Liquid−Liquid Equilibria for Binary Mixtures of Water + Acetophenone, + 1-Octanol, + Anisole, and + Toluene from 370 K to 550 K

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Liquid−liquid equilibria are reported for binary mixtures of water with acetophenone, 1-octanol, anisole, and toluene in the temperature range of 370 K to 550 K. The data were measured in a variable-volume windowed vessel by a traditional cloud point technique. These results are in good agreement with data reported in the literature. Above 450 K binary data for the water + anisole and water + acetophenone systems have not been reported previously.

Introduction

Liquid−liquid mutual solubility data for aqueous/organic systems are necessary for the design of a variety of high-temperature commercial separations such as petroleum processing, water pollution abatement,[1] and removal of waste petroleum and pesticides from soil.[2] These data are also of increasing interest as liquid water in the near-critical region (520−647 K) is proving to be a good solvent for chemical reactions. As the temperature is increased from room temperature to 550 K, the density decreases from 1.0 to 0.7 $g\cdot cm^{-3}$ and the dielectric constant decreases from 80 to 20.[3,4] With these properties that are more like ambient acetone than ambient water,[5] near-critical water readily dissolves even nonpolar organics such as toluene.[1,6,7]

In addition, the dissociation constant of water increases by 3 orders of magnitude from room temperature to 520 K,[8] making it a source of hydronium and hydroxide ions that may catalyze reactions. Thus, near-critical water can be used simultaneously as a reaction solvent, catalyst, and reactant for reactions that are traditionally acid- or base-catalyzed.[5] In many processes, this may eliminate the need to neutralize and dispose of conventional acids or bases otherwise used as catalysts. [9]

Near-critical water has been used as a solvent, catalyst, and reactant for a number of hydrolyses that require added mineral acid at ambient conditions.[5,10−13] It has also been successfully used for the Friedel−Crafts alkylation of phenol and *p*-cresol with *tert*-butyl alcohol.[14]

The special properties of water in the near-critical region make it an especially good solvent for carrying out organic chemical reactions that are heterogeneous at lower temperatures, as many of these reactions become homogeneous in near-critical water. In conventional reactions, this homogeneity generally results in a costly separation of products from traditional solvents. However, as the solubility of organics in water is tunable with temperature, products from a near-critical water reaction can be easily separated from the solvent by simply cooling and decanting. Thus the phase equilibria data are crucial for the design of any of such processes.

To aid in the development of predictive models for the phase equilibria of organic compounds + water at elevated temperature, the binary liquid−liquid equilibria of water with three model compounds—acetophenone, 1-octanol, and anisole—were measured up to the upper critical solution temperature. The already well-characterized water + toluene system[1,6,7,15−17] was measured at elevated temperature to verify our experimental procedure. Acetophenone, 1-octanol, and anisole were chosen to investigate the effects of hydrogen bonding functionality on liquid−liquid equilibria with water at elevated temperature. The liquid−liquid equilibria of water + 1-octanol were measured previously for the alcohol-rich phase at elevated temperature,[18] while the data for water + acetophenone and water + anisole have not been measured previously except at lower temperature.[17,19]

Experimental Section

Chemicals. Chemicals used in the measurements were the following with purities given in mass percent: acetophenone (Aldrich 99%), anisole (Aldrich 99%), 1-octanol (Aldrich 99%), toluene (Aldrich 99.8+%), and water (Aldrich HPLC grade). Each organic compound was analyzed by GC−MS both out of the bottle and after the solubility data had been taken. Based on the peak areas of our GC−MS results, most compounds studied were more pure than Aldrich suggests. Based on GC−MS peak areas, we estimate the purities out of the bottle to be acetophenone 99.45%, anisole 99.9+%, 1-octanol 99.3%, and toluene 99.3%. All compounds were found to be stable under measurement conditions. While anisole may hydrolyze to methanol and phenol,[20] and 1-octanol may isomerize to 2-octanol in high-temperature water over the course of many hours to days, we were able to measure the solubility of these compounds in only a few hours.

