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Isobaric Vapor−Liquid Equilibria of Octane + 1-Butanol, +2-Butanol, and +2-Methyl-2-propanol at 101.3 kPa

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Isobaric vapor−liquid equilibria were measured for three binary systems of 1-butanol + octane, 2-butanol + octane, and 2-methyl-2-propanol + octane at 101.3 kPa. The measurements were made in an equilibrium still with circulation of both the vapor and liquid phases. Both 1-butanol + octane and 2-butanol + octane form a minimum boiling azeotrope. 2-Methyl-2-propanol + octane is a nonazeotrope. The activity coefficients of three binary systems were best correlated with the Wilson equation.

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.*, 1992, 1994a−d, 1995a,b), the isobaric VLE of 1-butanol + octane, 2-butanol + octane, and 2-methyl-2-propanol + octane at 101.3 kPa of pressure were measured using a vapor and liquid recirculating still (Hiaki *et al.*, 1992). One set of isobaric data (Kogan *et al.*, 1959), which is consistent according to the results of thermodynamic consistency tests, at the same pressure condition and two sets of $x-P$ data at 373.2 and 383.2 K (Gierycz *et al.*, 1988) are available in the literature for 1-butanol + octane. For the 2-methyl-2-propanol + octane system, one set of isothermal data (Weidlich *et al.*, 1986) at 338.5 K and one set of $x-P$ data (Janaszewski *et al.*, 1982) at 313.2 K have been reported. No isobaric VLE data have been reported previously for 2-butanol + octane and 2-methyl-2-propanol + octane systems.

Experimental Section

Materials. Octane, 1- butanol, 2- butanol, and 2-methyl-2-propanol were special grade reagents, supplied by the Wako Pure Chemical Co. Ltd. Gas chromatographic analysis on all four materials indicated that each had a purity of at least 99.9 mol %. The purity was checked by comparing some of the measured properties with the values reported in the literature (Riddick *et al.*, 1986). The agreement was satisfactory. Normal boiling points were measured by an ebulliometer which has capacity of about 70 cm^3. Density values were determined using a vibrating tube density meter (Shibayama Kagaku SS-D-200-exp. type, Japan). The density was measured with an accuracy of $\pm 1.0 \times 10^{-5}$ g m^{-3}. The physical properties of compounds are listed in Table 1 along with literature values.

Procedure. The equilibrium still (Hiaki *et al.*, 1992) 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 (Pt 100Ω) with an accuracy of 0.03 K. A standard resistance thermometer (Chino Co. model R 800-2, Japan), based on IPTS-90, was used for this calibration.

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

	T_b/K		ρ/g cm^{-3}		
material	exptl	lit.[a]	exptl	lit.[a]	T/K
1-butanol	390.88	390.875	0.805 82	0.805 75	298.15
2-butanol	372.68	372.662	0.802 47	0.802 41	298.15
2-methyl-2-propanol	355.47	355.497	0.775 40	0.775 45	303.15
octane	398.86	398.823	0.698 68	0.698 62	298.15

[a] Riddick *et al.* (1986).

Table 2. Antoine Constants of the Components[a,b]

material	A	B	C
1-butanol	6.540 68	1335.028	−96.496
2-butanol	6.326 90	1157.363	−104.830
2-methyl-2-propanol	6.352 72	1105.198	−101.256
octane	6.043 94	1351.938	−64.030

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

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 PEG-20M (10% poly(ethylene 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

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

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 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).

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Table 3. Isobaric Vapor−Liquid Equilibrium Data, Temperature, *T*, Liquid Phase, x_1, and Vapor Phase, y_1, Mole Fractions, and Activity Coefficient, γ_i, for 1-Butanol (1) + Octane (2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
398.86	0.000	0.000		
389.12	0.077	0.290	4.0504	1.0038
387.89	0.100	0.323	3.6382	1.0161
387.29	0.110	0.340	3.5423	1.0199
385.62	0.157	0.388	3.0143	1.0477
384.89	0.178	0.408	2.8655	1.0621
383.97	0.228	0.444	2.5113	1.0923
383.38	0.272	0.458	2.2116	1.1494
383.04	0.329	0.477	1.9294	1.2158
382.63	0.403	0.500	1.6738	1.3234
382.40	0.449	0.515	1.5586	1.4023
382.35	0.485	0.528	1.4827	1.4620
382.32	0.512	0.533	1.4196	1.5274
382.32	0.541	0.542	1.3673	1.5917
382.43	0.605	0.565	1.2667	1.7552
382.57	0.646	0.581	1.2135	1.8799
382.62	0.658	0.588	1.2025	1.9116
382.86	0.712	0.612	1.1459	2.1262
383.21	0.755	0.636	1.1091	2.3168
383.80	0.810	0.674	1.0706	2.6412
385.19	0.873	0.735	1.0297	3.0869
385.59	0.887	0.752	1.0222	3.2152
386.00	0.901	0.769	1.0142	3.3704
386.25	0.908	0.782	1.0144	3.3963
387.30	0.937	0.833	1.0069	3.7400
387.56	0.943	0.846	1.0078	3.7544
390.88	1.000	1.000		

