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Vapor−Liquid Equilibria of Ethanol + Octane at 343.15 K and 1-Propanol + Octane at 358.15 K

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Isothermal vapor−liquid equilibria were measured for ethanol + octane at 343.15 K and 1-propanol + octane at 358.15 K. The measurements were made in a still with the aid of a computer for control of the temperature and measurement of the total pressure. The results were best correlated with the Wilson equation for the system of ethanol + octane and with the nonrandom two-liquid (NRTL) equations for the 1-propanol + octane system.

Introduction

In the present study, vapor−liquid equilibria (VLE) were measured for ethanol + octane at 343.15 K and 1-propanol + octane at 358.15 K, using an apparatus which was described in our previous work (*1*), with computer control of the temperature and the measurement of total pressure. For the ethanol + octane system, four sets of isothemal VLE data, at 318.15, 328.15, 338.15, and 348.15 K, are available in the literature (*2*). The isothermal VLE for the 1-propanol + octane system have been reported at 363.15 K in the literature (*3*).

Experimental Section

Materials. Octane, ethanol, and 1-propanol used in this work were special grade reagents, supplied by the Wako Pure Chemical Co. Ltd. Ethanol and 1-propanol were used after their minute water content was removed with molecular sieves having a pore diameter of 0.3 nm. A 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 data.

Procedure. The isothermal VLE apparatus and associated computer, which was described in our previous work (*1*), was used for the measurements. The equilibrium still (*4*) with a provision for both vapor and liquid recirculation was used for the determination of VLE. The still with a total capacity of about 100 cm^3 was used.

The ebulliometer was used for the determination of the total pressure. The platinum resistance thermometers placed in both the equilibrium still and the ebulliometer were linked with the 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. After establishing a steady state 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 the four solenoid valves and the vacuum pump.

The temperature was measured with a calibrated platinum resistance thermometer with an accuracy of 0.03 K.

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

material	T_b/K		ρ(298.15 K)/(g·cm^{-3})	
	exptl	lit. (*19*)	exptl	lit. (*19*)
ethanol	351.44	351.443	0.784 93	0.784 93
1-propanol	370.26	370.301	0.799 65	0.799 60
octane	398.80	398.823	0.698 68	0.698 62

Table 2. Antoine Constants of the Components[a] (*20*)

material	*A*	*B*	*C*
ethanol	7.242 22	1595.811	−46.702
1-propanol	6.870 65	1438.587	−74.598
octane	6.043 94	1351.938	−64.030

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

Table 3. Isothermal Vapor−Liquid Equilibrium Data, Vapor Pressure, *P*, Liquid Phase, x_1, and Vapor Phase, y_1, Mole Fractions, and Activity Coefficient, γ_i, for Ethanol (1) + Octane (2) at 343.15 K

P/kPa	x_1	y_1	γ_1	γ_2
15.951	0.0000	0.0000		
60.295	0.0830	0.7381	7.4719	1.0640
64.986	0.1114	0.7594	6.1610	1.0857
66.999	0.1311	0.7677	5.4517	1.1047
69.835	0.1807	0.7813	4.1905	1.1490
72.133	0.2243	0.7891	3.5185	1.2081
72.971	0.2601	0.7904	3.0736	1.2729
74.505	0.3225	0.7980	2.5535	1.3676
74.962	0.3514	0.7988	2.3599	1.4314
75.453	0.3859	0.8026	2.1727	1.4931
76.241	0.4521	0.8053	1.8796	1.6675
76.791	0.5206	0.8079	1.6490	1.8938
76.892	0.5793	0.8131	1.4932	2.1032
77.243	0.6380	0.8180	1.3699	2.3917
77.408	0.6699	0.8220	1.3137	2.5714
77.718	0.7310	0.8256	1.2138	3.1046
78.116	0.7818	0.8318	1.1490	3.7116
78.244	0.8124	0.8386	1.1164	4.1516
78.300	0.8392	0.8441	1.0885	4.6841
78.268	0.8653	0.8531	1.0663	5.2713
77.715	0.9072	0.8723	1.0325	6.6182
77.030	0.9380	0.8970	1.0178	7.9408
72.226	1.0000	1.0000		

The vapor pressure, *P*, of the sample was determined by the measurement of the boiling point of water on the basis of the published data of the vapor pressure of water (*5*). The accuracy of vapor pressure measurements is estimated to be 0.03 kPa.