Apparatus and Procedure. Mutual solubilities were measured in a variable-volume windowed vessel (1.59 cm i.d., 20 cm^3 maximum volume) similar to that used by McHugh.[21,22] The vessel window and variable-volume piston were sealed with fluorocarbon O-rings (Parker V 0747) capable of withstanding water and organics at temperatures exceeding 290 °C for short periods of time. Phase boundaries were measured by visually observing the

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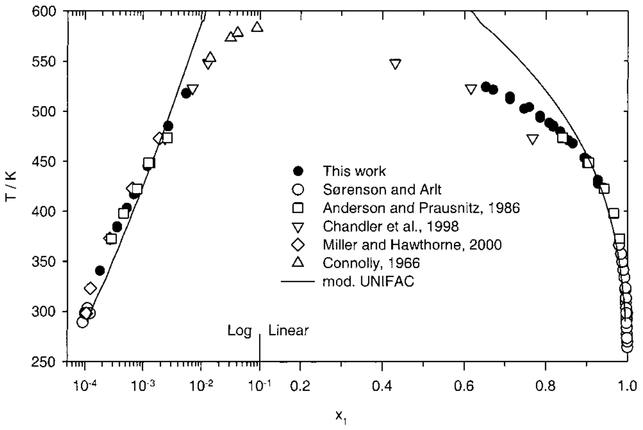

Figure 1. Liquid−liquid equilibria for toluene (1) + water (2). The data from this work were measured at 6.80 MPa. The literature data (Miller and Hawthorne,[16] Anderson and Prausnitz,[1] Chandler et al.,[6] Connolly,[7] Sørenson and Arlt[17]) were measured at a variety of pressures shown in Table 1.

cloud point through a 2.54 cm diameter sapphire window (1.27 cm viewable area) with a CCD camera (Sony) mounted on a 0.635 cm borescope (Olympus). The borescope and video camera not only allowed for safe observation of the phase equilibria, but also provided a significant magnification of the viewable area. The binary mixtures were stirred with a Teflon-coated stir bar coupled with an external magnet. The entire cell was placed in a thermostated air bath (modified Varian 3400 gas chromatograph) with temperature control better than ±0.5 K. Precise temperature control was not required as cloud points were induced and observed while cooling the vessel. The temperature was measured with a hand-held readout (HH-22 Omega) and thermocouple (Omega Type K) inserted into the center of the phase equilibria vessel. The thermocouple response time was on the order of seconds. The combination of thermocouple and readout was accurate to ±0.2 K and calibrated for each experiment against a platinum RTD (Omega PRP-4) with a DP251 precision RTD benchtop thermometer (DP251 Omega) accurate to ±0.025 K and traceable to NIST. Back-pressure was applied to the piston with a syringe pump (ISCO 100D) operated at constant pressure. To avoid any vapor phase, the pressure was held constant at 6.80 MPa (except where noted) measured with a Druck DPI 260 gauge with PDCR 910 transducer accurate to ±0.001 MPa. The pressure was measured on the back side of the piston and differed from the pressure of the aqueous−organic mixture by as much as 0.15 MPa. At temperatures below 520 K, however, pressure changes of less than 0.75 MPa made no measurable difference in the cloud points.

While visually obtaining a cloud point can be somewhat subjective, it avoids the challenges associated with sampling from pressurized, high-temperature systems. When making similar measurements of similar binary and ternary aqueous systems, Anderson and Prausnitz discuss sampling error.[1] Small droplets of one liquid can become entrained in another, solutes adsorb on the walls of the sampling lines, and changes in temperature and pressure while sampling can lead to liquid−liquid and vapor−liquid phase splits. Differences in the densities and viscosities of the resulting phases lead to physical separations that are sources of error.[1] While these problems can be overcome with sufficient time and attention to detail, the cloud point technique reduces this tedium by avoiding sampling altogether.

