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Isobaric Vapor–Liquid Equilibria for Three Binary Systems of 2-Butanone with 3-Methyl-1-butanol, 1-Butanol, or 2-Butanol

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A new apparatus for measuring vapor–liquid equilibria was constructed. Vapor–liquid equilibria for the three binary systems of 2-butanone with 3-methyl-1-butanol, 1-butanol, or 2-butanol were measured with the present recirculation still at 100.00 kPa of pressure. The isobaric vapor–liquid equilibrium data obtained were correlated with an equation of state and with the Wilson equation.

Introduction

We have previously reported vapor–liquid equilibrium (VLE) data obtained with several types of ebulliometers for measuring boiling points (*1–5*).

In the present study, a new apparatus for measuring VLE was constructed. Isobaric VLE data for the three binary systems of 2-butanone with 3-methyl-1-butanol, 1-butanol, or 2-butanol were measured at 100.00 kPa. VLE data for those systems have been published previously by Miller et al. (*6*), Amick et al. (*7*), and Aristovich et al. (*8*). However, there are significant differences between these measurements (*6–8*).

The data were successfully correlated with our pseudocubic equation of state (*9–11*) and the Wilson equation (*12*), with vapor-phase corrections according to Hayden and O'Connell (*13*).

Experimental Section

The present experimental apparatus for measuring vapor–liquid equilibria is schematically shown in Figure 1. The recirculation still is entirely constructed by borosilicate glass. The main parts are a boiling still (B), two condensers (C), two cocks (K), an overflow tube (O), a condensate chamber (S), and a thermometer (T). The structure of the boiling still (B) is essentially the same as the previous ones (*1–5*). The amount of solution required is about 45 cm^3 per determination. The reliability of the present apparatus was confirmed for the methanol–water system at atmospheric pressure. The experimental data obtained agreed fairly well with the data of Uchida and Kato (*14*).

At the start of the experiments, cocks K_1 and K_2 are closed. A prepared solution is charged to the boiling still (B) from the top of the condenser. The boiling vapor–liquid mixture flashes to the thermometer well in the boiling still. The vapor is condensed and introduced to the condensate chamber (S). The condensed vapor in the condensate chamber (S) recirculates to the boiling still (B) through the overflow tube (O).

After attainment of steady state, equilibrium temperatures were measured with a Hewlett-Packard 2804A quartz thermometer calibrated by the triple point of water in a reference cell with an accuracy of ±0.01 K. The steady state was confirmed with the constancy of the equilibrium temperature of ±0.01 K. The atmospheric pressures were evaluated from the boiling point temperatures of water. In order to analyze equilibrium compositions, both samples of liquid and vapor phases were individually taken from cocks K_1 and K_2, respectively. The analysis of the equilibrium composition was carried out with a Hitachi GC-163 gas chromatograph equipped with a 3.0-m dioctyl sebacate (DOS) 25% chromosorb W column. Helium was used as a carrier gas with the flow rate of 25 cm^3/min. The column temperature was about 373.15 K, and the current on thermal conductivity detector (TCD) was 100 mA. The total reproducibility of the composition analysis was ±0.001 mole fraction.

Special-grade reagents were supplied by Wako Pure Chemical Industries, Ltd. 2-Butanone was used without further purification. 3-Methyl-1-butanol and 2-butanol were purified by fraction distillation in a 30-plate Oldershaw column. The physical properties of the materials used are listed in Table I.

Results

The experimental equilibrium temperatures were corrected from the raw data to those at 100.00 kPa of pressure, using the linear approximation of the derivatives of temperature with pressure for the mixture, similar to the previous work (*2*). The experimental isobaric VLE data are given in Tables II–IV and shown in Figures 2–4. For the 2-butanone + 3-methyl-1-butanol system, large differences were observed between the present data and those of Miller et al. (*6*), as shown in Figure 2. For the 2-butanone + 1-butanol system, substantial differences were observed between the present data and those of Aristovich et al. (*8*), as shown in Figure 3. For the 2-butanone + 2-butanol system, the present experimental data agreed fairly well with the data of Amick et al. (*7*), as shown in Figure 4. For this system, large differences were observed between the present data and those of Miller et al. (*6*).

