Vapor–Liquid Equilibria of Ethanol with 2,2,4-Trimethylpentane or Octane at 101.3 kPa

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Isobaric vapor–liquid equilibria were measured for ethanol with 2,2,4-trimethylpentane or 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

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 two binary systems, ethanol + 2,2,4-trimethylpentane and ethanol + octane, at 101.3 kPa of pressure using a vapor and liquid recirculating still (*1, 2*). For ethanol + octane, one set of isobaric data is available in the literature (*3*), but these data are not consistent according to the results of a thermodynamic consistency test by Gmehling and Onken (*4*). New reliable data seem, therefore, to be required for this system. No isobaric VLE data have been reported previously for ethanol + 2,2,4-trimethylpentane.

Experimental Section

Materials. Ethanol, 2,2,4-trimethylpentane, and octane were special grade reagents, supplied by the Junsei Chemical Co. Ltd. Ethanol was 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. An equilibrium still (*1, 2*) 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.

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

	T_b/K		ρ(298.15 K)/(g·cm^{-3})	
component	exptl	lit (*17*)	exptl	lit. (*17*)
ethanol	351.44	351.443	0.794 93	0.794 93
2,2,4-trimethylpentane	372.40	372.388	0.687 64	0.687 81
octane	398.80	398.823	0.698 68	0.698 62

Table 2. Antoine Constants of the Components[a] (*18*)

component	A	B	C
ethanol	7.242 22	1595.811	−46.702
2,2,4-trimethylpentane	5.927 51	1252.340	−53.060
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 Ethanol (1) + 2,2,4-Trimethylpentane (2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
348.541	0.0874	0.5317	6.8808	1.0402
347.343	0.1166	0.5566	5.6536	1.0585
346.708	0.1474	0.5702	4.6954	1.0858
346.081	0.1746	0.5809	4.1383	1.1167
345.557	0.2608	0.6049	2.9430	1.1974
344.942	0.3375	0.6125	2.3595	1.3374
344.692	0.4062	0.6198	2.0032	1.4768
344.620	0.4633	0.6270	1.7814	1.6975
344.528	0.5020	0.6282	1.6532	1.7322
344.435	0.5938	0.6407	1.4301	2.0602
344.435	0.6317	0.6438	1.3507	2.2531
344.424	0.6683	0.6487	1.2868	2.4690
344.431	0.7114	0.6551	1.2201	2.7866
344.544	0.7468	0.6620	1.1689	3.1026
344.585	0.7722	0.6663	1.1357	3.4011
344.978	0.8363	0.6911	1.0698	4.3326
346.764	0.9296	0.7929	1.0257	6.4220

Results and Discussion

The activity coefficients γ_i were calculated from

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

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 (*5*). 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 (*6*).

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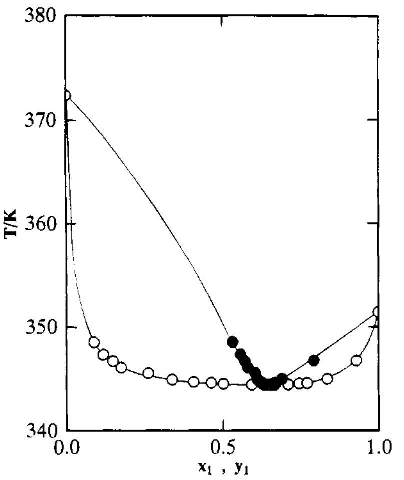

Figure 1. Temperature–composition diagram for ethanol (1) + 2,2,4-trimethylpentane (2) at 101.3 kPa: (○) x_1 and (●) y_1, this work; (—) Wilson equation.

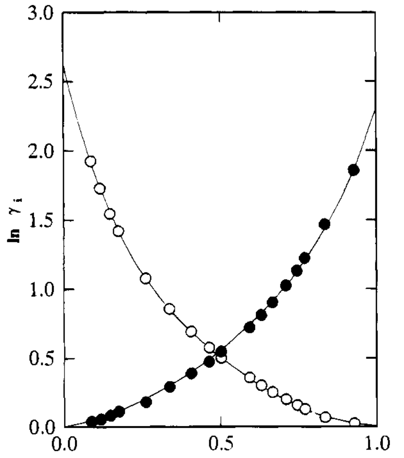

Figure 2. Activity coefficient–liquid composition diagram for ethanol (1) + 2,2,4-trimethylpentane (2) at 101.3 kPa: (○) ln γ_1 and (●) ln γ_2, this work; (—) Wilson equation.