Table 1. Liquid−Liquid Equilibrium for Toluene (1) + Water (2)

10^2 (x_1 ± error)	T/K (± 1 K)	P/MPa	10^2 (x_1 ± error)	T/K (±1 K)	P/MPa
		This Work			
0.0183 ± 0.0005	340.6	6.80	75.9 ± 0.3	504.2	6.80
0.0360 ± 0.0008	384.1	6.80	78.6 ± 0.3	494.7	6.80
0.0527 ± 0.0010	403.2	6.80	80.9 ± 0.2	488.4	6.80
0.0693 ± 0.0011	417.2	6.80	81.8 ± 0.3	485.1	6.80
0.118 ± 0.002	445.0	6.80	83.5 ± 0.2	479.8	6.80
0.268 ± 0.005	485.2	6.80	85.5 ± 0.2	470.9	6.80
0.547 ± 0.011	518.0	6.80	86.6 ± 0.2	467.8	6.80
65.3 ± 0.3	524.3	6.80	89.5 ± 0.2	453.3	6.80
67.1 ± 0.3	521.6	6.80	90.2 ± 0.2	451.1	6.80
71.2 ± 0.3	513.5	6.80	92.7 ± 0.3	429.2	6.80
74.7 ± 0.3	502.5	6.80	94.2 ± 0.2	422.8	6.80
		Literature			
0.0107[a] ± 0.0002	298.0	5.00	0.011[e]	298.2	0.10
0.0125[a] ± 0.0004	323.0	5.00	0.011[e]	303.2	0.10
0.0270[a] ± 0.0010	373.0	5.00	0.013[e]	298.2	0.10
0.0660[a] ± 0.003	423.0	5.00	97.92[e]	366.2	0.10
0.190[a] ± 0.010	473.0	5.00	98.42[e]	357.2	0.10
0.0286[b] ± 0.002	372.6	0.15	98.71[e]	349.2	0.10
0.0463[b] ± 0.002	398.0	0.38	98.98[e]	341.2	0.10
0.0794[b] ± 0.003	422.6	0.75	99.22[e]	333.7	0.10
0.13[b] ± 0.002	448.4	1.43	99.51[e]	321.2	0.10
0.123[b] ± 0.003	448.5	1.40	99.51[e]	323.2	0.10
0.259[b] ± 0.011	473.6	2.36	99.51[e]	323.2	0.10
84.08[b] ± 0.16	473.6	2.36	99.62[e]	313.2	0.10
90.17[b] ± 0.08	448.4	1.43	99.63[e]	313.2	0.10
90.48[b] ± 0.17	448.5	1.40	99.64[e]	311.7	0.10
94.21[b] ± 0.08	422.6	0.75	99.65[e]	308.2	0.10
96.59[b] ± 0.04	398.0	0.38	99.69[e]	303.2	0.10
98.08[b] ± 0.04	372.6	0.15	99.69[e]	303.2	0.10
0.238[c] ± 0.017	473.2	2.50	99.71[e]	298.2	0.10
0.703[c] ± 0.095	523.2	5.80	99.72[e]	303.2	0.10
1.29[c] ± 0.06	548.2	8.60	99.72[e]	298.2	0.10
43.1[c] ± 1.5	548.2	8.60	99.73[e]	303.2	0.10
61.6[c] ± 3.2	523.2	5.80	99.77[e]	298.2	0.10
76.8[c] ± 3.1	473.2	2.50	99.77[e]	293.2	0.10
0.714[c] ± 0.03	523.2	17.2	99.77[e]	293.2	0.10
1.29[c] ± 0.04	548.2	17.2	99.80[e]	298.2	0.10
54.7[c] ± 1.5	548.2	17.2	99.83[e]	291.2	0.10
66.5[c] ± 1.3	523.2	17.2	99.83[e]	283.2	0.10
1.4[d]	553.2	15.0	99.84[e]	283.2	0.10
3.1[d]	573.2	17.0	99.86[e]	277.2	0.10
4.1[d]	578.2	18.0	99.90[e]	283.7	0.10
8.8[d]	583.2	18.0	99.97[e]	270.2	0.10
0.010[e]	298.2	0.10	99.99[e]	264.2	0.10
0.010[e]	298.2	0.10			

