J. Chem. Eng. Data **2004,** *49,* 465−467

Isobaric Vapor−Liquid Equilibria of the Ternary System Toluene + Ethylbenzene + Amyl Acetate

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Isobaric vapor−liquid equilibria (VLE) was measured for the ternary system toluene + ethylbenzene + amyl acetate. Boiling temperature (T) − liquid composition (x) relations were obtained at (26.66, 53.33, and 79.99) kPa by using a semimicroebulliometer. The Wilson model was used to correlate the binary $T-x$ data and to predict VLE in the ternary system.

Introduction

A knowledge of multicomponent vapor−liquid equilibrium (VLE) data is important in the design of equipment for separation processes. In addition, such experimental information can be used to test and develop models for correlation and prediction thermodynamic properties of mixtures. In previous work, we have reported VLE in the ternary systems *o*-xylene + amyl acetate + nonane,[1] *o*-xylene + nonane + cyclohexanol,[2] hexan-2-one + *o*-xylene + nonane,[3] toluene + *p*-xylene + 1,2-dichloroethane,[4] and toluene + ethylbenzene + chlorobenzene.[5] To obtain further information regarding thermodynamic properties of ternary mixtures containing aromatic compounds, we present here VLE at pressures (26.66, 53.33, and 79.99) kPa for the system toluene + ethylbenzene + amyl acetate and two constituent binaries containing amyl acetate. We have not found information for VLE of this ternary system in the literature. Recently, we have published binary VLE data for the binary system toluene + ethylbenzene[5] and compared these data with those of Wohland and Pape,[6] Kutsarov et al.,[7] Makh and Azarova,[8] and Martirosyan et al.[9] at 101.32 kPa, finding a good agreement between our experiments and literature data. For the binary toluene + amyl acetate, the boiling temperatures are measured at 101.32 kPa by Fahmy and El-Ghannam.[10,11] No data are available for the system ethylbenzene + amyl acetate.

For the correlation of binary VLE data and prediction ternary VLE, the Wilson equation was used as a model giving in many cases the most reliable results.

Experimental Section

Materials. All substances, obtained from Reakhim (Kharkov, Ukraine), were twice purified by vacuum rectification. Their purity checked by gas chromatography was better than 99.5 mass %. Densities measured at 298.15 K in a capillary pycnometer were (862.2, 862.5, and 875.4) kg·m^{-3} for toluene, ethylbenzene, and amyl acetate, respectively, as reported by us earlier.[5,12]

Apparatus and Procedures. The boiling temperature liquid mole fraction measurements were performed by means of a semimicroebulliometer. The experimental arrangement and the procedure of determining the $T-x$ relation were described previously.[13] Uncertainties of the boiling temperature measurements were estimated to be <0.05 K. Equilibrium pressure was measured by a mercury manometer. The absolute accuracy of these measurements is probably within 13 Pa.

All mixtures were prepared by mass. Uncertainties of mole-fraction composition of a liquid mixture (x_i) were found to be <5 × 10^{-4}.

Table 1. Isobaric Vapor−Liquid Equilibrium Data: Liquid Phase Mole Fraction (x_1) and Boiling Temperatures (T) in Binary Systems

	T/K at P/kPa		
x_1	$P = 26.66$	$P = 53.33$	$P = 79.99$
	Toluene (1) + Amyl Acetate (2)		
0.000	380.05	400.72	414.20
0.219	369.47	390.07	404.15
0.292	366.18	387.15	400.83
0.350	363.16	384.33	398.04
0.411	360.77	381.58	395.21
0.491	357.67	378.28	391.86
0.699	350.58	370.96	384.25
0.859	346.02	366.14	379.31
1.000	342.65	362.63	375.66
	Ethylbenzene (1) + Amyl Acetate (2)		
0.000	380.05	400.72	414.20
0.251	376.09	396.93	410.43
0.346	374.69	395.57	409.28
0.496	372.35	393.34	407.03
0.668	370.02	391.05	404.83
0.792	368.39	389.45	403.22
0.902	367.03	388.16	401.90
1.000	365.86	386.94	400.70