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 Ethanol (1) + Octane (2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
359.280	0.0716	0.7141	7.4842	1.0382
355.599	0.1087	0.7517	5.9352	1.0722
352.433	0.2013	0.7842	3.7633	1.1690
352.222	0.2219	0.7880	3.4578	1.1884
351.537	0.2738	0.7952	2.9024	1.2623
351.424	0.3527	0.7985	2.2721	1.3995
350.753	0.4385	0.8098	1.9025	1.5620
350.730	0.4665	0.8108	1.7908	1.6378
350.452	0.5001	0.8142	1.6955	1.7348
350.470	0.5378	0.8216	1.5896	1.8018
350.194	0.6229	0.8287	1.3988	2.1439
349.981	0.6939	0.8295	1.2673	2.6500
350.002	0.7120	0.8300	1.2348	2.8063
349.869	0.7717	0.8396	1.1582	3.3602
349.792	0.8148	0.8486	1.1120	3.9207
349.773	0.8506	0.8577	1.0770	4.5808
349.811	0.8822	0.8661	1.0469	5.4641
349.918	0.9105	0.8840	1.0307	6.2182
350.160	0.9497	0.9159	1.0139	7.9790
350.233	0.9557	0.9216	1.0109	8.4284

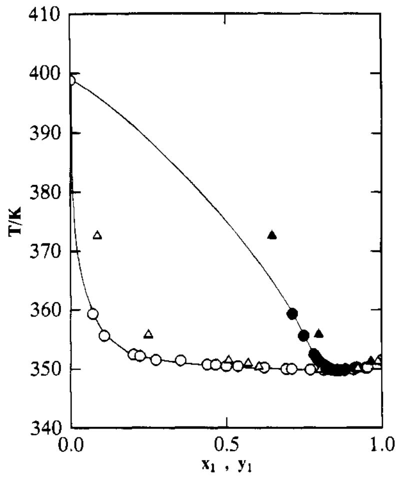

Figure 3. Temperature–composition diagram for ethanol (1) + octane (2) at 101.3 kPa: (○) x_1 and (●) y_1, this work; (—) NRTL equation; (△) x_1 and (▲) y_1, Koshelkov et al. (*3*).

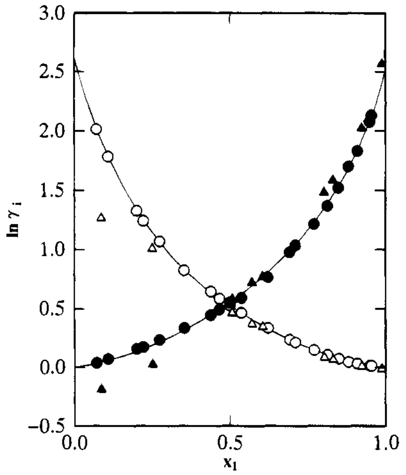

Figure 4. Activity coefficient–liquid composition diagram for ethanol (1) + octane (2) at 101.3 kPa: (○) ln γ_1 and (●) ln γ_2, this work; (—) NRTL equation; (△) ln γ_1 and (▲) ln γ_2, Koshelkov et al. (*3*).

The VLE results for ethanol (1) + 2,2,4-trimethylpentane (2) and ethanol (1) + octane (2) are reported in Tables 3 and 4 along with the activity coefficients calculated using eq 1. Both binary systems form a minimum boiling azeotrope. The azeotropic points were determined on the basis of the experimental VLE data, and at $P = 101.3$ kPa are $x_1(\mathrm{AZ}) = 0.645$ and $T(\mathrm{AZ}) = 344.42$ K for ethanol (1) + 2,2,4-trimethylpentane (2) and $x_1(\mathrm{AZ}) = 0.863$ and $T(\mathrm{AZ}) = 349.76$ K for ethanol (1) + octane (2).

The results were tested for thermodynamic consistency by using the point test of Fredenslund et al. (*7*) and of Van Ness et al. (*8*) and the area test of Herington (*9*) and of Redlich and Kister (*10*) as described by Gmehling and Onken (*4*). In addition, the results were checked by the Kojima (*11*) 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 three consistency tests indicate that the results for both systems are thermodynamically consistent.

The activity coefficients were correlated with the Wilson (*12*), modified Wilson (*13*), nonrandom two-liquid (NRTL) (*14*), and UNIQUAC (*15*) equations (see ref 4, Vol. I, Part 1). The parameters in each of these equations are obtained by using the Marquardt method (*16*). The sum of the squares of relative deviations in temperature and vapor composition was minimized during optimization of the parameters.

For ethanol (1) + 2,2,4-trimethylpentane (2), the Wilson equation yielded the lowest mean deviations between the experimental and calculated temperatures, 0.08 K, and vapor compositions, 0.005 mole fraction. The Wilson parameters for this system were found to be

$$\lambda_{12} - \lambda_{11} = 2111.251 \text{ cal·mol}^{-1}$$

$$\lambda_{12} - \lambda_{22} = 271.588 \text{ cal·mol}^{-1}$$

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

$$g_{12} - g_{11} = 1186.792 \text{ cal·mol}^{-1}$$

$$g_{12} - g_{22} = 1322.753 \text{ cal·mol}^{-1}$$

$$\alpha = 0.4775$$

Absolute average deviations of 0.003 in mole fraction and 0.05 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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