[a] Miller and Hawthorne.[16] [b] Anderson and Prausnitz.[1] [c] Chandler et al.[6] [d] Connolly.[7] [e] Sørenson and Arlt.[17]

To observe a cloud point, at each concentration the cell and contents were heated 10−20 K above the phase boundary. The vessel was then cooled at a rate between 1 and 5 K/min until opalescence was observed. When cooling too slowly, a second phase would form on the wall of the vessel without forming a cloud point. When cooling too quickly, we observed supersaturation. To verify that the phase splitting observed was at equilibrium, each cloud point was repeated at different cooling rates. These were reproducible to within a range of ±1 K, and the two values were averaged. While the cell would not go completely dark for mixtures extremely dilute in one component, the cloud point was clearly visible at compositions as low as 1×10^{-4} mole fraction. Each component was metered in with a syringe pump (ISCO 500D) able to measure a volume difference of ±0.005 cm^3. When less than 0.10 cm^3 was added, the small amounts of organic or water were added through a sample loop with a calibrated volume in order to measure the volume more exactly.

Table 2. Liquid−Liquid Equilibria for Acetophenone (1) + Water (2)

10^2 (x_1 ± error)	T/K (± 1 K)	P/MPa
0.145 ± 0.003	339.9	6.80
0.179 ± 0.004	351.4	6.80
0.281 ± 0.006	383.7	6.80
0.317 ± 0.011	392.2	6.80
0.439 ± 0.012	411.0	6.80
0.693 ± 0.017	436.0	6.80
1.822 ± 0.040	479.3	6.80
6.54 ± 0.12	500.8	6.80
12.2 ± 0.2	502.1	6.80
15.5 ± 0.2	500.9	6.80
20.5 ± 0.3	498.3	6.80
21.0 ± 0.3	497.6	6.80
31.4 ± 0.4	488.1	6.80
42.5 ± 0.4	471.2	6.80
51.5 ± 0.4	454.0	6.80
59.1 ± 0.5	437.4	6.80
66.8 ± 0.4	416.0	6.80
74.6 ± 0.4	388.5	6.80
79.9 ± 0.4	363.0	6.80
83.9 ± 0.3	342.2	6.80

Table 3. Liquid−Liquid Equilibria for 1-Octanol (1) + Water (2)

10^2 (x_1 ± error)	T/K (± 1 K)	P/MPa
0.0122[a] ± 0.0004	354.3	6.80
0.0236 ± 0.0005	381.4	6.80
0.0540 ± 0.0011	428.2	6.80
0.0995 ± 0.0020	452.2	6.80
0.183 ± 0.004	477.9	6.80
0.368 ± 0.019	499.0	6.80
0.736 ± 0.027	522.1	6.80
1.28 ± 0.03	537.9	6.80
10.3 ± 0.1	542.7	6.80
21.5 ± 0.3	526.4	6.80
34.0 ± 0.5	501.9	6.80
42.2 ± 0.6	480.5	6.80
47.9 ± 0.7	461.2	6.80
57.7 ± 0.9	419.3	6.80
68.6 ± 0.9	356.1	6.80

Table 4. Liquid−Liquid Equilibria for Anisole (1) + Water (2)

10^2 (x_1 ± error)	T/K (± 1 K)	P/MPa
0.0768 ± 0.003	373.7	6.80
0.292 ± 0.004	440.9	6.80
0.622 ± 0.007	477.9	6.80
1.28 ± 0.01	507.3	6.80
3.19 ± 0.04	536.3	7.48
7.67 ± 0.09	548.4	8.16
26.4 ± 0.3	551.8	8.16
49.2 ± 0.6	524.8	6.80
69.2 ± 1.0	487.6	6.80
89.1 ± 1.3	415.8	6.80
97.3 ± 1.1	344.7	6.80

