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High Temperature VLE for the Benzene−Ethylbenzene System

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We used a continuous flow apparatus designed for vapor−liquid equilibrium (VLE) data measurements at high temperatures up to 400 °C, previously used to measure VLE data along three isotherms for the tetralin−quinoline system. In this work, the apparatus was slightly modified for measurements of four high-temperature (180 °C, 210 °C, 250 °C, 280 °C) VLE isotherms for the benzene−ethylbenzene system. The data were successfully tested for thermodynamic consistency by using the area test.

Introduction

High-temperature VLE data available in the literature are quite limited. Even for a common system such as benzene−ethylbenzene, the only VLE data sets available in the literature are those of Kesselmann et al.[1] and Kutsarov et al.,[2] who measured isobaric *T*, *X*, *Y* data at atmospheric pressure. Makh and Azarova[3] were the first to report VLE data on this system, but their measurements were only approximate, resulting in an average relative volatility at atmospheric pressure. In this work, we report four higher temperature isotherms for this system. The data have been tested and proven to be thermodynamically consistent.

Experimental Section

The experimental apparatus and the procedure used for the measurements were described in a previous article.[4] After the previous VLE measurements for the tetralin−quinoline system, the apparatus was modified by bringing the sampling points closer to the VLE cell. Also, one-way check valves were introduced in the liquid and the vapor outlet lines at a distance 30 cm downstream from the sampling points. The latter was done because we suspected the existence of backflow of the liquid into the vapor line at lower pressures and at low vapor flow rates. At these conditions, the measured vapor compositions showed larger uncertainties. The benzene and ethylbenzene used in the measurements were obtained from Sigma-Aldrich Chemical Co. and were 99.9% pure.

The analysis of the samples (benzene, ethylbenzene mixtures) obtained from the VLE apparatus were carried out by the gas chromatographic method. The method specifically designed for the benzene−ethylbenzene binary system used a Perkin-Elmer AutoSystem gas chromatograph, a programmed split-splitless (PSS) injector with a narrow glass liner, a Supelco Beta-Dex 110 fused silica capillary column 30 m long and with a 0.25 mm i.d., a flame ionization detector (FID), helium carrier gas, a 0.1 μL injection size, methanol dilution solvent, 200 °C injector temperature, 50 °C column temperature, 260 °C detector temperature, and Waters Maxima chromatographic software for data analysis. The standard used for calibration was a solution of equal volumes of benzene and ethylbenzene. The solution was diluted by methanol solvent so that 0.1 μL of the solution would contain approximately 100 ng each of benzene and ethylbenzene, a limit as recommended by Supelco, the manufacturer of the GC column. Assuming a linear relation between the response and concentration, the concentration of benzene in an unknown solution would then be given by

$$\text{vol fraction benzene in unknown} = \text{RB}/(\text{RB} + k(\text{REB})) \tag{1}$$

where RB and REB are the responses of benzene and ethylbenzene in the unknown sample in μV·s and *k* is the calibration constant which represents the ratio of the response factor of ethylbenzene to that of benzene corresponding to the standard solution. After a few calibration runs, the following values of *k* were determined for two different concentration ranges: 1.135 for mixtures with vol % benzene greater than 50%, and 1.168 for mixtures with vol % benzene less than 50%. With this method the mole fractions in the vapor and the liquid samples were analyzed with an accuracy of 1%.

Results and Discussion

Pure benzene and pure ethylbenzene have been well studied, and thermophysical property data such as vapor pressures, liquid and vapor densities, and heat capacities are available in the literature. A good review of all the data available for benzene is given by Goodwin.[5] For ethylbenzene, the vapor pressure data of Chirico et al.,[6] Osborn and Scott,[7] and Ambrose[8] cover the temperature range 306 K to the critical temperature. From these data, constants in the Wagner equation were regressed by Wang and Kabadi.[9] The Wagner equation and the constants are given below:

$$\ln(P_r^{\text{sat}}) = (A\tau + B\tau^{1.5} + C\tau^3 + D\tau^6)/T_r \tag{2}$$

where T_r and P_r are reduced temperature and pressure and $\tau = (1 - T_r)$

Benzene: $A = -6.957\,98$; $B = 1.277\,57$; $C = -2.564\,66$; $D = -3.403\,52$

Ethylbenzene: $A = -7.282\,89$; $B = 0.879\,44$; $C = -2.146\,24$; $D = -5.638\,93$