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 2-Butanol (1) + Octane (2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
398.86	0.000	0.000		
383.95	0.090	0.396	3.0403	1.0047
380.00	0.139	0.484	2.7307	1.0222
379.14	0.159	0.505	2.5566	1.0314
377.62	0.193	0.539	2.3631	1.0498
375.25	0.277	0.588	1.9540	1.1252
374.32	0.325	0.614	1.7903	1.1654
372.78	0.426	0.655	1.5394	1.2870
372.26	0.477	0.673	1.4381	1.3622
371.88	0.519	0.686	1.3656	1.4404
371.43	0.598	0.712	1.2484	1.6068
371.37	0.611	0.715	1.2301	1.6469
371.22	0.639	0.726	1.1995	1.7174
371.14	0.653	0.730	1.1839	1.7654
371.02	0.680	0.741	1.1592	1.8432
370.87	0.759	0.778	1.0955	2.1125
370.86	0.828	0.814	1.0497	2.4916
370.99	0.877	0.849	1.0293	2.8172
371.34	0.924	0.894	1.0143	3.1930
372.02	0.970	0.952	1.0046	3.5650
372.68	1.000	1.000		

The VLE data for 1-butanol + octane, 2-butanol + octane, and 2-methyl-2-propanol + octane are reported in Tables 3−5 along with the activity coefficients calculated using eq 1. The experimental data are shown graphically in Figures 1−6.

Both 1-butanol + octane and 2-butanol + octane systems form a minimum boiling azeotrope. The azeotropic points were determined on the basis of the experimental VLE data and are $x_1(\mathrm{AZ}) = 0.543$ and $T(\mathrm{AZ}) = 382.31$ K for 1-butanol (1) + octane (2) and $x_1(\mathrm{AZ}) = 0.798$ and $T(\mathrm{AZ}) = 370.84$ K for 2-butanol (1) + octane (2). For the system 2-methyl-2-propanol (1) + octane (2), the experimental VLE data indicate a nonazeotrope.

The results were tested for thermodynamic consistency by using the point test of Fredenslund *et al.* (1977) and of

Table 5. Isobaric Vapor−Liquid Equilibrium Data, Temperature, *T*, Liquid Phase, x_1, and Vapor Phase, y_1, Mole Fractions, and Activity Coefficient, γ_i, for 2-Methyl-2-Propanol (1) + Octane (2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
398.86	0.000	0.000		
374.52	0.103	0.553	2.7867	1.0037
371.37	0.135	0.605	2.5682	1.0185
366.10	0.223	0.687	2.1044	1.0688
365.88	0.229	0.689	2.0711	1.0773
362.80	0.336	0.739	1.6876	1.1669
362.27	0.354	0.744	1.6434	1.1961
360.33	0.459	0.777	1.4175	1.3344
359.28	0.532	0.797	1.3045	1.4538
358.54	0.592	0.814	1.2297	1.5698
357.60	0.677	0.838	1.1463	1.7820
357.12	0.728	0.854	1.1054	1.9474
356.81	0.764	0.866	1.0807	2.0767
356.47	0.806	0.882	1.0568	2.2513
356.28	0.830	0.893	1.0447	2.3682
356.04	0.867	0.909	1.0275	2.5895
355.77	0.913	0.934	1.0132	2.8888
355.55	0.963	0.968	1.0024	3.4267
355.52	0.971	0.974	1.0021	3.5001
355.49	0.983	0.984	1.0016	3.6118
355.50	0.984	0.985	1.0008	3.6633
355.47	1.000	1.000		

