High-Temperature VLE for the Ethylbenzene + Quinoline System

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In previous works, we constructed a continuous-flow apparatus designed for vapor−liquid equilibrium (VLE) data measurements at high temperatures up to 400 °C and used it to measure VLE data for the tetralin + quinoline and benzene + ethylbenzene systems. In this work, the apparatus was further modified and used for VLE measurements for the ethylbenzene + quinoline system along several isotherms (498.15, 523.15, 553.15, 583.15, 613.15, 638.15, 653.15) K. The data were successfully tested for thermodynamic consistency by using the area test.

Introduction

High-temperature vapor−liquid equilibrium (VLE) data available in the literature are quite limited. Previously, we reported VLE measurements for the tetralin−quinoline[1] and benzene−ethylbenzene[2] systems. Here, we present data for the ethylbenzene + quinoline system, for which no previous VLE measurements are available. The systems selected for our measurements consist of coal model compounds of different functionalities. This is consistent with our original objective to understand and model the VLE properties of coal liquid mixtures. The measured data for the ethylbenzene + quinoline system were successfully tested for thermodynamic consistency by using the area test.

Experimental Section

The experimental apparatus and the procedure used for the measurements were described in the previous articles.[1,2] The continuous-flow VLE apparatus consists of a feed tank, a positive displacement metering pump, a preheater oven, the main oven that houses the equilibrium cell, sensors for temperature, pressure, and liquid level measurement, bottles for sample collection, and a liquid chromatograph for sample analysis. Feed from the feed tank is continuously pumped through the preheater oven to the equilibrium cell. Temperature, pressure, and liquid levels in the equilibrium cell are accurately measured and controlled to their desired values. Liquid and vapor streams exit the equilibrium cell continuously. Sampling points are provided on the two outlets to withdraw liquid and vapor samples for analysis. The two streams are combined downstream and returned back to the feed tank.

Previously, the liquid level in the equilibrium cell was measured by an electrical conductivity sensor made by Delta-M Corporation. The sensor gave a (4−20) mA signal, which was used to control the liquid level to the desired value by manipulating the flow rate of the liquid leaving the equilibrium cell. This sensor was quite tedious to use; it required frequent calibrations and was erratic at temperatures exceeding 300 °C. It was replaced by a much simpler spherical borosilicate glass float. The float was tested, and it was confirmed to withstand temperatures up to 400 °C and pressures up to 13.75 MPa. A cross section
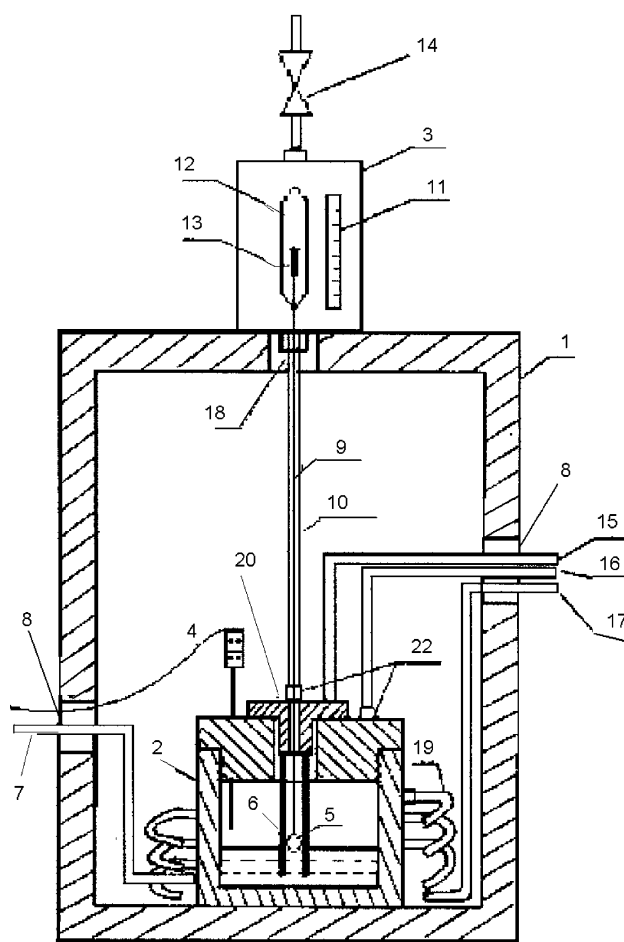
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Figure 1. Internal structure of the VLE cell and the oven. 1, main over; 2, VLE cell; 3, Jerguson level gauge (insulated; 4, thermocouple; 5, glass ball float; 6, solid rod to hold the float in place; 7, liquid-phase outlet tubing; 8, oven opening; 9, tungsten wire; 10, $^{1}/_{4}$ in. tubing; 11, ruler; 12, level gauge window; 13, level indicator; 14, plug valve; 15, pressure-sensing tube to transducer; 16, vapor-phase outlet ($^{1}/_{4}$ in. tubing); 17, feed inlet tubing ($^{1}/_{4}$ in.); 18, $^{1}/_{2}$ in. NPT male connector; 19, $^{1}/_{4}$ in. tubing coils; 20, flange; 21, top lid; 22, Swagelok tubing fitting.