The three-parameter pseudocubic equation of state previously proposed by us (*9–11*) and the Wilson equation (*12*) with

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Table I. Normal Boiling Points T_b, Densities ρ, and Refractive Indexes n_D of the Materials Used

material	T_b/K exptl	T_b/K lit.	ρ(298.15 K)/(g cm^{-3}) exptl	ρ(298.15 K)/(g cm^{-3}) lit.	n_D(298.15 K) exptl	n_D(298.15 K) lit.
2-butanone	352.67	352.75 (*22*)	0.7996	0.7995 (*22*)	1.3763	1.3761 (*22*)
3-methyl-1-butanol	403.53	403.65 (*20*)	0.8069	0.8070 (*20*)	1.4053	1.4052 (*20*)
1-butanol	390.80	390.85 (*21*)	0.8056	0.8057 (*21*)	1.3976	1.3974 (*21*)
2-butanol	372.59	372.65 (*20*)	0.8023	0.8026 (*21*)	1.3952	1.3950 (*20*)

Table II. Experimental Vapor–Liquid Equilibrium Data, Liquid-Phase (X_1) and Vapor-Phase (Y_1) Mole Fractions, and Equilibrium Temperatures T, for the 2-Butanone (1) + 3-Methyl-1-butanol (2) System at 100.00 kPa

X_1	Y_1	T/K	X_1	Y_1	T/K
0.000	0.000	403.39	0.456	0.818	372.05
0.053	0.172	398.92	0.573	0.887	366.06
0.110	0.333	394.33	0.714	0.934	361.05
0.169	0.484	389.29	0.853	0.971	356.45
0.253	0.625	383.43	0.926	0.986	354.18
0.346	0.741	377.29	1.000	1.000	352.26

Table III. Experimental Vapor–Liquid Equilibrium Data, Liquid-Phase (X_1) and Vapor-Phase (Y_1) Mole Fractions, and Equilibrium Temperatures T, for the 2-Butanone (1) + 1-Butanol (2) System at 100.00 kPa

X_1	Y_1	T/K	X_1	Y_1	T/K
0.000	0.000	390.41	0.512	0.788	365.23
0.058	0.170	386.45	0.629	0.849	361.77
0.126	0.325	382.42	0.750	0.906	358.28
0.215	0.471	378.13	0.873	0.953	355.39
0.294	0.587	374.08	0.939	0.978	353.75
0.399	0.703	369.36	1.000	1.000	352.26

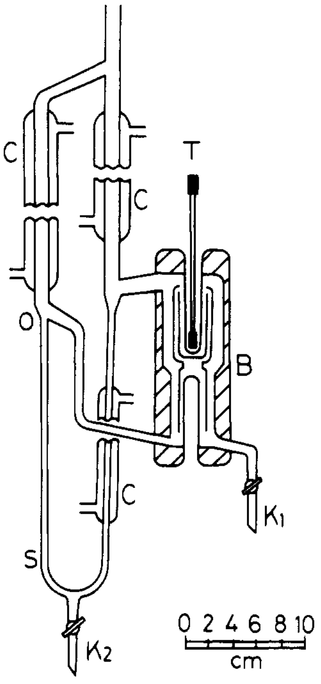

Figure 1. Experimental apparatus for measuring isobaric vapor–liquid equilibria: (B) boiling still; (C) condenser; (K) cock; (O) overflow tube; (S) condensate chamber; (T) quartz thermometer.

