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Vapor–Liquid Equilibria of 1-Propanol or 2-Propanol with Octane at 101.3 kPa

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Isobaric vapor–liquid equilibria were measured for 1-propanol or 2-propanol with octane at 101.3 kPa in an equilibrium still with circulation of both the vapor and liquid phases. The results were correlated with the Wilson and nonrandom two-liquid (NRTL) equations.

Introduction

As a continuation of our studies on the vapor–liquid equilibria (VLE) of alkane + alkanol mixtures (*1–4*), the VLE of 1-propanol + octane and 2-propanol + octane at 101.3 kPa of pressure were measured using a vapor and liquid recirculating still (*1*). One set of isobaric data at the same condition is available in the literature (*5*) for 1-propanol + octane. For 2-propanol + octane, one set of isobaric VLE at 53.3 kPa of pressure is available in the literature (*6*). However, these data are not consistent according to the results of a thermodynamic consistency test by Gmehling and Onken (*7*). New reliable data seem, therefore, to be required for these systems.

Experimental Section

Materials. Octane, 1-propanol, and 2-propanol were special grade reagents, supplied by the Wako Pure Chemical Co. Ltd. 1-Propanol and 2-propanol were used after water was reduced with molecular sieves having a pore diameter of 0.3 nm. Gas-chromatographic analysis on all three materials indicated that each had a purity of at least 99.9 mol %. Table 1 compares some of the measured properties with literature values.

Procedure. The equilibrium still (*1*) with a provision for both vapor and liquid recirculation was used for the measurements. The still had a total capacity of about 100 cm^3. 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 with an accuracy of ±0.03 K.

Analysis. The equilibrium composition of the samples was determined using a Shimadzu gas chromatograph, type GC-14A, equipped with a flame ionization detector. The column packing was PEG-20M (10% polyethylene glycol on chromosorb W-AW 60/80). 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 was estimated as ±0.002.

Results and Discussion

The activity coefficients γ_i were calculated from

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

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(*8*). The vapor pressures of the pure components, P_i°, were obtained using the Antoine equation constants (Table 2). The liquid molar volumes V_i were calculated from the Rackett equation as modified by Spencer and Danner (*9*).

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

	T_b/K		ϱ(298.15 K)/(g·cm^{-3})	
material	exptl	lit. (*20*)	exptl	lit. (*20*)
1-propanol	370.26	370.301	0.799 65	0.799 60
2-propanol	355.42	355.392	0.780 86	0.781 26
octane	398.80	398.823	0.698 68	0.698 62

Table 2. Antoine Constants of the Components^a (*21*)

material	A	B	C
1-propanol	6.870 65	1438.587	−74.598
2-propanol	6.866 34	1360.183	−75.557
octane	6.043 94	1351.938	−64.030

^{a} $\log(P/\text{kPa}) = A - B/[(T/\text{K}) + C\,]$.

Table 3. Isobaric Vapor–Liquid Equilibrium Data: Temperature, T, Liquid Phase, x_1, and Vapor Phase, y_1, Mole Fractions, and Activity Coefficients, γ_i, for 1-Propanol (1) + Octane (2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
398.80	0.0000	0.0000		
375.71	0.0943	0.5285	4.6543	1.0126
373.01	0.1356	0.5767	3.8834	1.0378
369.45	0.2451	0.6331	2.6817	1.1563
368.38	0.3041	0.6539	2.3220	1.2264
368.11	0.3489	0.6617	2.0682	1.2930
367.63	0.3980	0.6685	1.8642	1.3922
367.21	0.5059	0.6894	1.5358	1.6133
367.12	0.5293	0.6953	1.4850	1.6665
366.97	0.5817	0.7059	1.3792	1.8200
366.92	0.6284	0.7174	1.2995	1.9730
366.79	0.6632	0.7198	1.2414	2.1680
366.72	0.7399	0.7418	1.1493	2.5965
366.73	0.7606	0.7504	1.1305	2.7279
366.76	0.7950	0.7682	1.1054	2.9584
366.84	0.8472	0.7885	1.0613	3.6173
367.20	0.8780	0.8112	1.0391	4.0030
367.63	0.9191	0.8502	1.0232	4.7352
368.36	0.9497	0.8945	1.0134	5.2537
370.26	1.0000	1.0000		

The VLE data for 1-propanol (1) + octane (2) and 2-propanol (1) + octane (2) are reported in Tables 3 and 4 along with the activity coefficients calculated using eq 1.

