Liquid−Liquid Equilibria for Binary Mixtures of Water + Benzene, Water + Toluene, and Water + *p*-Xylene from 273 K to 458 K

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Mutual solubilities for benzene + water, toluene + water, and *p*-xylene + water and the vapor pressures have been measured from (273 to 458) K. The results for benzene and toluene are in good agreement with previous data and with correlations. The data for *p*-xylene are in good agreement with older data, but not with recent experiments.

Introduction

Equilibria between water and hydrocarbons are important in the processing of oil and gas and in evaluating environmental contamination. The present work was undertaken as part of a study of the solubility of aromatic hydrocarbons in aqueous alkanolamine solutions.

Experimental Work

The measurements were made in an apparatus[1] previously used in this laboratory for studies of phase equilibria; hence, only a brief description is necessary. The windowed equilibrium cell was mounted in an air bath. The contents of the cell were mixed using a magnetically driven piston pump.[2] The hydrocarbon-rich phase was drawn off the top of the cell and pumped into the bottom of the cell. The temperature of the contents of the cell was measured by a calibrated iron−constantan (type J) thermocouple, and the pressure in the cell was measured by digital Heise gauges (0−10 MPa and 0−35 MPa). The thermocouple was calibrated against a platinum resistance thermometer and found to be accurate within ±0.1 K over the range of temperatures studied. The pressure gauges had an accuracy of 0.1% of full scale by calibration against a dead weight gauge.

The chemicals were obtained from the following sources and had the purity described: benzene (Aldrich, HPLC 99.9+%), toluene (Fisher, Certified 99.8%), *p*-xylene (Aldrich, HPLC 99+%), heptane (Aldrich, HPLC 99+%), ethylene glycol (Aldrich, anhydrous, 99.8%), and water (double distilled).

To perform an experiment, water was fed into the system and a vacuum was drawn to remove dissolved air. The hydrocarbon was then injected into the cell, the temperature controller was set, and the pump was started. The system was allowed to circulate for 24 h to ensure that equilibrium was reached. The pump was then stopped, and the pressure and temperature were recorded. A sample of the lower (aqueous) phase was taken into a 40 mL bomb containing a magnetic stirring bar and 2−5 g of heptane. At temperatures below 60 °C, the lower portion of the bomb was immersed in dry ice. Alternatively, the system pressure was raised to 50 kPa. These measures ensured that no heptane vapor passed into the equilibrium cell. After thorough mixing in the sample bomb, the aqueous portion was decanted to a capped vial and the hydrocarbon portion to a 2 mL vial closed with a septum. A syringe was used to inject 2 μL of the hydrocarbon phase into an HP 5890A gas chromatograph equipped with a thermal conductivity detector. The column was a 2 m × 3.125 mm stainless steel tube packed with 80/100 mesh Chromosorb 104. For the heptane and benzene/toluene/xylene (BTX) analysis, the oven was kept at 200 °C.

A similar procedure was used to analyze the hydrocarbon phase for water. A bomb containing about 2 g of ethylene glycol was used to take a sample of the upper (hydrocarbon) phase. In the analysis of the glycol phase, the oven started at 200 °C for 3.5 min and was then ramped to 250 °C until the ethylene glycol eluted. Calibrations were prepared for binary mixtures of BTX in heptane for mole ratios from 10^{-4} to 10^{-2}. Similar calibrations were made for mixtures of water and ethylene glycol. The background water in the ethylene glycol was also determined. The newly opened bottle of ethylene glycol contained 0.038 mass % water. After 3 months, the water content was 0.061 mass %. This background water was corrected for in all experiments. The accuracy of the data is about ±10% by replicate measurements and comparison with literature data.