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Table 4. Isothermal Vapor–Liquid Equilibrium Data, Vapor Pressure, *P*, Liquid Phase, x_1, and Vapor Phase, y_1, Mole Fractions, and Activity Coefficient, γ_i, for 1-Propanol (1) + Octane (2) at 358.15 K

P/kPa	x_1	y_1	γ_1	γ_2
27.991	0.0000	0.0000		
52.230	0.0649	0.4849	6.2946	1.0126
57.314	0.0933	0.5358	5.2954	1.0305
61.074	0.1315	0.5722	4.2673	1.0550
64.344	0.1737	0.5981	3.5520	1.0961
65.403	0.1901	0.6040	3.3299	1.1195
66.239	0.2112	0.6116	3.0724	1.1415
69.001	0.2859	0.6369	2.4586	1.2270
70.357	0.3469	0.6534	2.1179	1.3056
71.500	0.4160	0.6624	1.8185	1.4448
72.226	0.4545	0.6693	1.6982	1.5303
72.515	0.4860	0.6756	1.6091	1.5997
72.773	0.5318	0.6881	1.5025	1.6953
73.358	0.5842	0.6945	1.3911	1.8847
73.812	0.6533	0.7078	1.2751	2.1761
73.957	0.6848	0.7151	1.2312	2.3390
73.935	0.7410	0.7314	1.1630	2.6851
73.690	0.7821	0.7481	1.1231	2.9862
73.424	0.8171	0.7626	1.0917	3.3438
73.007	0.8371	0.7725	1.0733	3.5800
73.787	0.8524	0.7823	1.0641	3.7719
72.324	0.8895	0.8098	1.0487	4.3814
70.893	0.9266	0.8500	1.0358	5.1140
68.357	0.9622	0.9004	1.0193	6.3836
62.849	1.0000	1.0000		

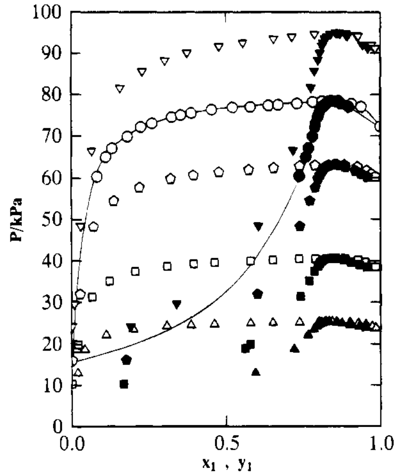

Figure 1. Pressure–composition diagram for ethanol (1) + octane (2) at 343.15 K: (○) x_1 and (●) y_1, this work; (—) Wilson equation; (△) x_1 and (▲) y_1 at 318.15 K, (□) x_1 and (■) y_1 at 328.15, (⬠) x_1 and (⬟) y_1 at 338.15, (▽) x_1 and (▼) y_1 at 348.15 K, Boublikova et al. (*2*).