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Table 4. Isobaric Vapor–Liquid Equilibrium Data: Temperature, *T*, Liquid Phase, x_1, and Vapor Phase, y_1, Mole Fractions, and Activity Coefficients, γ_i, for 2-Propanol (1) + Octane (2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
398.80	0.0000	0.0000		
368.87	0.0853	0.6202	4.4670	1.0067
365.51	0.1178	0.6678	3.9152	1.0214
363.42	0.1475	0.6939	3.5001	1.0457
360.90	0.2148	0.7270	2.7594	1.1053
358.72	0.2958	0.7553	2.2572	1.1937
357.81	0.3833	0.7691	1.8349	1.3289
357.10	0.4215	0.7790	1.7357	1.3911
356.62	0.4768	0.7882	1.5809	1.5004
356.39	0.5177	0.7945	1.4801	1.5926
355.92	0.5919	0.8056	1.3364	1.8123
355.73	0.6257	0.8127	1.2846	1.9179
355.43	0.6757	0.8219	1.2166	2.1289
355.10	0.7194	0.8310	1.1701	2.3645
354.86	0.7807	0.8466	1.1084	2.7737
354.69	0.8400	0.8675	1.0622	3.3100
354.64	0.8923	0.8952	1.0337	3.9068
354.66	0.9309	0.9230	1.0204	4.4819
355.42	1.0000	1.0000		

Table 5. Results of Thermodynamic Consistency Tests for the 1-Propanol (1) + Octane (2) System at 101.3 kPa

test	criterion of consistency (character: +)	results of this work
method 1 (*10, 11*)	$D_y < 0.01$	0.006 (+)
method 2 (*12, 13*)	$D - J < 10\%$	−13.01(+)
method 3 (*14*)	[point test] $\delta < 5$	4.0 (+)
	[area test] $A < 3$	2.2 (+)
	[infinite dilution test] $I_1 < 30$	13.4 (+)
	$I_2 < 30$	10.2 (+)

Table 6. Results of Thermodynamic Consistency Tests for the 2-Propanol (1) + Octane (2) System at 101.3 kPa

test	criterion of consistency (character: +)	results of this work
method 1 (*10, 11*)	$D_y < 0.01$	0.004 (+)
method 2 (*12, 13*)	$D - J < 10\%$	−17.93 (+)
method 3 (*14*)	[point test] $\delta < 5$	2.9 (+)
	[area test] $A < 3$	2.6 (+)
	[infinite dilution test] $I_1 < 30$	12.4 (+)
	$I_2 < 30$	10.9 (+)

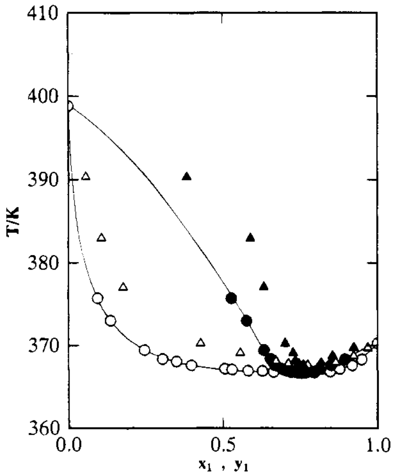

Figure 1. Temperature–composition diagram for 1-propanol (1) + octane (2) at 101.3 kPa: (○) x_1 and (●) y_1, this work; (—) Wilson equation; (△) x_1 and (▲) y_1, Timofeev et al. (*5*).

For the alkane + alcohol system, it is quite difficult to determine VLE at the infinite dilution region, especially at low concentrations of alcohol because the equilibrium temperature vibrates within a wide range at these concentration regions. Therefore, data of $x_1 < 0.05$ mole fraction were eliminated from the tables.

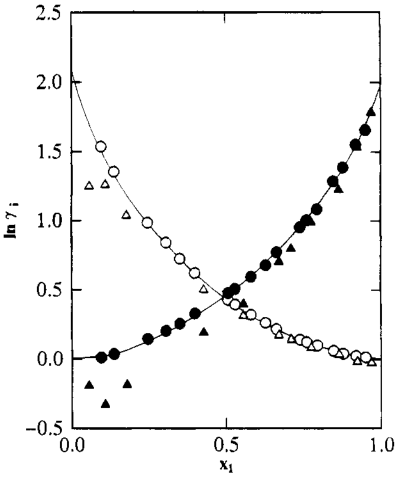

Figure 2. Activity coefficient–liquid composition diagram for 1-propanol (1) + octane (2) at 101.3 kPa: (○) ln γ_1 and (●) ln γ_2, this work; (—) Wilson equation; (△) ln γ_1 and (▲) ln γ_2, Timofeev et al. (*5*).