The Wagner equation with the constants given above represents the vapor pressure data for the two liquids with

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Table 1. Experimental VLE Data for the Benzene (1) + Ethylbenzene (2) System

t/°C	P/bar	X_1	Y_1	γ_1	γ_2	G^E/RT
180	3.452	0.078 ± 0.003	0.220 ± 0.005	1.0846	1.00	0.0063
	3.950	0.141 ± 0.004	0.350 ± 0.007	1.078	1.0081	0.0175
	5.702	0.370 ± 0.007	0.644 ± 0.007	1.0545	1.0307	0.0387
	7.750	0.642 ± 0.007	0.837 ± 0.004	1.0322	1.0620	0.0419
	8.817	0.786 ± 0.005	0.910 ± 0.003	1.0218	1.0825	0.0339
	9.082	0.823 ± 0.004	0.927 ± 0.003	1.0188	1.0853	0.0298
	9.857	0.939 ± 0.002	0.976 ± 0.001	1.0054	1.0912	0.0104
210	6.220	0.092 ± 0.003	0.220 ± 0.005	1.0643	1.0007	0.0064
	7.100	0.171 ± 0.004	0.360 ± 0.007	1.0506	1.0024	0.0104
	9.409	0.374 ± 0.007	0.607 ± 0.008	1.0320	1.0146	0.0208
	12.26	0.611 ± 0.007	0.793 ± 0.004	1.0224	1.0397	0.0287
	14.27	0.780 ± 0.004	0.892 ± 0.003	1.0130	1.0574	0.0223
	15.01	0.845 ± 0.004	0.925 ± 0.003	1.0086	1.0625	0.0167
	16.35	0.952 ± 0.002	0.978 ± 0.001	1.0062	1.0722	0.0092
250	11.35	0.063 ± 0.002	0.131 ± 0.003	1.0518	1.0021	0.0052
	13.40	0.180 ± 0.004	0.323 ± 0.006	1.0380	1.0026	0.0088
	16.86	0.364 ± 0.007	0.542 ± 0.009	1.0279	1.0134	0.0185
	21.27	0.593 ± 0.008	0.739 ± 0.006	1.0141	1.0256	0.0186
	25.16	0.774 ± 0.005	0.862 ± 0.004	1.0113	1.0441	0.0185
	26.37	0.834 ± 0.004	0.900 ± 0.003	1.0075	1.0466	0.0138
	28.76	0.950 ± 0.002	0.971 ± 0.001	1.0013	1.0545	0.0039
280	17.35	0.064 ± 0.002	0.113 ± 0.003	1.0375	1.00	0.0023
	19.20	0.141 ± 0.004	0.231 ± 0.005	1.0331	1.0036	0.0077
	24.70	0.368 ± 0.007	0.500 ± 0.009	1.0184	1.0102	0.0131
	31.46	0.611 ± 0.008	0.715 ± 0.006	1.0135	1.0204	0.0160
	37.20	0.789 ± 0.005	0.847 ± 0.004	1.0109	1.0329	0.0154
	39.00	0.843 ± 0.004	0.886 ± 0.003	1.0092	1.0359	0.0133
	42.34	0.955 ± 0.002	0.967 ± 0.002	1.0018	1.0404	0.0036

