Registry No. 2-Pentanol, 6032-29-7; 2-butanone, 78-93-3.

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Mutual Solubilities in Six Binary Mixtures of Water + a Heavy Hydrocarbon or a Derivative

William A. Leet, Ho-Mu Lin, and Kwang-Chu Chao*

School of Chemical Engineering, Purdue University, West Lafayette, Indiana 47907

Mutual solubilities at the three-phase vapor–liquid–liquid equilibrium pressure were experimentally determined for six binary mixtures of water with *m*-cresol, quinoline, indoline, 1,2,3,4-tetrahydroquinoline (THQ), thianaphthene, or 9,10-dihydrophenanthrene at temperatures from 293 to 502 K. The equilibrium compositions of both liquid phases, temperature, and three-phase equilibrium pressure are reported.

Introduction

The fluid phase equilibrium of hydrocarbon and water mixtures is of fundamental interest in the chemical, petroleum, and natural gas industries. Much is known about the solubilities of hydrocarbons and water at temperatures close to ambient. High-temperature data are available only for a limited number of paraffinic, olefinic, and naphthenic hydrocarbons and for a few aromatic hydrocarbons.

Schneider and co-workers (*1–6*) reported solubility data for binary mixtures of water with several alkanes, alkylated benzenes, phenol, biphenyl, tetralin, and *cis*- and *trans*-decalin at temperatures up to 693 K and pressures to 370 MPa. Skripka and co-workers (*7–11*) studied the phase behavior of water in mixtures with heavy *n*-alkanes (up to *n*-eicosane) at temperatures from 323 K to the three-phase critical point and at pressures to 79 MPa. Wilson and co-workers (*12*, *13*) recently investigated the mutual solubilities of hydrocarbons and water along the three-phase locus to temperatures and pressures approaching the critical end point. Compositions, temperature, and pressure were reported for aqueous hydrocarbon systems of several paraffins, olefins, naphthenes, light aromatics, 1-methylnaphthalene, and 1-ethylnaphthalene.

We report in this work the mutual solubilities of water and six polycyclic aromatic hydrocarbons, which are of interest to the processing of coal and heavy oils. The hydrocarbons studied include N-, O-, and S-containing heteronuclear aromatics and a three-ring aromatic.

Experimental Apparatus

The measurements of this work were made in a recirculating static apparatus. Figure 1 shows the schematic diagram. The heart of the apparatus is the equilibrium cell, which is made from a clear flat insert gauge (Eugene Ernst Products Model EEPWT-15) rated to 10 MPa at 593 K. The cell body is 316 stainless steel and has an internal volume of approximately 100 cm^3. Tempered glass windows enclose the cell on opposing sides for visual observation of the phases. All feed and sample tubing connections to the cell, including a dip tube for sampling of the upper liquid layer, are mounted into the cell end plugs. Samples are withdrawn from the equilibrated phases through $^1/_{16}$-in. 316 stainless steel tubing. The cell temperature is measured by a calibrated type K thermocouple inserted into the cell body. The thermocouple was calibrated to an accuracy of ±0.1 K. A Model CMM 0–500 psi Heise gauge measures pressure in the cell to 0.1% of the maximum range. The cell is submerged in a thermostated silicone oil bath (Dow Corning 550 silicone fluid) controllable to within ±0.1 K over the range of 333–513 K.

To promote the attainment of equilibrium, the cell contents are mixed by means of a magnetic recirculation pump submerged in the oil bath. The pump is similar to that described by Ruska and co-workers (*14*). The function of the pump is to withdraw the fluid of the heavier phase from the bottom of the equilibrium cell and discharge the fluid into the headspace of the cell. By judicious adjustment of pump drive speed, adequate mixing is achieved without the creation of stable emulsions. Recirculation rates on the order of 10–30 cm^3/min have been found satisfactory.

The hydrocarbon of interest and water were fed to the equilibrium cell by positive displacement pumps. Enough feed material was added to diminish the cell vapor volume to a mere indicator bubble and to position the liquid–liquid interface at about the center of the cell. The cell contents were then recirculated by magnetic pump and heated to the desired temperature. The liquids were degassed by repeatedly bleeding vapor from the top of the cell until the cell pressure no longer changed with bleeding.

