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Vapor–Liquid Equilibria of Ethanol + 2,2,4-Trimethylpentane at 333.15 K and 1-Propanol + 2,2,4-Trimethylpentane at at 343.15 K

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Isothermal vapor–liquid equilibria were measured for ethanol + 2,2,4-trimethylpentane at 333.15 K and 1-propanol + 2,2,4-trimethylpentane at 343.15 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 experimental results were best correlated with the Wilson equation.

Introduction

Vapor–liquid equilibria (VLE) are required for engineering use such as in the design and operation of separation processes. In the present study, VLE were measured for ethanol + 2,2,4-trimethylpentane at 333.15 K and 1-propanol + 2,2,4-trimethylpentane at 343.15 K, using an apparatus with computer control of the temperature and the measurement of total pressure. For the ethanol + 2,2,4-trimethylpentane system, three sets of data, at 298.15, 313.15, and 323.15K, are available in the literature (*1, 2*). The VLE for the 1-propanol + 2,2,4-trimethylpentane system have been reported at two temperatures, 328.37 and 348.52 K, in the literature (*3*).

Experimental Section

Materials. 2,2,4-Trimethylpentane, ethanol, and 1-propanol used in this work were special grade reagents, supplied by the Junsei 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 gives compares some of the measured properties with literature data.

Procedure. 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 mL was used.

A schematic diagram of the isothermal VLE apparatus and associated computer is shown in Figure 1. The apparatus, which was modified in our previous work (*5*), consists of a VLE still, an ebulliometer for the determination of the total pressure, a Hewlett-Packard Model 3421A data acquisition/control unit, a NEC personal computer, four solenoid valves for pressure control, two surge tanks, and a vacuum pump. The modification consisted of increasing the number of solenoid valves. The broken line represents a GP-IB (IEEE488) instrument bus. 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.

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. (*20*)	exptl	lit. (*20*)
ethanol	351.44	351.443	0.784 93	0.784 93
1-propanol	370.26	370.301	0.799 65	0.799 60
2,2,4-trimethylpentane	372.40	372.388	0.687 64	0.687 81

The sample was introduced into the VLE still and water into the ebulliometer for the determination of vapor pressure. 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. 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 (*6*). The accuracy of vapor pressure measurements is estimated to be ±0.03 kPa.

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 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:

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

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 (*7*). The vapor pressures of the pure

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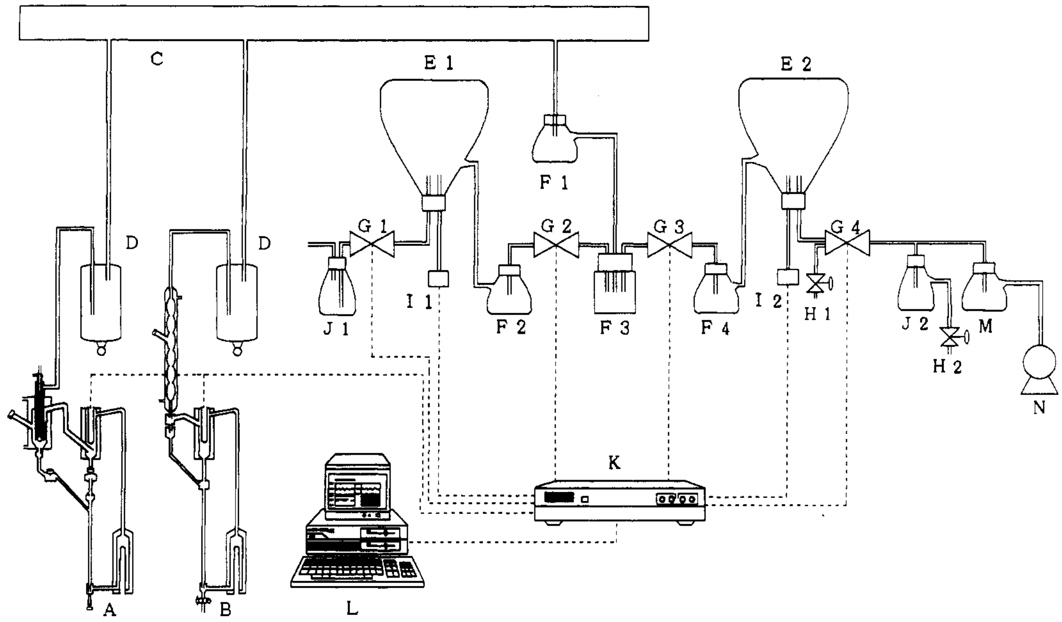

Figure 1. Schematic diagram of the isothermal VLE measurement system: (A) VLE still, (B) ebulliometer, (C) vacuum line, (D) cold trap, (E1, E2) surge tanks, (F1–F4) buffer tanks, (G1–G4) solenoid valves, (H1, H2) needle valve, (I1, I2) pressure transducers, (J1, J2) silica gel tanks, (K) data acquisition/control unit, (L) computer, (M) oil trap, (N) vacuum pump, (- - -) GP-IB (IEEE488) instrument bus.