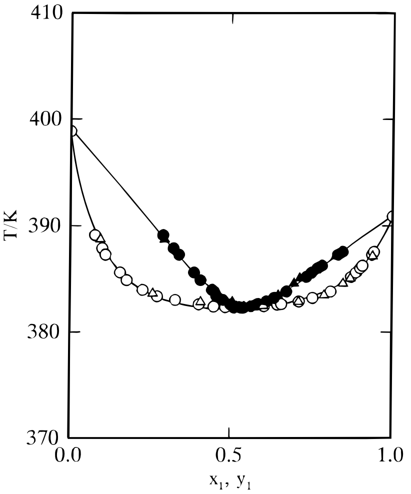

Figure 1. Temperature−composition diagram for 1-butanol (1) + octane (2) at 101.3 kPa: (○) x_1 and (●) y_1, this work; (—) Wilson equation;(△) x_1 and (▲) y_1, Kogan et al. (1959).

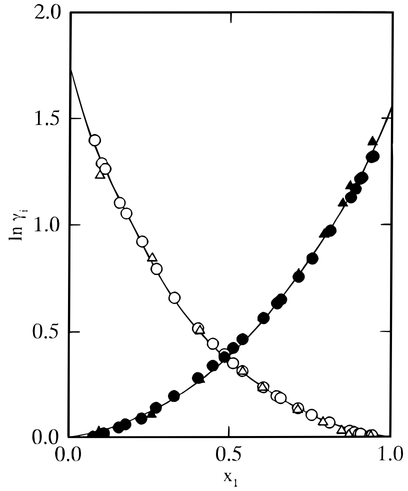

Figure 2. Activity coefficient−liquid composition diagram for 1-butanol (1) + octane (2) at 101.3 kPa: (○) ln γ_1 and (●) ln γ_2, this work; (—) Wilson equation; (△) ln γ_1 and (▲) ln γ_2, Kogan et al. (1959).

Table 6. Results of the Consistency Tests for the VLE of 1-Butanol (1) + Octane (2), 2-Butanol (1) + Octane (2), and 2-Methyl-2-propanol (1) + Octane (2) at 101.3 kPa

test	criterion of consistency (character: +)	1-butanol (1) + octane (2)	2-butanol (1) + octane (2)	2-methyl-2-propanol (1) + octane (2)
method 1[a,b]	$\Delta y < 0.01$	0.004 (+)	0.003 (+)	0.003 (+)
method 2[c,d]	$D < 10\%$	−6.5 (+)	−11.0 (+)	−12.7 (+)
method 3[e]				
[point Test]	$\delta < 5$	2.1 (+)	2.6 (+)	3.0 (+)
[area Test]	$A < 3$	1.9 (+)	1.8 (+)	1.7 (+)
[infinite dilution test]	$I_1 < 30$	7.3 (+)	12.8 (+)	15.1 (+)
	$I_2 < 30$	0.9 (+)	8.3 (+)	3.1 (+)

[a] Fredenslund *et al.* (1977). [b] Van Ness *et al.* (1973). [c] Herington (1951). [d] Redlich and Kister (1948). [e] Kojima *et al.* (1990).

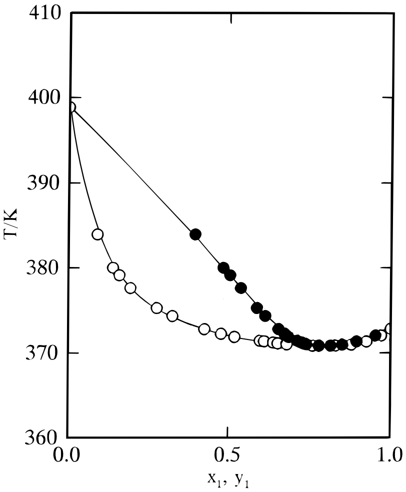

Figure 3. Temperature−composition diagram for 2-butanol (1) + octane (2) at 101.3 kPa: (○) x_1 and (●) y_1, this work; (—) Wilson equation.

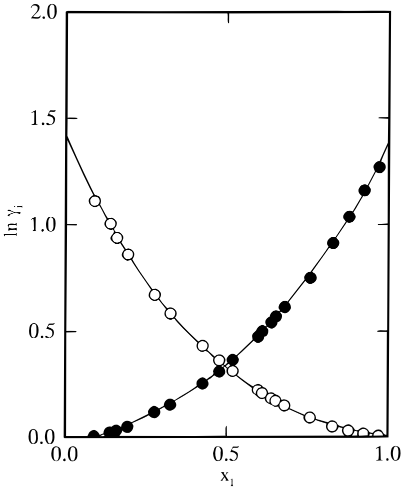

Figure 4. Activity coefficient−liquid composition diagram for 2-butanol (1) + octane (2) at 101.3 kPa: (○) ln γ_1 and (●) ln γ_2, this work; (—) Wilson equation.