Before withdrawal of the samples from the liquid phases at equilibrium, the liquids in the cell were recirculated for 5–30 min and then allowed to stand and settle. The temperature and pressure were recorded. Liquid samples of each phase were withdrawn from the cell via insulated $^1/_{16}$-in. tubing under cell pressure. In case the three-phase equilibrium pressure was lower than atmospheric pressure, the cell was pressurized with

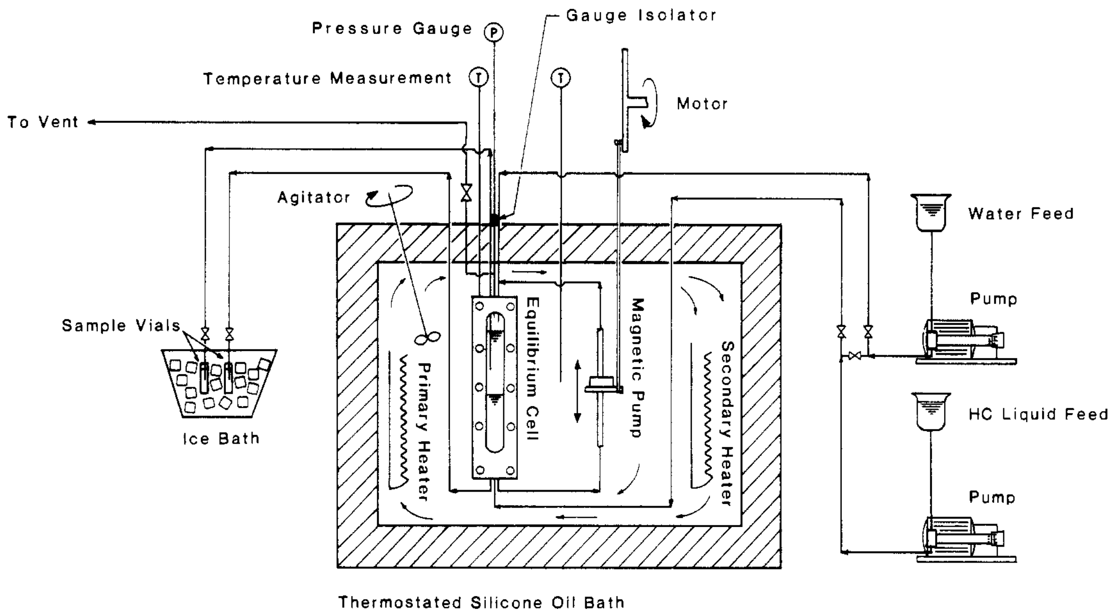

Figure 1. Liquid-liquid mutual solubility apparatus.

nitrogen to about 0.2 MPa to develop adequate pressure for sampling. The sample line was first purged with about 1 cm^3 of sample. A sample of 1-3 cm^3 was then withdrawn into a tared, septum-capped sample vial. The sample vial was reweighed to determine the amount of sample collected prior to analysis of the composition as described below.

To extend the measurement to lower temperatures than can be conveniently obtained in the liquid bath, water and hydrocarbon mixtures were prepared and left to stand at room temperature (293.5 ± 0.5 K) or in a thermostated air bath at 311.2 ± 0.2 K for 24 h. For each of the mixtures prepared, the aqueous layers were sampled and analyzed, and the remaining aqueous layer was decanted. The more dense hydrocarbon liquid layer was then sampled and analyzed.

At a fixed temperature, a sufficient number of samples were taken from each liquid phase until at least two consecutive samples yielded nearly the same analysis. A total of three or four samples were generally required. The reported compositions in Tables I-VI are average values from replicate samples that gave replicable analyses.

Analysis of Samples

Tsonopoulos and Wilson (*12*) discussed the major problems in the measurement of mutual solubilities of water and hydrocarbon. Hydrocarbon solubilities are extremely low at the low temperatures. At all temperatures, trace contamination of one phase with small amounts of the other phase can lead to serious sampling error.

Samples of the aqueous layer are analyzed for hydrocarbon by gas chromatography (GC). For the case of quinoline and *m*-cresol, which are relatively soluble in water at room temperature, the collected sample was first homogenized by addition of 1-3 g of accurately weighed dry pyridine (Aldrich Chemical Co., 99.9+% pure material dried over 3Å molecular sieves) or ethylene glycol (Aldrich Chemical 99.9+% dried by similar method) and subsequent agitation. The GC analysis was carried out on a Varian Model 3701 gas chromatograph with flame ionization detector using a $^1/_8$ in. × 6 ft. 304 SS column packed with 10% Dexil 300 GC on 60/80 mesh Anakrom ABS. GC response to the hydrocarbon was calibrated with quinoline + pyridine or *m*-cresol + ethylene glycol standards prepared by weight. The GC analysis gave the concentration of quinoline in pyridine (or *m*-cresol in ethylene glycol). From the amount of pyridine (ethylene glycol) charged to the sample and the total weight of the sample, the concentration of the hydrocarbon in the sample was calculated.

