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Ternary Vapor−Liquid Equilibria of Ethanol + Acetone + Benzene at 318.15 K

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Isothermal vapor−liquid equilibria of ethanol + acetone + benzene were measured using a modified Boublik still at 318.15 K. The experimental results are compared with those calculated using the UNIQUAC associated-solution model with binary parameters, and a good agreement between the experimental and calculated values is obtained.

Introduction

This work reports experimental vapor−liquid equilibrium (VLE) results for ethanol + acetone + benzene at 318.15 K, because no experimental data were available from the literature. The measured results are compared with those calculated from the UNIQUAC associated-solution model with binary parameters obtained from three constituent binary VLE systems. The binary VLE results at 318.15 K for ethanol + acetone (Chaundry et al., 1980), ethanol + benzene (Brown and Smith, 1954), and acetone benzene (Brown and Smith, 1957), selected from among the binary systems measured by many researchers, are of good quality.

Experimental Section

Materials. Special grade ethanol was refluxed over calcium oxide and then fractionally distilled. Analytical-grade acetone was dried by fractional distillation from anhydrous copper sulfate. First grade benzene was purified by repeated recrystallization. A gas chromatographic analysis indicated that the purities of chemicals used were better than 99.9 mol %. The densities of the chemicals used, measured with an Anton-Paar densimeter at 298.15 K, and the boiling points agreed well with literature values (Riddick and Bunger, 1970), as shown in Table 1. The vapor pressures of the pure components measured were in good agreement within ±0.01 kPa with the values calculated by the Antoine equation whose constants are available from the literature (Riddick and Bunger, 1970).

Procedure. VLE measurements at 318.15 K were carried out using a modified Boublik vapor-recirculating still as described previously (Nagata, 1985b). The compositions of ternary equilibrated samples were analyzed with a Shimadzu glc (GC-8A) and a Shimadzu Chromatopac (C-R6A). The experimental errors of the measured variables were mole fraction, ±0.002; pressure, ±0.0133 kPa; and temperature, ±0.05 K.

Table 1. Densities d and Boiling Points T_b of the Components

component	d(298.15 K)/g·cm^{-3} exptl	d(298.15 K)/g·cm^{-3} lit.[a]	T_b(101.325 kPa)/K exptl	T_b(101.325 kPa)/K lit.[a]
ethanol	0.784 90	0.785 04	351.4	351.44
acetone	0.784 52	0.784 40	329.3	329.44
benzene	0.873 60	0.873 70	353.2	353.25

[a] Riddick and Bunger, 1970.

Table 2. Antoine Coefficients A, B, and C[a]

component	A	B	C
ethanol	7.445 99	1718.10	−35.63
acetone	6.356 47	1277.03	−35.92
benzene	6.030 55	1211.033	−52.36

$$\log(P_i^0/\mathrm{kPa}) = A - B/[(T/\mathrm{K}) + C]$$

[a] Riddick and Bunger, 1970.

Table 3. Vapor Pressures P_i^0, Liquid Molar Volumes V_i^0, Structural Parameters r_i and q_i, and Second Virial Coefficients B_{ij} at 318.15 K

	ethanol	acetone	benzene
P_i^0/kPa	23.160	67.874	29.798
V_i^0/cm^3·mol^{-1}	59.43	76.35	91.60
r_i	1.69	2.06	2.56
q_i	1.55	1.85	2.05
$-B_{ii}$/cm^3·mol^{-1}	1517	1510	1257
	ethanol + acetone	ethanol + benzene	acetone + benzene
$-B_{ij}$/cm^3·mol^{-1}	1276	664	1092

Results and Analysis

The following equations were used to calculate the activity coefficients γ_i and fugacity coefficients ϕ_i

$$\gamma_i = P y_i \phi_i / [x_i P_i^0 \phi_i^0 \exp\{V_i^0 (P - P_i^0)/RT\}] \qquad (1)$$

$$\ln \phi_i = (2\sum_j y_j B_{ij} - \sum_i \sum_j y_i y_j B_{ij}) P/RT \qquad (2)$$

where P is the total pressure, P_i^0 and V_i^0 are the pure-component vapor pressure calculated from the Antoine equation with coefficients given in Table 2 and the liquid molar volume calculated from a modified Rackett equation