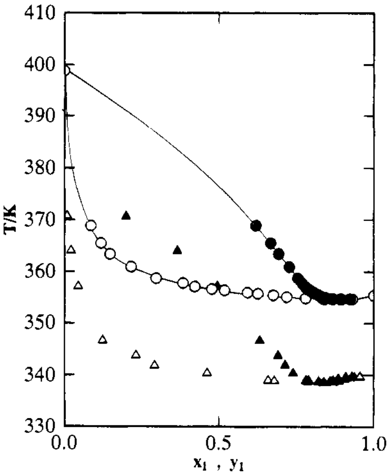

Figure 3. Temperature–composition diagram for 2-propanol (1) + octane (2) at 101.3 kPa: (○) x_1 and (●) y_1, this work; (—) NRTL equation; (△) x_1 and (▲) y_1, Prabhu et al. (*6*).

Both binary systems form a minimum boiling azeotrope. The azeotropic points were determined on the basis of the experimental VLE data, and are $x_1(\mathrm{AZ}) = 0.743$ and $T(\mathrm{AZ}) = 366.71$ K for 1-propanol (1) + octane (2), and $x_1(\mathrm{AZ}) = 0.899$ and $T(\mathrm{AZ}) = 354.63$ K for 2-propanol (1) + octane (2).

The results were tested for thermodynamic consistency by using the point test of Fredenslund et al. (*10*) and of Van Ness et al. (*11*) and the area test of Herington (*12*) and of Redlich and Kister (*13*) as described by Gmehling and Onken (*7*). In addition, the results were checked by the Kojima (*14*) method, which permits the overall check of the data by combining three tests, namely, the point test, the area test, and the infinite dilution test. The results of the consistency tests for the VLE of 1-propanol (1) + octane (2) and 2-propanol (1) + octane (2) are shown in Tables 5 and 6. Three consistency tests indicate that the VLE data for both systems are thermodynamically consistent.

The activity coefficients were correlated with the Wilson (*15*), modified Wilson (*16*), nonrandom two-liquid (NRTL) (*17*), and UNIQUAC (*18*) equations (see ref 7, Vol. I, Part 1). The parameters in each of these equations are obtained by using the Marquardt method (*19*). The sum of the squares of relative deviations in temperature and vapor composition was minimized during optimization of the parameters.

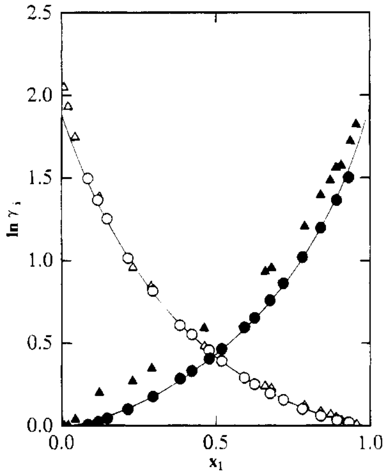

Figure 4. Activity coefficient–liquid composition diagram for 2-propanol (1) + octane (2) at 101.3 kPa: (○) ln γ_1 and (●) ln γ_2, this work; (—) NRTL equation; (△) ln γ_1 and (▲) ln γ_2, Prabhu et al. (*6*).

For 1-propanol (1) + octane (2), the Wilson equation yielded the lowest mean deviations between the experimental and calculated temperatures, 0.06 K, and vapor compositions, 0.004 mole fraction. The Wilson parameters for this system were found to be

$$\lambda_{12} - \lambda_{11} = 6.6495\ \mathrm{kJ{\cdot}mol^{-1}};\quad \lambda_{12} - \lambda_{22} = 1.2240\ \mathrm{kJ{\cdot}mol^{-1}}$$

The results for the system 2-propanol (1) + octane (2) were best correlated using the NRTL equation with the parameters

$$g_{12} - g_{11} = 3.8126\ \mathrm{kJ{\cdot}mol^{-1}};\quad g_{12} - g_{22} = 4.0552\ \mathrm{kJ{\cdot}mol^{-1}}$$

$$\alpha = 0.5618$$

Absolute average deviations of 0.002 in mole fraction and 0.07 K in temperature were observed. The calculated results using each of the activity coefficient equations are shown by solid lines in Figures 1–4.

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