Indoline, thianaphthene, and 1,2,3,4-tetrahydroquinoline are only slightly soluble in water at low temperatures. Analysis for the equilibrium water phase was made by first injecting 0.5-2.5 of accurately weighed *n*-decane (Aldrich Chemical Co., 99+% purity) into the sample vial. The vial was agitated to extract the hydrocarbon into the decane phase. The decane extract was then analyzed by GC in much the same way as quinoline and *m*-cresol.

Analysis for the concentration of water in the equilibrium hydrocarbon phase was carried out by Karl Fischer (KF) titration. The samples were first homogenized by addition of 1-3 g of accurately weighed dry pyridine or ethylene glycol and subsequently agitated. Aliquots of 1 μL-5 mL were then analyzed by standard Karl Fischer titration using a Labindustries aquameter equipped with a platinum electrode to indicate the titration end point. The reagent titre was standardized with reagent grade water.

The accuracy of both analytical techniques has been established by analysis of samples of known composition. Karl Fischer titrations are generally accurate to ±3%, while GC analyses for trace amount of hydrocarbon in water are reproducible to ±5%. Nevertheless, greater scatter exists in the measured solubility data due to sampling difficulties. Sequential samples of the hydrocarbon phase generally agree to within ±5% of the mole fraction of water at all but the lowest concentrations for which replicability decreases to ±10%. Such deterioration is limited to temperatures approaching the melting points of the heaviest hydrocarbons studied. The effect is exaggerated by the nearly equal densities of water and the aromatic species studied here. With respect to aqueous phase sampling, sample replicability is within ±5% of the mole fraction of hydrocarbon for concentrations of 0.7 mol % hydrocarbon and greater. For lower concentrations approaching the lower quantitative limit of the GC analyses, sample scatter increases to ±15%.

The hydrocarbons used in this work were purchased from Aldrich Chemical Co., with claimed purities of 99+% for *m*-cresol and quinoline, 99% for indoline and 9,10-dihydrophenanthrene, and 98+% for 1,2,3,4-tetrahydroquinoline and thianaphthene. All the chemicals were vacuum-distilled prior to use. The purities after distillation were better than 99% by GC analysis. Reagent grade water (16 MΩ cm^{-1}) was used in all experiments.

Table I. *m*-Cresol + Water Mutual Solubility Data

T, K	p, MPa	nonaq phase x_W	aq phase x_{Cr}
293.5		0.480	0.003 96
313.2		0.499	0.004 23
331.6		0.539	0.005 03
350.4		0.583	0.006 22
371.3		0.634	0.008 29
392.9	0.204	0.701	0.013 0
412.1	0.366	0.795	0.023 9

Table II. Quinoline + Water Mutual Solubility Data

T, K	p, MPa	nonaq phase x_W	aq phase x_Q
293.5		0.604	0.000 89
313.2		0.589	0.000 90
338.0		0.578	0.001 15
353.4		0.564	0.001 48
373.2		0.558	0.001 94
393.8	0.204	0.565	0.002 81
419.0	0.491	0.577	0.004 36
432.8	0.624	0.594	0.006 07
453.0	1.02	0.639	0.009 70
472.4	1.62	0.696	0.017 6
482.2		0.736	0.023 9
493.4		0.783	0.045 2
498.2		0.817	0.069 5

Table III. Indoline + Water Mutual Solubility Data

T, K	p, MPa	nonaq phase x_W	aq phase x_I
293.5		0.0992	0.000 53
313.2		0.105	0.000 66
332.6		0.108	0.000 83
352.2		0.119	0.001 04
373.2		0.143	0.001 48
391.8	0.202	0.187	0.001 99
411.7	0.353	0.239	0.002 70
432.4	0.621	0.303	0.003 85
450.5	0.970	0.356	0.005 75
470.5	1.56	0.415	0.008 66
479.6	1.87	0.433	0.011 7
490.3	2.30	0.460	0.019 9