of the main oven and the modified equilibrium cell with the new liquid level sensor is shown in Figure 1. The glass

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

t/°C	P/ bar	X_1	Y_1	γ_1	γ_2	G^E/RT
225	4.13	0.436 ± 0.005	0.866 ± 0.003	1.290 4	1.137 7	0.183 9
	4.91	0.601 ± 0.005	0.897 ± 0.003	1.130 2	1.428 5	0.215 9
	5.76	0.774 ± 0.005	0.935 ± 0.003	1.049 6	1.809 0	0.171 4
	6.61	0.940 ± 0.003	0.978 ± 0.002	1.014 6	2.563 7	0.070 2
	6.81	1.0	1.0			
250	1.35	0.0	0.0			
	2.18	0.044 ± 0.001	0.390 ± 0.004	2.252 7	1.006 6	0.042 2
	4.95	0.300 ± 0.004	0.777 ± 0.006	1.413 4	1.047 7	0.136 4
	5.93	0.440 ± 0.008	0.836 ± 0.005	1.214 3	1.117 5	0.147 6
	7.22	0.585 ± 0.008	0.879 ± 0.004	1.135 5	1.298 3	0.182 7
	8.53	0.773 ± 0.004	0.927 ± 0.003	1.038 2	1.617 9	0.138 2
	9.88	0.942 ± 0.003	0.977 ± 0.002	1.007 2	2.205 0	0.052 7
	10.27	1.0	1.0			
280	2.45	0.0	0.0			
	2.99	0.022 ± 0.002	0.182 ± 0.004	2.037 0	1.004 3	0.019 7
	5.60	0.147 ± 0.003	0.580 ± 0.008	1.715 5	1.032 6	0.106 7
	7.16	0.288 ± 0.006	0.710 ± 0.006	1.327 8	1.044 9	0.112 9
	9.39	0.477 ± 0.008	0.811 ± 0.006	1.148 2	1.139 8	0.134 4
	11.20	0.608 ± 0.006	0.862 ± 0.004	1.100 6	1.254 0	0.147 0
	13.35	0.791 ± 0.005	0.923 ± 0.002	1.031 6	1.461 7	0.103 9
	15.32	0.942 ± 0.002	0.974 ± 0.001	1.005 0	1.912 3	0.042 3
	16.01	1.0	1.0			
310	4.16	0.0	0.0			
	4.71	0.019 ± 0.001	0.119 ± 0.003	1.757 3	1.002 9	0.013 7
	8.05	0.164 ± 0.003	0.515 ± 0.009	1.433 1	1.019 4	0.075 1
	10.21	0.291 ± 0.006	0.651 ± 0.008	1.245 6	1.038 9	0.090 9
	12.48	0.420 ± 0.008	0.744 ± 0.006	1.157 0	1.073 3	0.102 3
	16.19	0.602 ± 0.006	0.832 ± 0.004	1.093 0	1.201 2	0.126 5
	18.94	0.775 ± 0.004	0.903 ± 0.003	1.022 5	1.323 9	0.080 4
	22.95	0.951 ± 0.002	0.975 ± 0.001	1.005 2	1.662 5	0.029 8
	23.87	1.0	1.0			
340	6.68	0.0	0.0			
	7.77	0.034 ± 0.001	0.147 ± 0.003	1.601 6	1.002 6	0.018 4
	11.12	0.163 ± 0.003	0.437 ± 0.007	1.334 6	1.014 6	0.059 2
	13.46	0.277 ± 0.005	0.571 ± 0.007	1.193 1	1.027 2	0.068 3
	17.23	0.433 ± 0.008	0.703 ± 0.006	1.127 0	1.061 2	0.085 4
	22.46	0.609 ± 0.007	0.800 ± 0.004	1.083 8	1.178 1	0.113 1
	25.90	0.769 ± 0.005	0.883 ± 0.003	1.024 9	1.222 3	0.065 3
	32.12	0.938 ± 0.002	0.961 ± 0.001	1.004 8	1.498 1	0.029 6
	34.51	1.0	1.0			
365	9.55	0.0	0.0			
	9.87	0.0038 ± 0.0002	0.015 ± 0.001			
	10.71	0.028 ± 0.001	0.131 ± 0.002			
	15.06	0.149 ± 0.002	0.422 ± 0.007			
	18.94	0.272 ± 0.005	0.552 ± 0.009			
	24.80	0.430 ± 0.006	0.680 ± 0.005			
	27.96	0.555 ± 0.009	0.742 ± 0.006			
380	11.66	0.0	0.0			
	11.95	0.0050 ± 0.0003	0.013 ± 0.001			
	13.65	0.042 ± 0.001	0.100 ± 0.002			
	17.73	0.151 ± 0.002	0.374 ± 0.005			
	22.69	0.288 ± 0.005	0.537 ± 0.009			
	28.89	0.428 ± 0.007	0.660 ± 0.006			