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Table 4. Isothermal Vapor−Liquid Equilibrium Data, Liquid Phase Mole Fractions x_i and Vapor Phase Mole Fractions y_i, Vapor Pressures P, Activity Coefficients γ_i, and Fugacity Coefficients ϕ_i for Ethanol (1) + Acetone (2) + Benzene (3) at 318.15 K

point	x_1	x_2	x_3	y_1	y_2	y_3	P/kPa	γ_1	γ_2	γ_3	ϕ_1	ϕ_2	ϕ_3
1	0.122	0.093	0.785	0.221	0.172	0.607	42.570	3.329	1.181	1.100	0.987	0.979	0.982
2	0.174	0.194	0.632	0.219	0.301	0.480	46.690	2.528	1.083	1.185	0.984	0.976	0.982
3	0.337	0.059	0.604	0.337	0.094	0.569	43.263	1.863	1.033	1.363	0.984	0.978	0.983
4	0.430	0.052	0.518	0.364	0.086	0.550	42.943	1.564	1.065	1.526	0.984	0.978	0.984
5	0.494	0.052	0.454	0.382	0.090	0.528	42.770	1.423	1.110	1.666	0.983	0.978	0.984
6	0.555	0.055	0.390	0.405	0.094	0.501	42.303	1.327	1.084	1.821	0.983	0.978	0.985
7	0.419	0.110	0.471	0.340	0.172	0.488	44.690	1.559	1.046	1.549	0.983	0.977	0.984
8	0.496	0.110	0.394	0.359	0.185	0.456	44.463	1.382	1.120	1.723	0.982	0.977	0.984
9	0.550	0.110	0.340	0.382	0.189	0.429	44.063	1.314	1.134	1.863	0.981	0.977	0.985
10	0.510	0.150	0.340	0.346	0.256	0.398	44.023	1.282	1.125	1.727	0.982	0.977	0.985
11	0.563	0.174	0.263	0.355	0.305	0.340	45.476	1.229	1.192	1.971	0.980	0.976	0.986
12	0.650	0.141	0.209	0.404	0.277	0.319	43.383	1.156	1.276	2.223	0.980	0.977	0.987
13	0.706	0.131	0.163	0.429	0.284	0.287	42.343	1.103	1.375	2.506	0.980	0.978	0.988
14	0.561	0.261	0.178	0.326	0.445	0.229	48.396	1.203	1.231	2.089	0.978	0.974	0.986
15	0.572	0.292	0.136	0.334	0.488	0.178	48.423	1.209	1.207	2.128	0.978	0.974	0.987
16	0.686	0.232	0.082	0.396	0.468	0.136	44.050	1.089	1.329	2.460	0.979	0.976	0.990
17	0.617	0.302	0.081	0.345	0.538	0.117	48.196	1.152	1.281	2.341	0.977	0.974	0.989
18	0.486	0.381	0.133	0.278	0.579	0.143	52.076	1.272	1.178	1.878	0.976	0.971	0.986
19	0.404	0.457	0.139	0.241	0.620	0.139	54.476	1.387	1.098	1.825	0.976	0.970	0.985
20	0.332	0.520	0.148	0.205	0.652	0.143	56.502	1.488	1.051	1.827	0.976	0.969	0.984
21	0.251	0.427	0.322	0.192	0.548	0.260	54.222	1.774	1.034	1.463	0.978	0.970	0.982
22	0.246	0.303	0.451	0.216	0.424	0.360	50.209	1.891	1.047	1.339	0.980	0.973	0.982
23	0.184	0.468	0.348	0.142	0.592	0.266	54.916	1.814	1.032	1.401	0.979	0.970	0.982
24	0.171	0.426	0.403	0.144	0.555	0.301	53.436	1.928	1.036	1.332	0.980	0.970	0.982

Table 5. Parameters and Root-Mean-Squared Deviations between Calculated and Experimental Pressures, Temperatures, Liquid Phase and Vapor Phase Mole Fractions Obtained Using the UNIQUAC Association Model for Binary Systems

binary mixture (A + B)	T/K	$K^0_{AB}(T)^a$	$-h_{AB}$/kJ·mol^{-1}	a_{AB}/K	a_{BA}/K	δP/kPa	δT/K	$10^3\delta x$	$10^3\delta y$
ethanol + acetone	323.15	35	21.0	314.2	−9.78	0.0347	0.00	0.1	
ethanol + benzene	318.15	3	8.3	−5.22	104.74	0.1107	0.02	0.6	3.7
acetone + benzene	318.15			−48.30	130.97	0.1307	0.04	0.4	2.7

$T = 323.15$ K.