Table IV. Experimental Vapor–Liquid Equilibrium Data, Liquid-Phase (X_1) and Vapor-Phase (Y_1) Mole Fractions, and Equilibrium Temperatures T, for the 2-Butanone (1) + 2-Butanol (2) System at 100.00 kPa

X_1	Y_1	T/K	X_1	Y_1	T/K
0.000	0.000	372.23	0.545	0.693	358.93
0.079	0.145	369.83	0.658	0.775	357.05
0.166	0.277	367.53	0.770	0.856	355.27
0.250	0.398	365.27	0.889	0.928	353.72
0.348	0.506	363.15	0.944	0.964	353.02
0.438	0.609	360.81	1.000	1.000	352.26

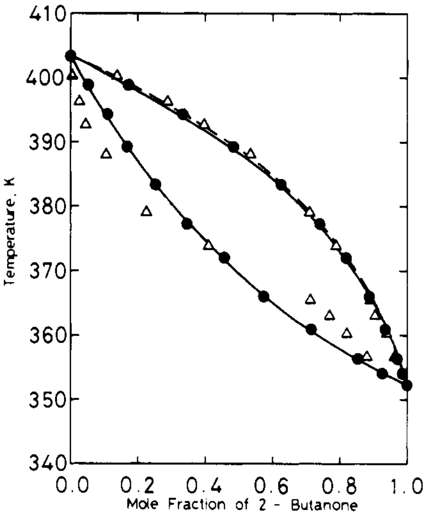

Figure 2. Experimental vapor-liquid equilibria for the 2-butanone + 3-methyl-1-butanol system: (●) this work, 100.00 kPa; (△) Miller et al. (*6*), 101.33 kPa; (—) calculated by the pseudocubic equation of state; (- - -) calculated by the Wilson equation.

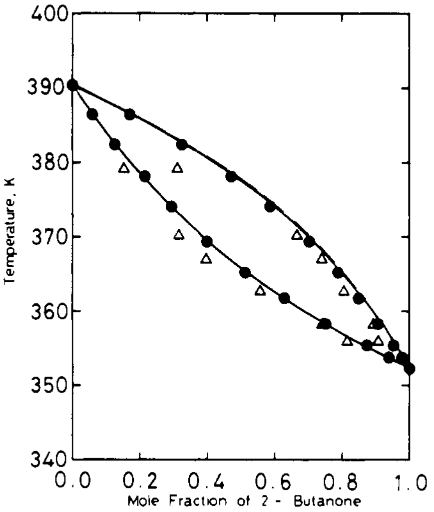

Figure 3. Experimental vapor-liquid equilibria for the 2-butanone + 1-butanol system: (●) this work, 100.00 kPa; (△) Aristovich et al. (*8*), 101.33 kPa; (—) calculated by the pseudocubic equation of state; (- - -) calculated by the Wilson equation.

vapor-phase corrections was successfully applied for the data reduction in the present study.

The pseudocubic equation of state used in the present study and the procedure to determine the binary interaction parameters k_{ij} and l_{ij} were the same as described previously (*9–11*). The mean absolute deviations of equilibrium temperature and vapor composition between the experimental data and calculated ones are shown in Table V. In the present calculations, the critical constants T_c, P_c, and V_c were obtained from Reid et al. (*15*). In Figures 2–4, the solid lines show the results calculated by the pseudocubic equation of state.

The VLE data were further correlated by the Wilson equation (*12*). The vapor-phase correction was made with the method of Hayden and O'Connell (*13*), using the parameters shown in

Table V. Interaction Parameters of the Pseudocubic Equation of State k_{ij} and l_{ij}, the Wilson Parameters Λ_{ij}, and Mean Absolute Deviations in Equilibrium Temperature ΔT and Vapor-Phase Composition ΔY_1 Obtained from the VLE Data[a]

	pseudocubic equation of state						Wilson equation					
system	k_{ij}	l_{ij}	ΔY_1	N_+	N_-	ΔT/K	Λ_{12}	Λ_{21}	ΔY_1	N_+	N_-	ΔT/K
I	0.0310	0.0396	0.005	6	6	0.16	1.8082	0.3478	0.006	3	9	0.19
II	0.0291	0.0275	0.008	3	9	0.13	1.4064	0.4898	0.010	2	10	0.13
III	0.0971	0.1000	0.009	2	10	0.06	1.4112	0.4724	0.011	2	10	0.08

[a] Systems: I, 2-butanone (1) + 3-methyl-1-butanol (2); II, 2-butanone (1) + 1-butanol (2); III, 2-butanone (1) + 2-butanol (2). Λ_{ij} is defined in ref 12. $\Delta Y_1 = \sum|Y_{1,\mathrm{calc}} - Y_{1,\mathrm{exptl}}|/N$; $\Delta T = \sum|T_{\mathrm{calc}} - T_{\mathrm{exptl}}|/N$ (N, number of experimental points); N_+, number of data points for positive deviation on Y_1; N_-, number of data points for negative deviation on Y_1.