Figure 2. VLE data for the ethylbenzene (1) + quinolene (2) system: ●, 225 °C; ▲, 280 °C; ▼, 340 °C; ◆, 380 °C. Bold lines show liquid compositions, and dotted lines are for vapor compositions.

injection valve, a Perkin-Elmer UV spectrophotometric detector (254 nm), and a Perkin-Elmer 3 cm × 3 cm C-18 LC column. A mixture containing 70% methanol and 30% water was used as the mobile phase with a flow rate of 1.8 mL·min^{-1}. The sample preparation involved diluting 5 μL of the sample into 1 mL of pure methanol. An injection size of 3 μL was used. The column pressure was maintained around 13.75 MPa. Data analysis was done using Perkin-Elmer Turbochrome 4 Rev. 4.1 software.

For calibration, nine standard solutions in the concentration range from 10 mol % ethylbenzene to 90 mol % ethylbenzene were prepared, and reproducible chromatograms were generated. A plot of molar ratio vs area ratio of ethylbenzene to quinolene was found to be linear with a slope (calibration constant K) of 11.585. The mole fraction of ethylbenzene in an unknown solution was then obtained from the equation

$$X_{eb} = KA_r/(1 + KA_r) \tag{1}$$

where X_{eb} is the mole fraction of ethylbenzene, K is the calibration constant, and A_r is the area ratio of ethylbenzene to quinolene. With this method, the mole fractions in the vapor and the liquid samples were analyzed to within 1.5% accuracy.

In the measurements involving hydrocarbons at such high temperatures, there is always a concern about the thermal decomposition. During our experiments, thermal degradation could be easily detected by the multiple unidentified peaks occurring in the chromatogram. No degradation of the chemicals was observed for all the lower temperature isotherms up to 340 °C. However, once each during the measurements of the 365 °C and 380 °C isotherms, the feed was found to be contaminated. In each case, the system was emptied, thoroughly cleaned, and recharged with fresh feed. Although no effort was made to

float is attached at the top by a thin tungsten wire which passes through $^1/_4$ in. tubing and moves freely within it. The top of the tungsten wire is visible in the view window of an insulated Jerguson gauge mounted on the top of the oven. The 15 cm long view window of the gauge is calibrated from empty to a liquid level of 15 cm in the equilibrium cell. Although the new technique is very simple and accurate, the liquid level must be controlled to the desired value by manual operation of a metering valve on the liquid line leaving the equilibrium cell. The rest of the apparatus was the same as described in our previous work.[1,2] Ethylbenzene and quinoline used in the measurements were obtained from Sigma-Aldrich Chemical Co. and had a purity of 99.9% and 99%, respectively.