(Spencer and Danner, 1972), and B_{ii} and B_{ij} are the pure and unlike-interaction second virial coefficients estimated by the Hayden−O'Connell method (1975). Table 3 gives the values of P_i^0 calculated from the Antoine equation (Riddick and Bunger, 1970), V_i^0, and B used in the analysis of the experimental results. Table 4 shows the experimental results for ethanol + acetone + benzene at 318.15

The experimental VLE results were analyzed with the UNIQUAC associated-solution model (Nagata, 1985a) with binary parameters obtained from the binary VLE results. The model assumes that in a ternary mixture alkanol self-associates to form open chains of any length, which produce many chemical complexes with two other active nonassociated components. The equilibrium constants for chemical-complex formation are independent of the numbers of associated and solvated molecules, the association constant for ethanol $K_A^0 = 110.4$ at 323.15 K (Brandani, 1983); the enthalpy of a hydrogen bond $h_A = -23.2$ kJ·mol^{-1} (Stokes et al., 1973). The van't Hoff equation fixes the temperature dependence of the equilibrium constants. The pure-component molecular-size and molecular-area parameters r and q, calculated from the method of Vera et al. (1977) are given in Table 3. The binary energy parameters of the model were obtained using a computer program based on the maximum-likelihood principle (Prausnitz et al., 1980). Standard deviations for the experimental values, taken as 0.13 kPa for pressure, 0.05 K for temperature, 0.001 for liquid mole fraction, and 0.003 for vapor mole fraction, were the same as those used by Prausnitz et al. (1980). Table 5 shows the solvation constant K^0_{AB} and enthalpy h_{AB} of complex formation taken from previous papers (Nagata, 1985a; Nagata and Miyazaki, 1992), the binary energy parameters a_{AB} and a_{AB}, and the root-mean-squared deviations (δP for pressure; δT for temperature; δx for liquid mole fraction; and δy for vapor mole fraction) between the experimental results and the values calculated from the binary data reduction. Figure 1 shows the experimental and calculated tie lines. Table 6 shows the deviations between the ternary experimental results and those cal-

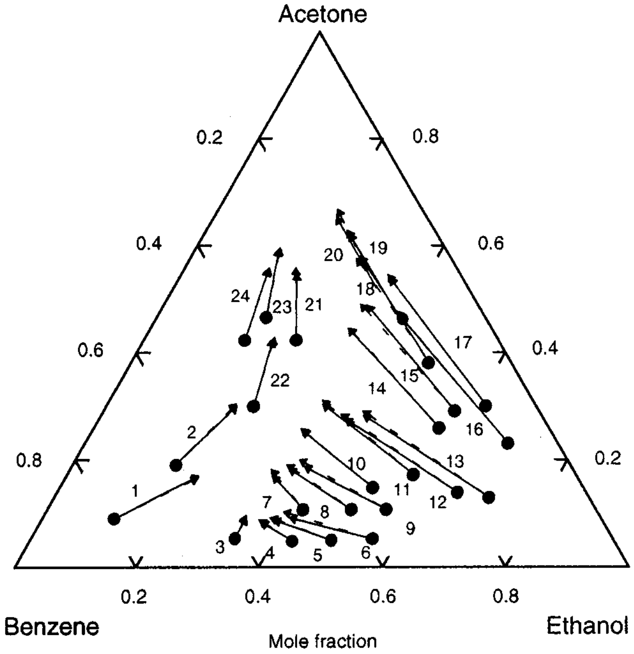

Figure 1. Equilibrium tie lines: (▲) vapor; (●) liquid; (—) experimental; (- - -) calculated.

Table 6. Deviations between Calculated and Experimental Vapor Phase Mole Fractions and Pressures for Ethanol (1) + Acetone (2) + Benzene (3) at 318.15 K

deviation	$10^3\delta y_1$	$10^3\delta y_2$	$10^3\delta y_3$	δP/kPa	$10^2\delta P/P$
mean	6.7	6.9	3.1	0.307	0.7
root-mean-square	7.7	7.7	4.3	0.383	0.8

culated from the UNIQUAC associated-solution model with only the binary parameters.

Conclusion

Experimental VLE data for ethanol + acetone + benzene at 318.15 K were well compared with those calculated by using the UNIQUAC associated-solution model with only binary parameters and were found to be thermodynamically consistent.

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