Table VI. Parameters Used for Vapor-Phase Correction: Critical Pressure P_c, Critical Temperature T_c, Molar Volume V, Mean Radius of Gyration R', Molecular Dipole Moment μ, and Association Parameter η

material	P_c/MPa	T_c/K	$V^a/(10^{-3}\ \mathrm{m^3\ mol^{-1}})$	R'/Å	μ/D	η^d
2-butanone	4.154 (*15*)	535.6 (*15*)	0.0902	3.139 (*23*)	3.3 (*15*)	0.90 (*23*)
3-methyl-1-butanol	3.850 (*15*)	579.5 (*15*)	0.1093	3.504[b]	1.8 (*15*)	2.20[c]
1-butanol	4.418 (*15*)	562.9 (*15*)	0.0920	3.225 (*23*)	1.8 (*15*)	2.20 (*23*)
2-butanol	4.195 (*15*)	536.0 (*15*)	0.0924	3.182 (*23*)	1.7 (*15*)	1.75 (*23*)

[a] Experimental data. [b] Evaluated from its parachor. [c] Assumed as 2.20. [d] $\eta_{12} = (\eta_{11} + \eta_{22})/2$.

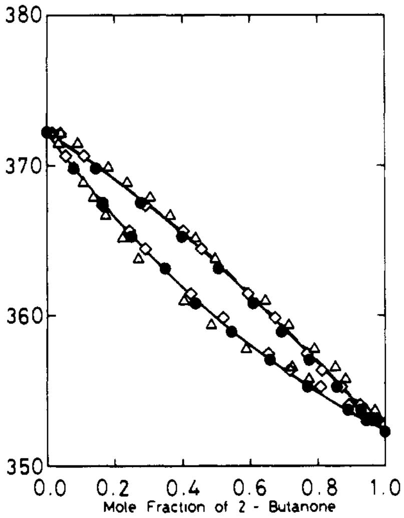

Figure 4. Experimental vapor–liquid equilibria for the 2-butanone + 2-butanol system: (●) this work, 100.00 kPa; (△) Miller et al. (*6*), 101.33 kPa; (◇) Amick et al. (*7*), 101.33 kPa; (—) calculated by the pseudocubic equation of state; (- - -) calculated by the Wilson equation.

Table VI. The association parameters of unlike molecules were estimated as the arithmetic mean of the constituent pure components. The Wilson parameters Λ_{12} and Λ_{21} were determined to minimize the sum of squares of the deviations in boiling point temperatures. The vapor pressures of the pure components were calculated by using the Antoine equation. For 2-butanone, 1-butanol, and 2-butanol, the Antoine constants were obtained by comparing the vapor pressure data of Boublik et al. (*16*) with the vapor pressure data of Ambrose et al. (*17*), Kemme and Kreps (*18*), and Biddiscombe et al. (*19*), respectively. For 3-methyl-1-butanol, the Antoine constants were obtained from the TRC-Thermodynamic Tables (*20*). Table V shows the Wilson parameters obtained and their deviations. The broken lines in Figures 2–4 show the calculation results by the Wilson equation.

Conclusions

In the present study, a new apparatus for measuring vapor–liquid equilibria was constructed. The isobaric vapor–liquid equilibrium data for the three binary systems made of 2-butanone with 3-methyl-1-butanol, 1-butanol, or 2-butanol at 100.00 kPa of pressure were measured with the present recirculation still. The vapor–liquid equilibrium data obtained in the present study were successfully correlated with the pseudocubic equation of state and with the Wilson equation.

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Registry No. 2-Butanone, 78-93-3; 3-methyl-1-butanol, 123-51-3; 1-butanol, 71-36-3; 2-butanol, 78-92-2.

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