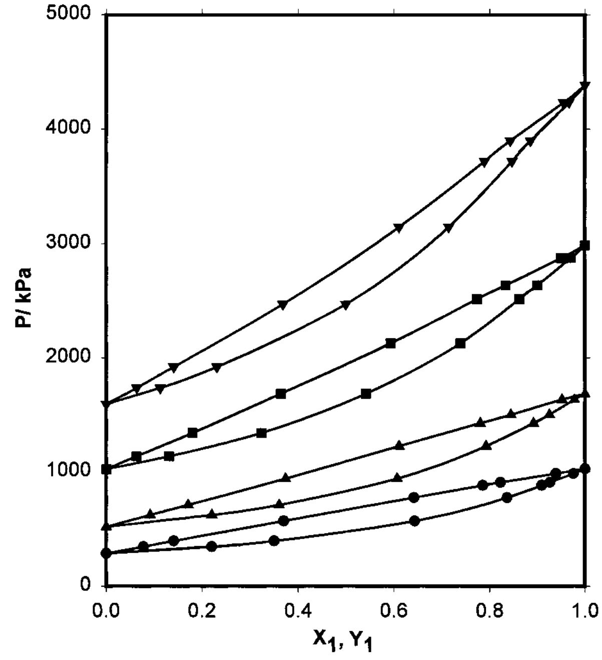

Figure 1. VLE data for the benzene–ethylbenzene system: ●, 180 °C; ▲, 210 °C; ■, 250 °C; ▼, 280 °C.

an accuracy of 0.5%. Therefore, no vapor pressure measurements for the two pure liquids were carried out in this work.

The temperature, pressure, mole fraction of benzene in liquid (X_1), and mole fraction of benzene in vapor (Y_1) are given in Table 1. The $P-X-Y$ diagram is shown in Figure 1. The uncertainties in the reported temperatures and pressures are $\Delta T = \pm 1$ K and $\Delta P = \pm 0.4\%$ which corresponds to ±1.4 kPa at a pressure of 3.5 bar and ±18 kPa at a pressure of 45 bar. The reported liquid and vapor mole fractions represent average values of four sample measurements each; the upper and lower limits of the measurements are also given. The area test for thermodynamic consistency was applied, and activity coefficients were calculated using the method described by Mahmood et al.[4] The following critical properties[10] were used:

$$\text{Benzene:}\quad T_c = 562.16\ \text{K};\quad P_c = 48.98\ \text{bar};\quad \omega = 0.212$$

$$\text{Ethylbenzene:}\quad T_c = 617.2\ \text{K};\quad P_c = 36.1\ \text{bar};\quad \omega = 0.302$$

The Peng–Robinson equation of state[11] with $k_{ij} = 0$ was used to calculate the fugacity coefficients. The liquid molar volumes necessary for calculation of the Poynting correction factors were calculated using the modified Rackett equation of Spencer and Danner[12] with $Z_{RA} = 0.2698$ for benzene and 0.2600 for ethylbenzene. The vapor pressures of the two components were calculated with the Wagner equation and the coefficients given above.

The calculated activity coefficients and the excess Gibbs free energies are shown in Table 1. Figure 2 shows a plot of $\ln(\gamma_2/\gamma_1)$ versus x_1. Although it does not cover the entire range from $x_1 = 0$ to $x_1 = 1$, the curves cross the X-axis at around $x_1 = 0.5$. For each isotherm, the positive and the negative areas under the curve were evaluated between $X_1 = 0.06$ and $X_1 = 0.94$, and the difference between the two numbers was found to be 5% in the worst case. On the basis of this quantitative result, the VLE data were judged to be thermodynamically consistent.

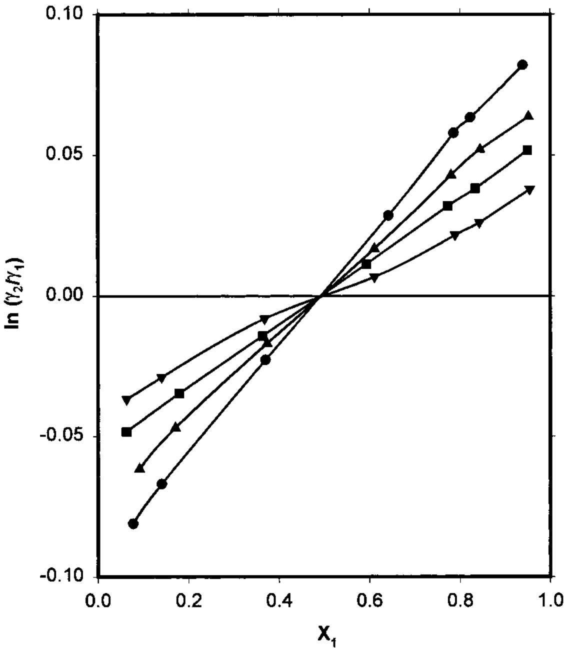

Figure 2. Area test for thermodynamic consistency of the benzene–ethylbenzene data: ●, 180 °C; ▲, 210 °C; ■, 250 °C; ▼, 280 °C.

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