Results and Discussion

The experimental values of boiling-temperature measurements for binary systems at three pressures (26.66, 53.33, and 79.99) kPa are reported in Table 1. The $T-x$ data of binary systems were fitted with the Wilson model,[14] traditionally used when VLE data have to be reduced. The expressions for activity coefficients are given, as follows

$$\ln \gamma_1 = -\ln(x_1 - \Lambda_{12}x_2) + x_2\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1}\right) \tag{1}$$

$$\ln \gamma_2 = -\ln(x_2 - \Lambda_{21}x_1) + x_1\left(\frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} - \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2}\right) \tag{2}$$

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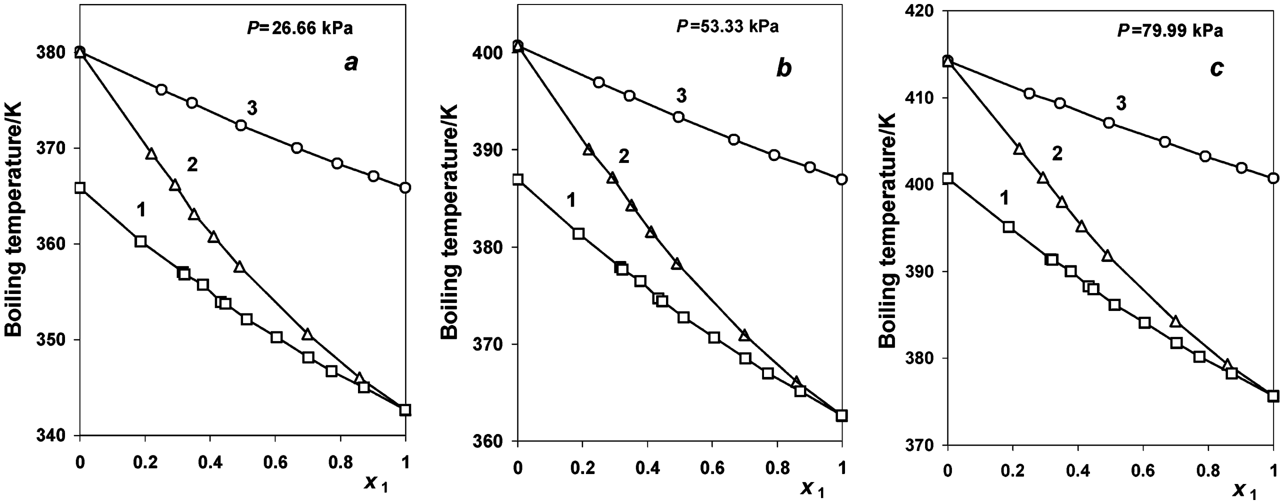

Figure 1. Boiling temperature−composition diagram for binaries at a, 26.66; b, 53.33; and c, 79.99 kPa. □, lines 1, Kuus et al.,[5] toluene (1) + ethylbenzene; △, lines 2, this work, toluene (1) + amyl acetate (2); ○, lines 3, this work, ethylbenzene (1) + amyl acetate (2).

Table 2. Fitted Parameters of the Wilson Equation and Calculated Standard Deviations (σP) and Absolute Mean Deviations (ΔP) of Pressure for Binary Systems

system	ratio of molar volumes V_1/V_2 at 333.15 K	values of Wilson parameters Λ_{12}	Λ_{21}	σP/kPa	ΔP/%
toluene (1) + ethylbenzene (2)	0.870	0.694	1.440	0.22	0.23
toluene (1) + amyl acetate (2)	0.714	0.555	1.801	0.26	0.39
ethylbenzene (1) + amyl acetate (2)	0.820	1.084	0.923	0.09	0.12