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

material	*A*	*B*	*C*
ethanol	7.242 22	1595.811	−46.702
1-propanol	6.870 65	1438.587	−74.598
2,2,4-trimethylpentane	5.927 51	1252.340	−53.060

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

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) + 2,2,4-Trimethylpentane (2) at 333.15 K

P/kPa	x_1	y_1	γ_1	γ_2
56.955	0.0877	0.5060	7.0334	1.0596
59.002	0.1087	0.5275	6.1196	1.0738
62.044	0.1955	0.5710	3.8631	1.1352
63.565	0.2733	0.5863	2.9039	1.2411
64.043	0.3251	0.5946	2.4932	1.3194
64.292	0.3548	0.5990	2.3099	1.3706
65.059	0.4458	0.6032	1.8725	1.5972
65.117	0.4708	0.6031	1.7743	1.6745
65.234	0.5126	0.6065	1.6415	1.8059
65.272	0.5489	0.6091	1.5403	1.9396
65.332	0.5800	0.6094	1.4597	2.0835
65.194	0.6621	0.6164	1.2904	2.5391
64.974	0.7253	0.6294	1.1984	3.0097
64.446	0.7775	0.6442	1.1347	3.5424
63.685	0.8359	0.6628	1.0728	4.5050
61.864	0.8871	0.6959	1.0310	5.7533
59.853	0.9187	0.7422	1.0271	6.5778

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 (*8*).

The VLE data for ethanol (1) + 2,2,4-trimethylpentane (2) at 333.15 K and 1-propanol (1) + 2,2,4-trimethylpentane (2) at 343.15 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 $x_1(\mathrm{AZ}) = 0.612$ and $\mathrm{P(AZ)} = 65.36$ kPa for ethanol (1) + 2,2,4-trimethylpentane (2), and $x_1(\mathrm{AZ}) = 0.414$ and $\mathrm{P(AZ)} = 60.11$ kPa for 1-propanol (1) + 2,2,4-trimethylpentane (2).

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) + 2,2,4-Trimethylpentane (2) at 343.15 K

P/kPa	x_1	y_1	γ_1	γ_2
52.395	0.0454	0.2466	8.7503	1.0055
56.634	0.1023	0.3287	5.5723	1.0274
58.250	0.1515	0.3553	4.1773	1.0728
59.350	0.2106	0.3753	3.2308	1.1379
59.421	0.2363	0.3805	2.9222	1.1678
59.656	0.2592	0.3847	2.7035	1.2004
59.898	0.3025	0.3987	2.4093	1.2511
60.001	0.3294	0.4015	2.2316	1.2974
60.074	0.3665	0.4071	2.0358	1.3623
60.074	0.4905	0.4222	1.5768	1.6512
59.579	0.5549	0.4313	1.4120	1.8461
59.391	0.6007	0.4399	1.3259	2.0210
58.597	0.6605	0.4544	1.2288	2.2867
57.542	0.7057	0.4700	1.1681	2.5193
56.857	0.7387	0.4859	1.1398	2.7220
55.391	0.7848	0.5134	1.1043	3.0530
52.765	0.8425	0.5583	1.0657	3.6181
49.402	0.8892	0.6187	1.0480	4.1733
45.923	0.9248	0.6821	1.0334	4.7849
42.040	0.9557	0.7560	1.0157	5.7328

The experimental data were tested for thermodynamic consistency by using the point test of Fredenslund et al. (*9*) and of Van Ness et al. (*10*) and the area test of Herington (*11*) and of Redlich and Kister (*12*) as described by Gmehling and Onken (*13*). In addition, the data 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 three consistency tests indicate that the experimental 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 13, Vol. I). The parameters in each of these equations are obtained by using the Marquardt method (*19*). The sum of the squares of