Table 1. Water (1) + Benzene (2) Mutual Solubilities

T/K	P/kPa	10^3x_1	10^4x_2	T/K	P/kPa	10^3x_1	10^4x_2
279.15	5.8	1.68	4.06	363.15	205	20.4	7.59
288.15	9.5	2.23, 2.34	4.08	373.15	280	25.8	8.79
298.15	16	3.20, 3.20	4.06	398.15	565	46.1	13.2
313.15	32	4.92	4.41	413.15	830	63.0	17.9
333.15	70	9.01	5.31	433.15	1320	87.1	26.1
343.15	104	11.3	6.10	453.15	2020	130.	38.4
353.15	146	15.7	6.73				

Results and Discussion

Data for the mutual solubility of benzene + water, together with the vapor pressure, are given in Table 1 over the range of temperatures from (279 to 453) K. Similar results for toluene + water and *p*-xylene + water are given in Tables 2 and 3.

Many studies of the solubilities of hydrocarbons in water and water in hydrocarbons have been made. The results are not always in accord, because of the small concentrations in both phases. Wagner[3] made a critical review of the literature and prepared correlations for the solubility of

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Table 2. Water (1) + Toluene (2) Mutual Solubilities

T	P			T	P		
K	kPa	10^3x_1	10^4x_2	K	kPa	10^3x_1	10^4x_2
273.15	1.5	1.18	1.24	373.15	175	22.6, 23.9	2.84
283.15	2.9	1.69	1.14	398.15	383	42.7, 42.5	4.45
298.15	7.0	2.73	1.16, 1.11	413.15	580	59.8	6.60
305.35	10.2	3.34	1.20	423.15	750	69.2	8.28
313.15	15	4.32	1.23	453.15	1520	120.	15.1
333.15	38	7.92	1.52	458.15	1700	133.	17.0
348.15	71	12.2	1.89				

Table 3. Water (1) + *p*-Xylene (2) Mutual Solubilities

T	P			T	P		
K	kPa	10^3x_1	10^5x_2	K	kPa	10^3x_1	10^5x_2
288.15	2.4	2.45	2.98	373.15	136	21.6	9.29
298.15	4.4	3.28	3.15	398.15	310	39.8	15.3
313.15	10.3	4.65	3.98	423.15	630	65.6	29.1
333.15	27	8.22	5.30	448.15	1170	102.	56.0
348.15	52	12.4	6.38				

hydrocarbons in water and water in hydrocarbons. This review is an update of the earlier reviews of Young[4] and Hefter.[5] Another review was prepared by Tsonopoulos,[6] who also presented correlations useful over a wider range of temperature. The present data will be compared with the correlations of Wagner and Tsonopoulos and with recent data which have appeared since the reviews were published.

Benzene + Water. The present data are compared with the correlations of Wagner and Tsonopoulos in Figure 1. The results are in good accord with both correlations. The recent data of Marche et al.[7] are in good agreement at the lower temperatures but deviate slightly at their highest temperatures. Direct comparisons with the data of Miller and Hawthorne[8] are not possible because their results were obtained at elevated pressures, but the data are consistent with the present work.

Toluene + Water. The present data are compared with the correlations of Wagner and Tsonopoulos in Figure 2. The data for toluene in water are in good agreement with the correlation of Tsonopoulos, but the data for water in toluene are slightly higher than the correlation of Wagner. The recent data of Dohányosová et al.[9] are lower than the present results at temperatures below 300 K but agree well at higher temperatures. Chandler et al.[10] presented data at temperatures from (473 to 550) K for toluene + water. Their lowest temperature value is in agreement with the present work.

