{22} = 1.2840 \text{ kJ·mol}^{-1}$$

$$\alpha = 0.47$$

The data for the isothermal system of 2-methyl-1-propanol (1) + octane (2) were best correlated using the Wilson equation and with the parameters

$$\lambda_{12} - \lambda_{11} = 2.3244 \text{ kJ·mol}^{-1}$$

$$\lambda_{12} - \lambda_{22} = 0.3520 \text{ kJ·mol}^{-1}$$

Average absolute deviations of 0.005 mole fraction in vapor composition and 0.30 kPa in vapor pressure were obtained. The maximum absolute deviations are 0.017 mole fraction and 0.76 kPa. The calculated results using each of the activity coefficient equations are shown by solid lines in Figures 1−4.

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