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

Results and Discussion

The activity coefficients γ_i were calculated using the following rigorous equation:

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

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 (*6*). The vapor pressures of the pure components, P_i°, were obtained using the Antoine equation constants (Table 2). The liquid molar volumes

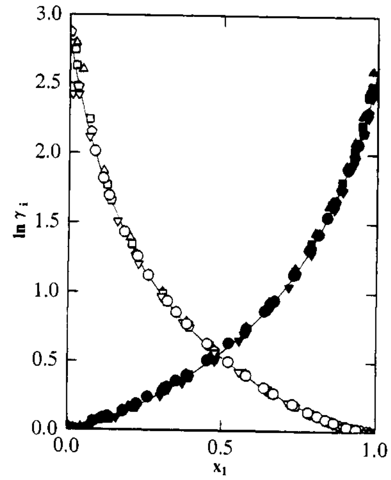

Figure 2. Activity coefficient–liquid composition diagram for ethanol (1) + octane (2) at 343.15 K: (○) ln γ_1 and (●) ln γ_2, this work; (—) Wilson equation; (△) ln γ_1 and (▲) in γ_2 at 318.15 K, (□) ln γ_1 and (■) ln γ_2 at 328.15 K, (⬠) ln γ_1 and (⬟) ln γ_2 at 338.15 K, (▽) ln γ_1 and (▼) ln γ_2 at 348.15 K, Boublikova et al. (*2*).

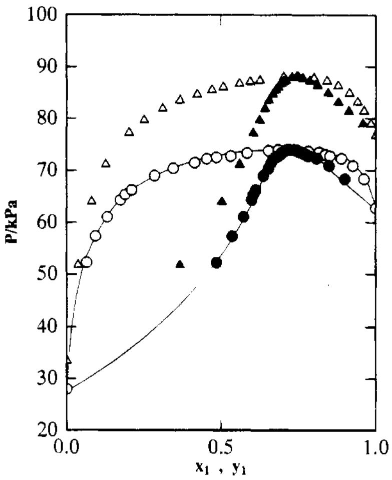

Figure 3. Pressure–composition diagram for 1-propanol (1) + octane (2) at 358.15 K: (○) x_1 and (●) y_1, this work, (—) NRTL equation; (△) x_1 and (▲) y_1 at 363.15 K, Berro (*3*).

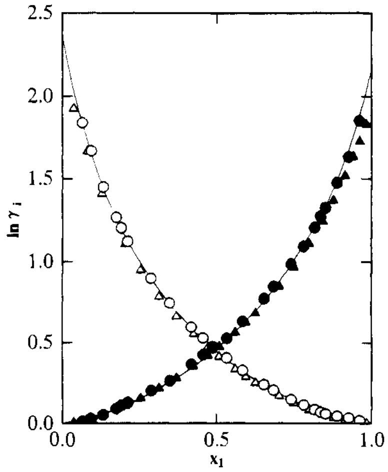

Figure 4. Activity coefficient–liquid composition diagram for 1-propanol (1) + octane (2) at 358.15 K: (○) ln γ_1 and (●) ln γ_2, this work; (—) NRTL equation; (△) ln γ_1 and (▲) ln γ_2 at 363.15 K, Berro (*3*).

V_i were calculated from the Rackett equation as modified by Spencer and Danner (*7*).

The VLE data for ethanol (1) + octane (2) at 343.15 K and 1-propanol (1) + octane (2) at 358.15 K are reported in Tables 3 and 4 along with the activity coefficients calculated using eq 1. Both binary systems form a maximum pressure azeotrope. The azeotropic points were determined on the basis of the experimental VLE data, and are $x_1(\mathrm{AZ}) = 0.846$ and $P(\mathrm{AZ}) = 78.31$ kPa for ethanol (1) + octane (2), and $x_1(\mathrm{AZ}) = 0.726$ and $P(\mathrm{AZ}) = 74.01$ kPa for 1-propanol (1) + octane (2).

The experimental data were tested for thermodynamic consistency by using the point test of Fredenslund et al. (*8*) and of Van Ness et al. (*9*) and the area test of Herington (*10*) and of Redlich and Kister (*11*) as described by Gmehling and Onken (*12*). The data were also checked by the Kojima (*13*) 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 three consistency tests indicate that the experimental data for both systems are thermodynamically consistent.