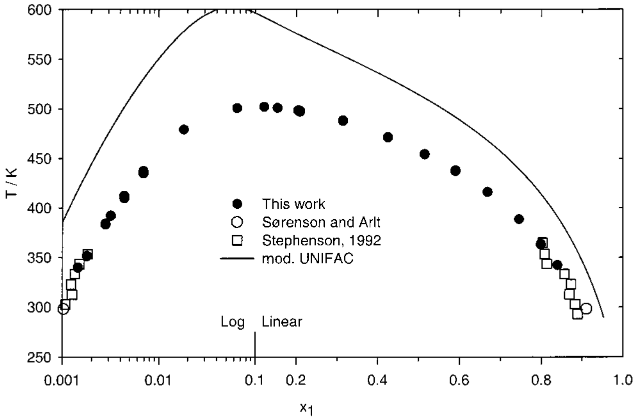

Figure 2. Liquid−liquid equilibria for acetophenone (1) + water (2). The data from this work were measured at 6.80 MPa. The literature data from Sørenson and Arlt[17] and from Stephenson[19] were measured at 0.10 MPa.

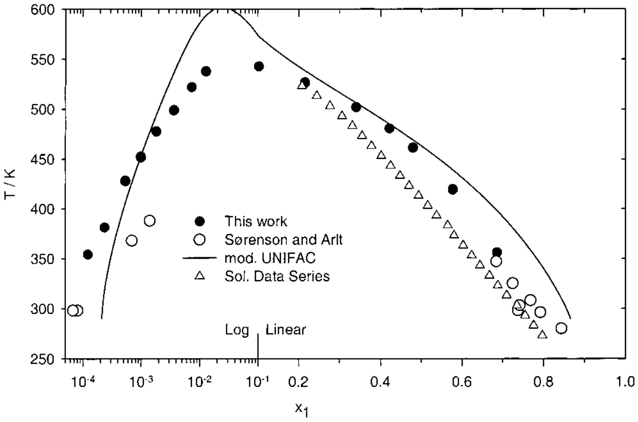

Figure 3. Liquid−liquid equilibria for 1-octanol (1) + water (2). The data from this work were measured at 6.80 MPa. The literature data from Sørenson and Arlt[17] and Stephenson, Stuart, and Tabak[27] were taken at 0.10 MPa. The literature data from the Solubility Data Series[18] were taken at three-phase pressure.

Results and Discussion

To verify the accuracy of our experimental procedure, the liquid−liquid equilibria of the already well-characterized toluene−water system was measured and compared with data from the literature (Figure 1, Table 1). The toluene-rich side of the liquid−liquid phase equilibria curve was repeated to verify that the reproducibility falls within the error that we report. The data sets are combined and shown in Table 1 and Figure 1. Nucleation of the vapor phase made the observation of the liquid−liquid immiscibility cloud point difficult, so the pressure was increased beyond the three-phase pressure to avoid this phenomenon. The pressure was held at a constant 6.80 MPa except where three-phase pressures were higher than 6.80 MPa. For the anisole−water system, the pressure was increased to 8.16 MPa to avoid the formation of a vapor phase. Below 520 K, the water + organic systems were relatively incompressible and the overpressure made little difference in the cloud point. As can be seen in Figure 1, our data are in good agreement with those from the literature.[1,6,7,16,17,19] The mutual solubility data for water with acetophenone, 1-octanol, anisole, and toluene are presented in Tables 1−4 and Figures 1−4.

The variability in the cloud point temperatures observed (±1 K) was much larger than the precision of temperature measurement (±0.2 K) and was independent of composition. The uncertainty in composition was calculated using standard error analysis techniques (partial derivatives) assuming the sources of error are independent. The sources of error considered were uncertainties in initial loading, in each subsequent loading, and in the measured sample loop volume for each injection. Each of these errors depended on the accuracy of volumetric measurements, save the sample loop error. This error was equated to the standard deviation in the sample loop volume measurements.