The analysis of the samples (ethylbenzene, quinoline mixtures) obtained from the VLE apparatus were carried out by a liquid chromatographic method. This method was specifically designed for the ethylbenzene + quinoline binary system. It used a Perkin-Elmer LC410 liquid chromatographic pump with a rheodyne model 7125 sample
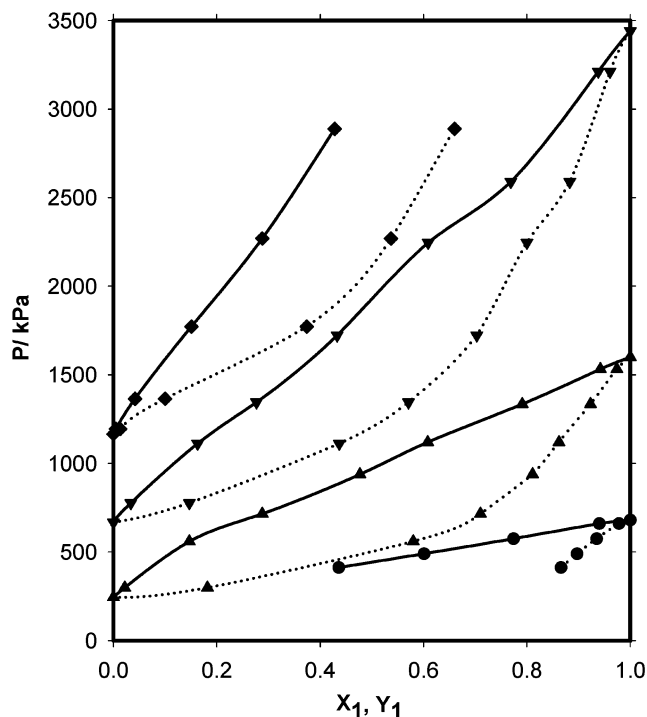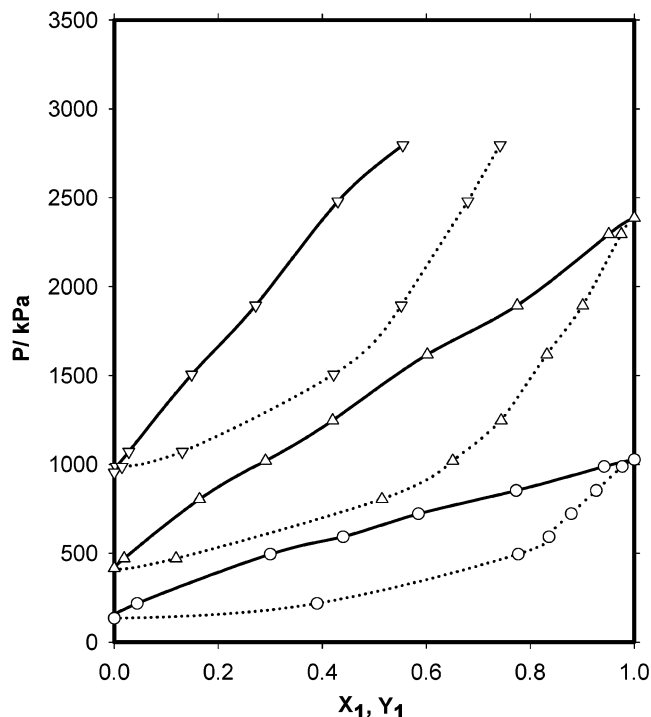
Figure 3. VLE data for ethylbenzene (1) + quinolene (2) system: ○, 250 °C; △, 310 °C; ▽, 365 °C.