Table 3. Experimental Vapor−Liquid Equilibria Data for the Ternary System Toluene (1) + Ethylbenzene (2) + Amyl Acetate (3) at Three Pressures and Values Calculated by the Wilson Equation[14] of Activity Coefficients (γ_1, γ_2, and γ_3), Vapor Mole Fractions (y_1 and y_2), Excess Gibbs Energy (G^E), Pressure (P_{calc}), and Boiling Temperature (T_{calc})

experimental data			calculated values							
liquid mole fraction			activity coefficients			vapor mole fractions				
x_1	x_2	T_{exp}/K	γ_1	γ_2	γ_3	y_1	y_2	G^E/J·mol^{-1}	P_{calc}/kPa	T_{calc}/K
P = 79.99 kPa										
0.562	0.219	387.00	0.983	0.984	0.929	0.769	0.144	−94.8	79.77	387.10
0.740	0.130	381.66	0.995	0.968	0.903	0.886	0.072	−67.8	79.25	381.98
0.242	0.379	397.67	0.934	1.002	0.995	0.423	0.352	−85.3	79.22	398.02
0.646	0.236	384.05	0.991	0.987	0.974	0.818	0.140	−72.1	79.94	384.07
0.420	0.387	390.54	0.971	0.975	0.913	0.626	0.286	−86.1	79.77	390.64
0.209	0.527	397.46	0.936	0.992	0.944	0.362	0.483	−66.7	79.68	397.60
0.622	0.126	385.77	0.986	1.002	0.924	0.825	0.080	−100.1	79.74	385.88
0.442	0.186	392.08	0.965	0.980	0.951	0.679	0.144	−115.5	80.27	391.96
0.387	0.204	393.96	0.956	0.997	0.959	0.622	0.168	−114.7	79.94	393.98
0.222	0.259	400.07	0.919	1.004	0.981	0.406	0.258	−92.7	79.20	400.42
P = 53.33 kPa										
0.562	0.219	373.62	0.983	0.984	0.929	0.779	0.141	−91.5	53.35	373.61
0.740	0.130	368.45	0.995	0.968	0.903	0.892	0.070	−65.5	52.95	368.68
0.242	0.379	383.93	0.934	1.002	0.995	0.436	0.350	−82.4	52.76	384.28
0.646	0.236	370.73	0.991	0.987	0.974	0.826	0.136	−69.6	53.40	370.69
0.420	0.387	377.25	0.971	0.975	0.913	0.638	0.281	−83.2	53.67	377.04
0.209	0.527	383.55	0.936	0.992	0.944	0.373	0.480	−64.4	52.81	383.87
0.622	0.126	372.43	0.986	1.002	0.924	0.835	0.077	−96.6	53.34	372.43
0.442	0.186	378.41	0.965	0.980	0.951	0.693	0.141	−111.5	53.46	378.33
0.387	0.204	380.35	0.956	0.997	0.959	0.637	0.165	−110.7	53.40	380.31
0.222	0.259	386.22	0.919	1.004	0.981	0.0.422	0.258	−89.5	52.59	386.68
P = 26.66 kPa										
0.562	0.219	353.12	0.983	0.984	0.929	0.797	0.134	−86.5	26.89	352.88
0.740	0.130	348.35	0.995	0.968	0.903	0.902	0.065	−61.9	26.77	348.24
0.242	0.379	363.11	0.934	1.002	0.995	0.460	0.345	−77.9	26.59	363.19
0.646	0.236	350.31	0.991	0.987	0.974	0.839	0.128	−65.8	26.83	350.14
0.420	0.387	356.42	0.971	0.975	0.913	0.658	0.270	−78.6	26.90	356.17
0.209	0.527	362.46	0.936	0.992	0.944	0.394	0.473	−60.8	26.35	362.80
0.622	0.126	351.70	0.986	1.002	0.924	0.851	0.073	−91.2	26.61	351.76
0.442	0.186	357.50	0.965	0.980	0.951	0.717	0.136	−105.3	26.78	357.38
0.387	0.204	360.28	0.956	0.997	0.959	0.662	0.161	−104.9	27.61	359.29
0.222	0.259	365.41	0.919	1.004	0.981	0.448	0.257	−84.7	26.54	365.55

