Solubility of Alkylbenzenes and a Model for Predicting the Solubility of Liquid Organics in High-Temperature Water

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The solubility of ethylbenzene, *m*-xylene, and benzene in water was determined using a laboratory-made system at temperatures ranging from 298 K to 473 K and a pressure of 50 bars. The solubility was enhanced by at least 1 order of magnitude by increasing the temperature from ambient to 473 K. A simple approximation model was developed to predict the solubility of liquid organics in high-temperature water. This model delivers an excellent estimation of the solubility of small molecules of liquid organic compounds in water at temperatures at or higher than 373 K.

Introduction

High-temperature water (also termed subcritical water, superheated water, and hot pressurized water in the literature) has unique properties and has been used for the successful extraction of polar and nonpolar analytes from a variety of matrixes.[1−10] The ability of water as an extraction solvent for nonpolar analytes is due to the effect of temperature on the polarity of water. By increasing the water temperature under moderate pressures to maintain the liquid state, the polarity of water is significantly reduced,[1−6] making water behave like an organic solvent.

The decreased polarity of high-temperature water dramatically increases the solubility of organic compounds, especially the nonpolar ones. Miller et al. and Rössling et al. reported that the solubility of polycyclic aromatic hydrocarbons and pesticides increased several orders of magnitude by raising the temperature from ambient to 473 K.[11−13] Yang et al. determined the solubility of toluene in high-temperature water while comparing the solubility trend to the partitioning of toluene from diesel fuel.[14] The solubility of other liquid organics (e.g., organics of environmental interest and fragrance compounds) in high-temperature water has also been reported by Miller et al.[15,16]

In this work, the solubility of ethylbenzene, *m*-xylene, and benzene in high-temperature water was determined using a homemade system that was significantly modified from the one used in the reference reported by Yang et al.[14] Solid-phase collection was employed during the sampling in this work. The temperatures used in this study ranged from 298 K to 473 K. Because the solubility data of liquid organics collected in our study and in refs 15 and 16 do not support the model for predicting the solubility of solid organics as described in the literature,[11] an improved model was developed to predict the solubility of small molecules of liquid organic compounds in high-temperature water. The new model is a better one in the higher-temperature range because it can be used to compare the predicted solubility with the experimental data for 10 different organic compounds reported in this work as well as in the literature.[14,15]

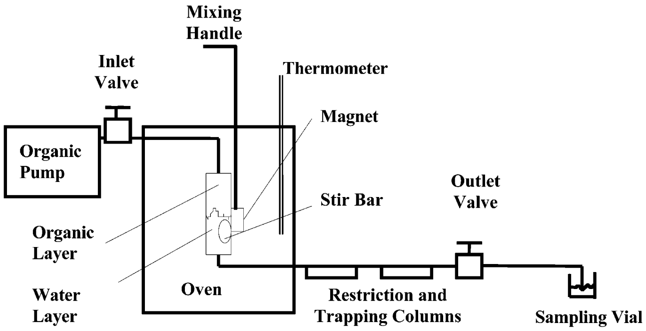

Figure 1. Schematic diagram of the solubility determination system.

Experimental Section

Chemicals. Benzene, toluene, ethylbenzene, *m*-xylene, and methylene chloride were obtained from Fisher Scientific (Fair Lawn, NJ). Deionized water (18 MΩ cm) was prepared in our laboratory using a four-stage reverse osmosis system (Sybron/Barnstead, Boston, MA).

Solubility Experiments. Solubility experiments were performed using a homemade laboratory system as shown in Figure 1. The components of the system include an organic pump (Spectra-Physics, Mountain View, CA); an equilibration cell (10 mL, 150 × 9.2 mm i.d., Keystone Scientific, Bellefonte, PA); stainless steel tubing ($^1/_{16}$”, Keystone Scientific); shut-off valves (HIP model 02-0120, High-Pressure Equipment Co., Erie, PA); a stirring bar ($^1/_2$” × $^5/_{16}$”, Fisher Scientific); collection columns packed with ODS (20 × 4 mm i.d., Keystone Scientific); an oven (Fisher Scientific Isotemp 500 Series); a magnet; and a rinse pump (model 8810-010, Spectra-Physics).