Table IV. 1,2,3,4-Tetrahydroquinoline + Water Mutual Solubility Data

T, K	p, MPa	nonaq phase x_W	aq phase x_{THQ}
293.5		0.0355	0.000 19
313.2		0.0428	0.000 25
333.0		0.0504	0.000 32
352.8		0.0583	0.000 42
373.6		0.0733	0.000 54
392.7	0.198	0.106	0.000 73
413.2	0.367	0.145	0.001 00
432.6	0.630	0.188	0.001 50
452.4	1.00	0.242	0.002 03
471.4	1.53	0.304	0.003 08
488.5	2.24	0.366	0.004 66
501.6	2.79	0.395	0.006 57

Table V. Thianaphthene + Water Mutual Solubility Data

T, K	p, MPa	nonaq phase x_W	aq phase x_T
332.2		0.0080	0.000 029
351.7		0.0126	0.000 047
372.2		0.0188	0.000 079
392.5	0.202	0.0308	0.000 14
410.6	0.347	0.0440	0.000 23
430.5	0.597	0.0756	0.000 40
450.0	0.963	0.117	0.000 73
469.3	1.49	0.154	0.001 2
490.5	2.30	0.186	0.002 1

Table VI. 9,10-Dihydrophenanthrene + Water Mutual Solubility Data

T, K	p, MPa	nonaq phase x_W
333.7		0.0092
353.7		0.0135
374.2		0.0232
392.5	0.195	0.0318
411.0	0.340	0.0455
429.2	0.559	0.0695
450.4	0.943	0.105
472.8	1.55	0.159
493.8	2.36	0.209

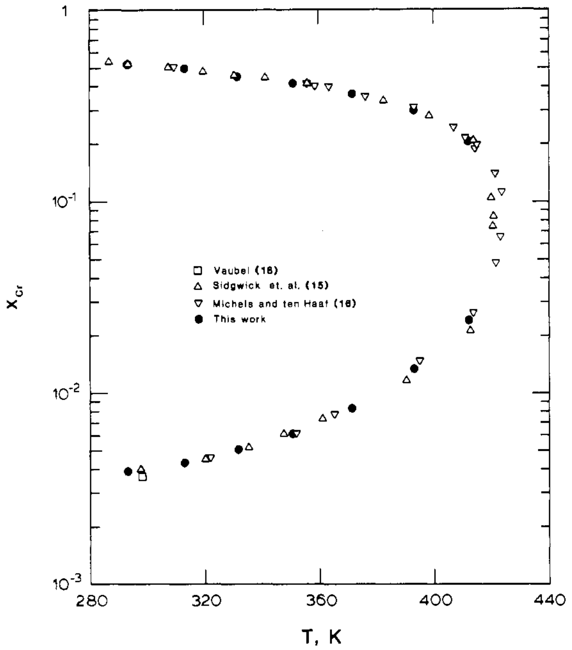

Figure 2. Mutual solubilities of *m*-cresol + water.

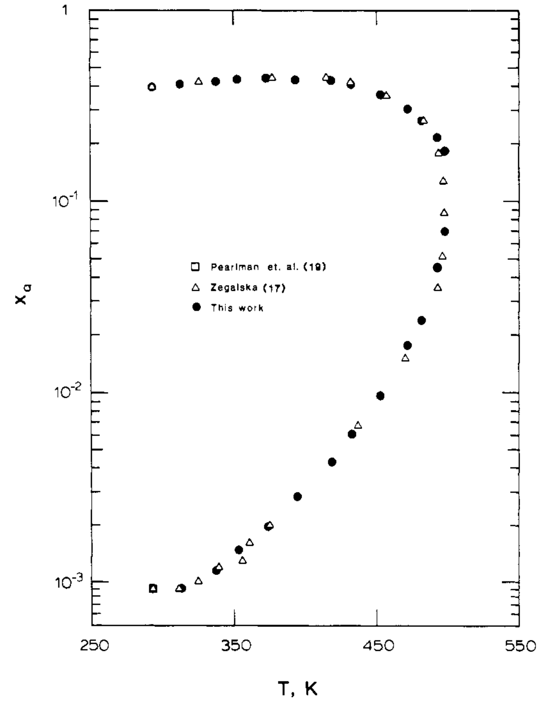

Figure 3. Mutual solubilities of quinoline + water.