The activity coefficients were correlated with the Wilson (*14*), modified Wilson (*15*), nonrandom two-liquid (NRTL) (*16*), and UNIQUAC (*17*) equations. The parameters in each of these equations are obtained by using the Marquardt method (*18*). The sum of the squares of relative deviations in temperature and vapor composition was minimized during optimization of the parameters.

For ethanol (1) + octane (2), the Wilson equation yielded the lowest mean deviations between the experimental and calculated pressures, 0.17 kPa, and vapor compositions, 0.003 mole fraction. The Wilson parameters for this system are found to be

$$\lambda_{12} - \lambda_{11} = 8.7063\ \mathrm{kJ{\cdot}mol^{-1}}$$

$$\lambda_{12} - \lambda_{22} = 2.0898\ \mathrm{kJ{\cdot}mol^{-1}}$$

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

$$g_{12} - g_{11} = 4.4197\ \mathrm{kJ{\cdot}mol^{-1}}$$

$$g_{12} - g_{22} = 4.9505\ \mathrm{kJ{\cdot}mol^{-1}}$$

$$\alpha = 0.547$$

and an absolute average deviation of 0.003 in mole fraction and of 0.18 kPa in pressure. The calculated results using each of the activity coefficient equations are shown by solid lines in Figures 1–4.

Literature Cited

(1) Hiaki, T.; Takahashi, K.; Tsuji, T.; Hongo, M.; Kojima, K. *J. Chem. Eng. Data,* in press.
(2) Boublikova, L.; Lu, B. C.-Y. *J. Appl. Chem.* **1969**, *19*, 89.
(3) Berro, C. *Int. Data Ser., Sel. Data Mixtures, Ser. A* **1987**, *1*, 73.
(4) Hiaki, T.; Yamato, K.; Kojima, K. *J. Chem. Eng. Data* **1992**, *37*, 203.
(5) Bridgeman, O. C.; Aldrich, E. W. *J. Heat Transfer* **1964**, 86, 279.
(6) Hayden, J. G.; O'Connell, J. P. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 209.
(7) Spencer, C. F.; Danner R. P. *J. Chem. Eng. Data* **1972**, *17*, 236.
(8) Fredenslund, A.; Gmehling, J.; Rasmussen, P. *Vapor-Liquid Equilibria Using UNIFAC*; Elsevier: Amsterdam, 1977.
(9) Van Ness, H. C.; Byer, S. M.; Gibbs, R. E. *AIChE J.* **1973**, *19*, 238.
(10) Herington, E. F. G. *J. Inst. Pet.* **1951**, *37*, 457.
(11) Redlich, O.; Kister, A. T. *Ind. Eng. Chem.* **1948**, *40*, 345.
(12) Gmehling, J.; Onken, U. *Vapor-Liquid Equilibrium Data Collection;* Chemistry Data Series; DECHEMA: Frankfurt, 1977.
(13) Kojima, K.; Moon, H. M.; Ochi, K. *Fluid Phase Equilib.* **1990**, *56*, 269.
(14) Wilson, G. M. *J. Am. Chem. Soc.* **1964**, *86*, 127.
(15) Tsuboka, T.; Katayama, T. *J. Chem. Eng. Jpn.* **1975**, *8*, 181.
(16) Renon, H.; Prausnitz, J. M. *AIChE J.* **1968**, *14*, 135.
(17) Abrams, D. S.; Prausnitz, J. M. *AIChE J.* **1975**, *21*, 116.
(18) Marquardt, D. W. *J. Soc. Ind. Appl. Math.* **1963**, *11*, 431.
(19) Riddick, J. A.; Bunger, W.; Sakano, T. K. *Organic Solvents Physical Properties and Methods of Purification,* 4th ed.; John Wiley & Sons: New York, 1986.
(20) Boublik, T.; Fied, V.; Hala, E. *The vapour pressures of pure substances,* 2nd ed.; Elsevier: Amsterdam, 1984.

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