Figure 4. Area test for thermodynamic consistency of ethylbenzene (1) + quinolene (2) data: ●, 225 °C; ○, 250 °C; ▲, 280 °C; △, 310 °C; ▼, 340 °C.

study the chemistry of thermal decomposition, quinoline is known to thermally degrade at such high temperatures.

Results and Discussion

The temperature, pressure, mole fraction of ethylbenzene in liquid (X_1), and mole fraction of ethylbenzene in vapor (Y_1) are given in Table 1. The $P-X-Y$ diagrams are shown in Figures 2 and 3. Two figures are provided to prevent overlap of curves corresponding to different isotherms. The uncertainties in the reported temperatures and pressures are $\Delta T = \pm 1$ K and $\Delta P = \pm 0.5\%$, which corresponds to ± 0.65 kPa at a pressure of 1.3 bar and ± 17.5 kPa at a pressure of 35 bar. The reported liquid and vapor mole fractions represent average values of four sample measurements each; upper and lower limits of the measurements are also given. The area test for thermodynamic consistency was applied to isotherms (498.15, 523.15, 553.15, 583.15, and 613.15) K, and activity coefficients were calculated using the method described in our previous articles.[1,2] The parameters for the Wagner vapor pressure correlation and the critical properties of ethylbenzene and quinolene were also given in these articles. The thermodynamic consistency test was not applied to the 638.15-K and 653.15-K isotherms, because these temperatures are in excess of the critical temperature of ethylbenzene, which is 617.2 K. The measured vapor pressures given in Table 1 agree with the values calculated from the Wagner equation to within 0.5%.
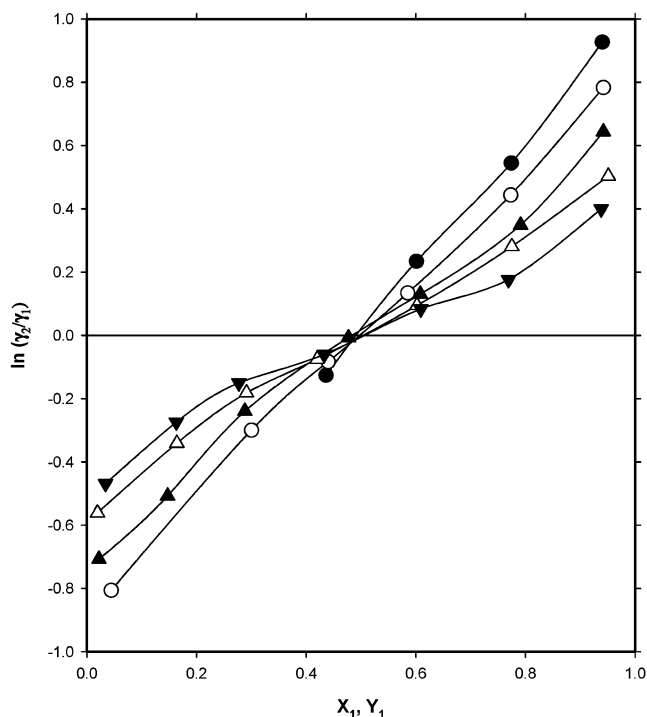
The calculated activity coefficients and the excess Gibbs free energies are shown in Table 1. Figure 4 shows plots of $\ln(\gamma_2/\gamma_1)$ vs x_1 for five isotherms. All the curves seem to cross the X axis at around $X_1 = 0.5$. For each isotherm (except 498.15 K), the positive and the negative areas under the curve were evaluated between $X_1 = 0.05$ and $X_1 = 0.95$ by numerical integration using the simple trapezoidal rule, and the differences between the two numbers were found to be 2.85%, 4.98%, 1.83%, and 3.44% for the four temperatures 250 °C, 280 °C, 310 °C, and 340 °C, respectively. On the basis of these approximate quantitative results, the VLE data were judged to be thermodynamically consistent. More accurate analysis for thermodynamic consistency using the area test or alternative tests (such as the point test) would require more data points for each isotherm.

Literature Cited

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