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). In addition, the results were checked by the Kojima method (Kojima *et al.*, 1990), 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-butanol (1) + octane (2), 2-butanol (1) + octane (2), and 2-methyl-2-propanol (1) + octane (2) are shown in Table 6. The results from the three consistency tests indicate that the VLE data for three binary systems are thermodynamically consistent.

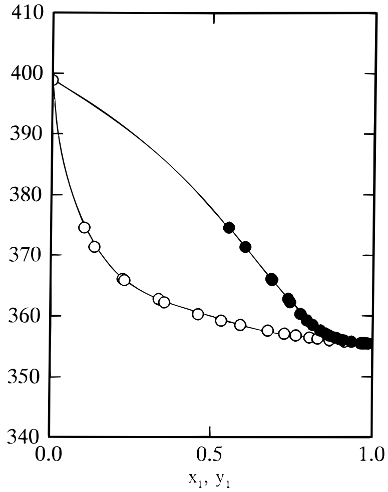

Figure 5. Temperature−composition diagram for 2-methyl-2-propanol (1) + octane (2) at 101.3 kPa: (○) x_1 and (●) y_1, this work; (—) Wilson equation.

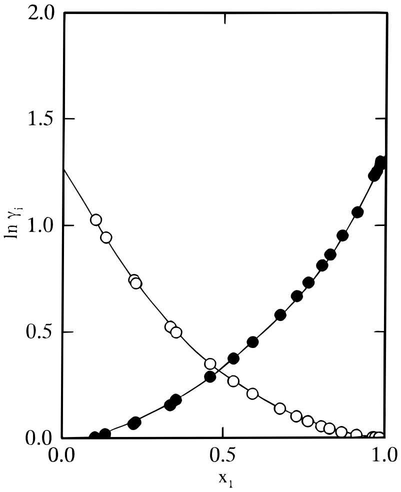

Figure 6. Activity coefficient−liquid composition diagram for 2-methyl-2-propanol (1) + octane (2) at 101.3 kPa: (○) ln γ_1 and (●) ln γ_2, this work; (—) Wilson equation.

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 deviations in temperature and vapor composition was minimized during optimization of the parameters.

For the experimental three binary systems of 1-butanol (1) + octane (2), 2-butanol (1) + octane (2), and 2-methyl-2-propanol (1) + octane (2), the Wilson equation yielded

Table 7. Wilson Parameters and Deviations between Calculated and Experimental Vapor Phase Mole Fractions, Δy_1, and Temperatures, ΔT, for 1-Butanol (1) + Octane (2), 2-Butanol (1) + Octane (2), and 2-Methyl-2-propanol (1) + Octane (2) at 101.3 kPa[a]

Wilson parameters/ J mol^{-1}		deviation			
		av		max	
		Δy_1	ΔT/K	Δy_1	ΔT/K
1-Butanol (1) + Octane (2) system					
$\lambda_{12} - \lambda_{11}$	5546.26	0.003	0.07	0.008	0.16
$\lambda_{12} - \lambda_{22}$	950.55				
2-Butanol (1) + Octane (2) system					
$\lambda_{12} - \lambda_{11}$	4285.18	0.002	0.06	0.007	0.23
$\lambda_{12} - \lambda_{22}$	925.09				
2-Methyl-2-propanol (1) + Octane (2) system					
$\lambda_{12} - \lambda_{11}$	4119.14	0.002	0.10	0.007	0.27
$\lambda_{12} - \lambda_{22}$	529.58				

[a] $\Delta y_1 = \sum^N |(y_{1,\mathrm{obs}} - y_{1,\mathrm{calc}})|/N$, $\Delta T = \sum^N |(T_{\mathrm{obs}} - T_{\mathrm{calc}})|/N$, N = number of data points.

the lowest mean deviations between the experimental and calculated activity coefficients. The parameter values and average and maximum absolute deviations using the Wilson equation are shown in Table 7. The calculated results of the Wilson equation are shown by solid lines in Figures 1−6.

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