Results

The mutual solubilities of water + hydrocarbon at the three-phase equilibrium pressures are reported in Tables I–VI for the six binary mixtures studied in this work. Figures 2 and 3 show the experimental results for water + *m*-cresol and water + quinoline, respectively. Literature data from different sources are also shown in the figures for comparison. The new data in general agree well with the literature values. For the *m*-cresol + water mixture, the data of Sidgwick et al. (*15*) and

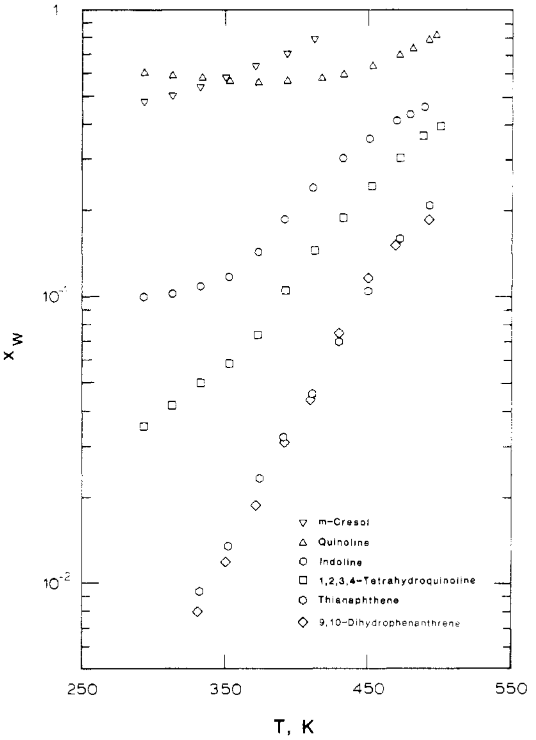

Figure 4. Saturated mole fraction of water in the nonaqueous phase.

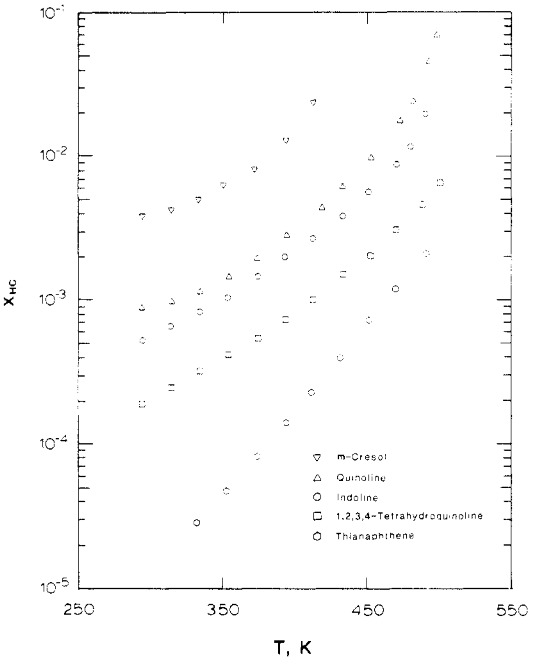

Figure 5. Saturated mole fraction of hydrocarbon in the aqueous phase.

Michels et al. (*16*) show some discrepancy. Our data are in better agreement with those of Michels and ten Haaf. For the water + quinoline mixture, the new data project a slightly higher critical end-point temperature than that reported by Zegalska (*17*).

Figure 4 shows the saturated mole fraction of water, x_W, in the nonaqueous liquid phase of the three-phase equilibrium mixture. The x_W values generally appear in the descending order: *m*-cresol, quinoline, indoline, tetrahydroquinoline, thianaphthene, and dihydrophenanthrene. The quinoline curve is unique in showing a minimum.

Figure 5 shows the saturated mole fraction of the hydrocarbon, x_{HC}, in the aqueous liquid phase. The x_{HC} values appear in the same descending order mentioned above. The solubility of 9,10-dihydrophenanthrene in water is not reported; the experiments were not completed due to sampling and analytical difficulties.

Glossary

p	pressure, MPa
T	temperature, K
x	mole fraction in liquid phase

Subscripts

Cr	*m*-cresol
D	9,10-dihydrophenanthrene
HC	hydrocarbon
I	indoline
Q	quinoline
T	thianaphthene
THQ	1,2,3,4-tetrahydroquinoline
W	water

Registry No. THQ, 635-46-1; Cr, 108-39-4; I, 496-15-1; Q, 91-22-5; T, 95-15-8; D, 776-35-2.

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