Impurities in the compounds used are also sources of error. Each organic compound was analyzed by GC−MS both out of the bottle and again after phase equilibria measurements at high temperature had been taken. The estimated impurities in mass percent are as follows: anisole contained 0.1% of 2-methyl anisole, 1-octanol

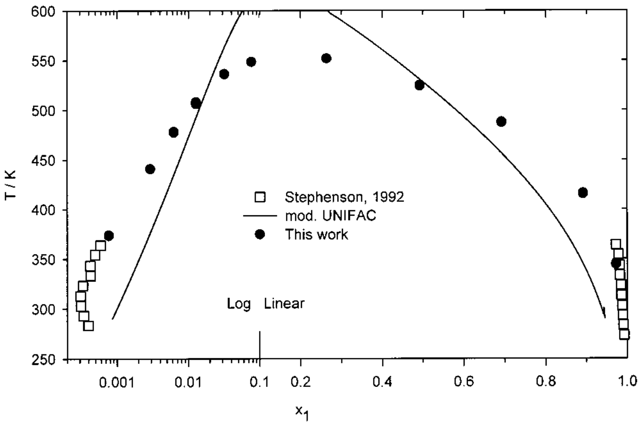

Figure 4. Liquid−liquid equilibria for anisole (1) + water (2). The data from this work below 530 K were measured at 6.80 MPa. Above 530 K, the pressure was increased slightly beyond the three-phase pressure to avoid the formation of a vapor phase. The pressure associated with each data point is shown in Table 4. The literature data from Stephenson[19] were measured at 0.10 MPa.

contained 0.5% of 2-octanol and 0.2% of tridecane, toluene contained 0.4% cyclohexane and 0.3% 1,3-dimethylcyclohexane, and acetophenone contained 0.5% of 2-phenyl-2-propanol and 0.05% of 1-phenyl ethanol. All compounds and impurities were stable in high-temperature water for several hours with the exception of 2-phenyl-2-propanol and 1-phenyl ethanol, which dehydrated to α-methylstyrene and styrene, respectively. Impurities were expected to have the most pronounced effect on measurements at or near the upper critical solution temperature.[23] Due to the dilution with water at the upper critical solution temperature, the total mole fraction of impurities was never larger than 1×10^{-3}. Snyder and Eckert investigated the effect of a third component on a binary liquid−liquid upper critical solution temperature. They found that third component mole fractions in excess of 2×10^{-3} were required to make even a 1 K change in the measured upper critical solution temperature of the hexane + nitrobenzene system.[23] Admittedly, impurities may have a greater effect in aqueous + organic systems.

We examined techniques for predicting high-temperature water + organic equilibria. The only model that was somewhat successful was modified UNIFAC,[24−26] and it fit the data with only varying success at lower temperature. These results are shown in Figures 1−4. Toluene, the compound with the least functionality and no hydrogen bonding capacity, is the most closely approximated by the modified UNIFAC at lower temperatures with good agreement up to 500 K. The modified UNIFAC shows a rough fit for the binary LLE of water with 1-octanol and anisole—overpredicting the solubility at lower temperature and underestimating the mutual solubilities at higher temperature. The modified UNIFAC fails to predict the LLE of water with acetophenone, underpredicting the mutual solubilities at all temperatures measured. In all cases, the modified UNIFAC grossly overpredicts the upper critical solution temperature. This is due, in part, to the fact that the modified UNIFAC does not take into account the radical decrease in density, dielectric constant, and hydrogen bonding that take place when water is heated from ambient to over 470 K.

Conclusion

We have measured liquid−liquid equilibria for hydrocarbons and water, useful for design of industrial reaction and separations equipment at elevated temperature and pressure. For systems where literature data were available, our measurements are in good agreement. The visual observation of a cloud point allows for rapid determination of water−organic mutual solubility data. Like traditional sampling techniques, these data were subject to errors in loading precision, temperature control/measurement, and impurities, but the myriad of errors associated with sampling high-temperature, high-pressure systems are completely eliminated.

Acknowledgment

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