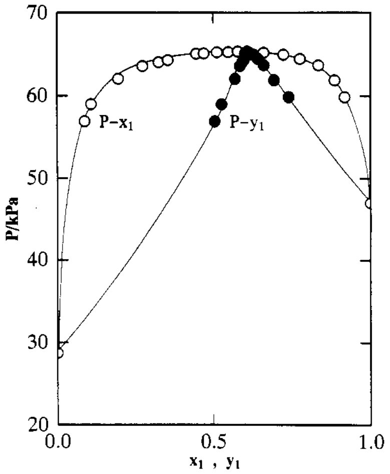

Figure 2. Pressure–composition diagram for ethanol (1) + 2,2,4-trimethylpentane (2) at 333.15 K: (○) x_1 and (●) y_1, this work; (—) Wilson equation.

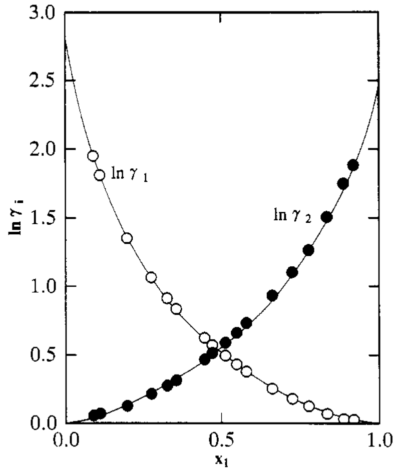

Figure 3. Activity coefficient–liquid composition diagram for ethanol (1) + 2,2,4-trimethylpentane (2) at 333.15 K: (○) ln γ_1 and (●) ln γ_2, this work; (—) Wilson equation.

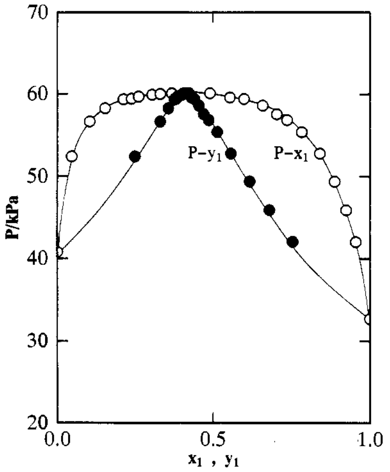

Figure 4. Pressure–composition diagram for 1-propanol (1) + 2,2,4-trimethylpentane (2) at 343.15 K: (○) x_1 and (●) y_1, this work; (—) Wilson equation.

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

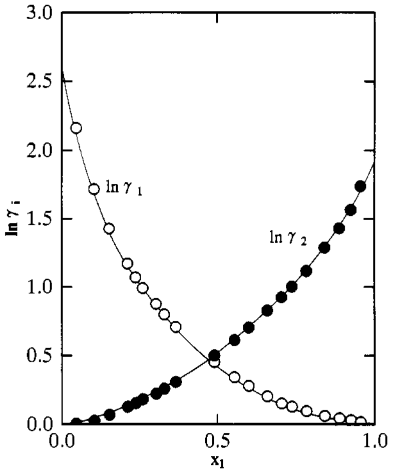

Figure 5. Activity coefficient–liquid composition diagram for 1-propanol (1) + 2,2,4-trimethylpentane (2) at 343.15 K: (○) ln γ_1 and (●) ln γ_2, this work; (—) Wilson equation.

For ethanol (1) + 2,2,4-trimethylpentane (2), the Wilson equation yielded the lowest mean deviations between the experimental and calculated pressures, 0.17 kPa, and vapor compositions, 0.004 mole fraction. The Wilson parameters for this system are found to be

$$\lambda_{12} - \lambda_{11} = 2064.349\ \mathrm{J{\cdot}mol^{-1}} \qquad \lambda_{12} - \lambda_{22} = 361.290\ \mathrm{J{\cdot}mol^{-1}}$$

The data for the system 1-propanol (1) + 2,2,4-trimethylpentane (2) were also least correlated using the Wilson equation with parameters

$$\lambda_{12} - \lambda_{11} = 1886.969\ \mathrm{J{\cdot}mol^{-1}} \qquad \lambda_{12} - \lambda_{22} = 147.080\ \mathrm{J{\cdot}mol^{-1}}$$

and an absolute average deviation of 0.007 in mole fraction and of 0.16 kPa in pressure. The calculated results using the Wilson equation are shown by solid lines in Figures 2–5.

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