Coefficients for the Antoine vapor pressure equation (kPa, K) were reported earlier,[1,5] being equal to 14.0841, 3148.177, and −51.1715 for toluene, 13.7078, 3083.502, and −70.0678 for ethylbenzene, and 14.0180, 3215.228, and

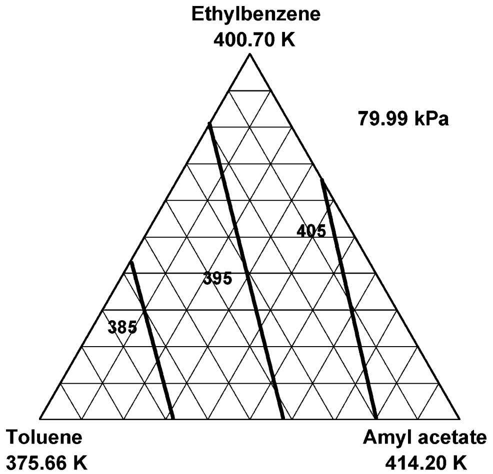

Figure 2. Calculated boiling temperature isotherms for the ternary system toluene + ethylbenzene + amyl acetate at 79.99 kPa.

−80.5320 for amyl acetate. Molar volumes of components were calculated from densities at 333.15 K given in literature: 0.8293 $g\cdot cm^{-3}$ for toluene,[15] 0.8317 $g\cdot cm^{-3}$ for ethylbenzene,[16] and 0.8375 $g\cdot cm^{-3}$ for amyl acetate.[17] In Table 2, the ratios of molar volumes, values of Wilson parameters, standard deviation, and mean relative error of pressure calculation as the results of correlation are presented. For the system toluene + ethylbenzene, the experimental data from our earlier work[5] were used for calculations. Standard deviations σP were calculated by using the relation

$$\sigma P = (\sum(P_{\mathrm{calc}} - P_{\mathrm{exp}})^2/(N - 2))^{1/2} \tag{3}$$

where N is number of experimental points.

Wilson parameters for binaries were calculated as unified values for all boiling temperatures at each of the three experimental pressures. It was found that a calculation of parameters separately for each pressure did not appreciably improve the correlation results. Therefore it is not reasonable to increase the number of Wilson parameters from 6 to 18 for correlation of ternary VLE data.

The isobaric VLE data for the ternary system are given in Table 3. Table 3 shows the experimental $T-x$ data together with calculated values of activity coefficients, vapor compositions, excess Gibbs energy, temperatures, and total pressures predicted by the Wilson equation using the binary parameters. P_{calc} is calculated assuming corresponding temperature equal to T_{exp}, and T_{calc} is calculated at P_{exp}. Mean (absolute) deviations between experimental and calculated temperature and pressure were equal to 0.20 K and 0.30 kPa, respectively.

As shown in Figure 1, the $T-x$ curves of binaries differ only slightly from straight lines. Systems are nearly ideal. There is no possibility for the formation of azeotropes.

The ternary system is also nearly ideal, showing only a weak negative deviation from Raoult's law. As seen from Table 3, all calculated G^E values have negative values and activity coefficients have values <1. For the illustration in Figure 2, the calculated boiling temperature isotherms for the ternary system at 79.99 kPa are presented in the form of the Gibbs triangle.

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Received for review June 3, 2003. Accepted February 12, 2004. Financial support of this work by the Estonian Ministry of Education and Science under Theme No. 0351456s00 is gratefully acknowledged.

JE0301850