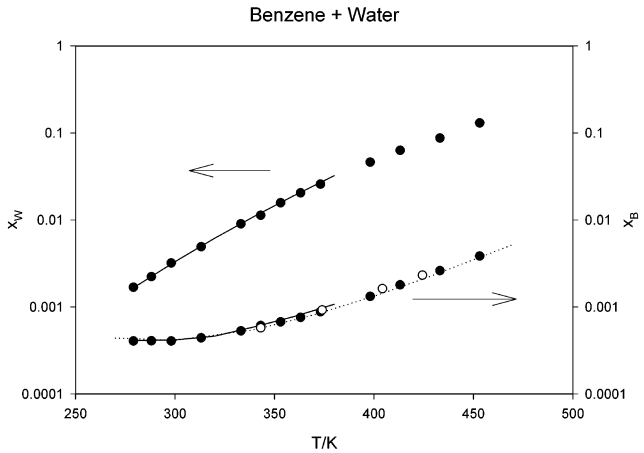

Figure 1. Mutual solubilities of water and benzene as a function of temperature: ●, this work; ○, Marche et al. (ref 7); —, Wagner (ref 3); ···, Tsonopoulos (ref 6).

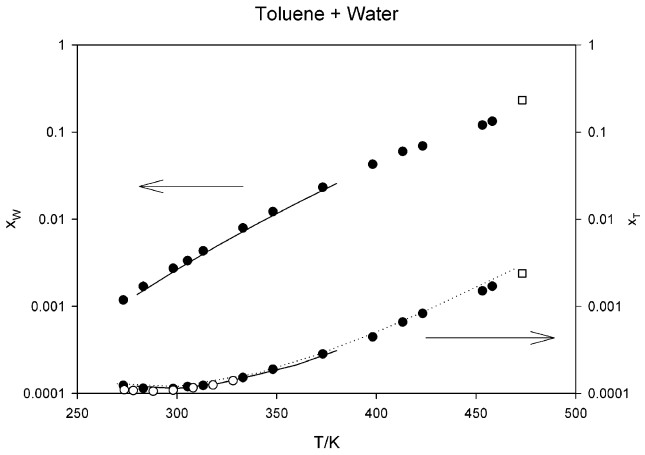

Figure 2. Mutual solubilities of water and toluene as a function of temperature: ●, this work; ○, Dohányosová et al. (ref 9); □, Chandler et al. (ref 10); —, Wagner (ref 3); ···, Tsonopoulos (ref 6).

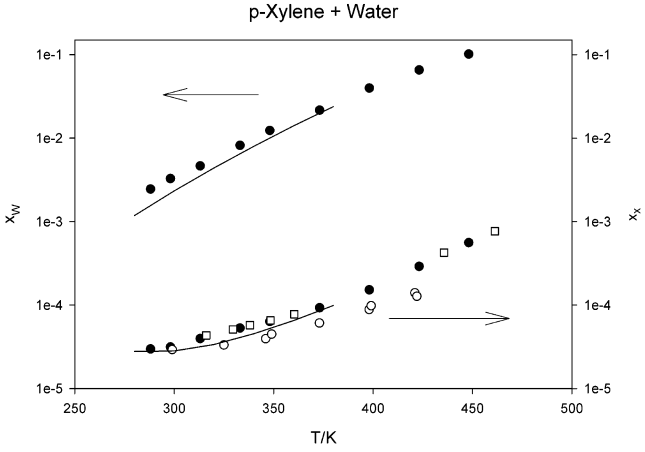

Figure 3. Mutual solubilities of water and *p*-xylene as a function of temperature: ●, this work; ○, Knauss and Copenhaver (ref 11); □, Pryor and Jentoft (ref 12); —, Wagner (ref 3).

p-Xylene + Water. The present data are compared with the correlations of Wagner in Figure 3. The agreement is not as good as that for benzene and toluene. The recent data of Knauss and Copenhaver[11] also deviate increasingly with increasing temperature. However, the older data of Pryor and Jentoft[12] are in good agreement with the present work. These data were obtained by the observation of the formation and disappearance of a cloud of finely dispersed xylene. Previous reviews have discounted these data as being too high, but they are in good agreement with the present work.

Conclusions

New data for the mutual solubilities of benzene + water, toluene + water, and *p*-xylene + water have been measured in the temperature range from (273 to 458) K. The data for benzene and toluene are in good agreement with new data and correlations. The data for *p*-xylene are in good agreement with older data but deviate from the most recent results.

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