The equilibration cell was completely filled with deionized water. The mixing magnet trapped the stir bar inside the cell. The manipulation of the stir bar by the magnet (outside the cell) was visually checked before fastening the top cap on the equilibration cell. Both end caps of the cell were tightened to prevent leakage. The water-loaded cell was connected to the system and placed inside the oven.

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The oven was then heated to the test temperature. During the heating process, approximately 5 mL of a pure liquid organic was loaded into the equilibration cell using the organic pump at 0.2 ± 0.02 mL/min by pushing out the preloaded water through the outlet of the equilibration cell. Approximately 10 min after the oven temperature reached the set value, the flow rate of the pump was adjusted to obtain 50 bars, and then both the inlet and the outlet valves were closed.

To ensure that the desired temperature inside the cell was achieved, mixing was started 10 min after the oven reached the set temperature. Dynamic mixing involved manipulating the stir bar inside the equilibration cell to break the interface between water and the organic with the magnet as shown in Figure 1. Dynamic mixing with the magnet and stir bar was done by hand for 10 min using the mixing handle at a rate of one length of the equilibration cell per second. The system was allowed to equilibrate (no mixing for 10 min) before the collection of the aqueous phase. Note that the inlet and outlet valves were closed during the dynamic mixing and the equilibration time. After the equilibration step, approximately 2 mL of the saturated water phase was collected into a 7-mL vial that contained 2 mL of methylene chloride. The collection was completed by pumping additional organic phase into the top of the cell at a very low flow rate (e.g., 0.2 mL/min) to prevent contamination of the saturated water phase. This was accomplished by opening the outlet valve while the cell was still heated and pressurized under the same conditions used in the equilibration step. Once the sampling of the saturated water phase was complete, the oven was turned off to allow the system to cool. The volume of the water phase sampled was accurately determined.

After cooling, the outlet tubing and collection columns were disconnected from the equilibration cell and attached to the rinse pump that contained methylene chloride. The outlet tubing, collection columns, and outlet valve were rinsed with methylene chloride. Approximately 2 mL of the rinsing methylene chloride was collected in an empty vial.

Toluene, as the internal standard, was added to the first collection vial that contained water and 2 mL of methylene chloride. The saturated water and methylene chloride in the vial was shaken ca. 100 times by hand. The methylene chloride layer was placed into the vial containing the rinsing methylene chloride. A second liquid−liquid extraction was performed by adding another 2 mL of fresh methylene chloride to the water vial. The organic layer was again removed and combined with the other two fractions of methylene chloride for GC analysis.

Gas Chromatography Analysis. Gas chromatography analyses were performed using a Hewlett-Packard model 6890 gas chromatograph (GC) with a flame ionization detector (FID) (Hewlett-Packard, Avondale, PA). An HP-5 column (30 m × 0.32 mm i.d., 0.25-μm film thickness, Hewlett-Packard) was used in this work. The GC oven temperature was set to 120 °C for benzene, 140 °C for ethylbenzene, and 160 °C for *m*-xylene. Injections were performed using an autosampler in split mode with a ratio of 1:40. The FID temperature was set to 275 °C.

Results and Discussion

Temperature Effect on Organic Solubility. Previous reports by Hawthorne et al.[1] and Yang et al.[2] have shown that the water temperature has a greater influence on extraction efficiencies of nonpolar organics than the pressure. Therefore, the temperature effect on solubility was studied while the pressure was maintained at 50 bars.

Table 1. Comparison of Mole Fraction Solubility x_2 for Liquid Organics in Water with Equations 1, 2, and 3

T/K	exptl(x_2 ± sd)	eq 1	eq 2	eq 3
Ethylbenzene, $10^5 x_2$ at 50 Bars				
298	2.8 ± 0.2	2.8	2.8	0.38
323	4.1 ± 0.8	6.3	6.4	1.3
373	9.2 ± 0.6	23	29	8.3
423	24 ± 2	62	190	31
473	81 ± 10	140	280	82
m-Xylene, $10^5 x_2$ at 50 Bars				
298	3.7 ± 0.2	3.7	3.7	0.50
373	8.0 ± 0.9	29	37	11
423	27 ± 1	76	230	38
473	102 ± 9	160	3400	99
Benzene, $10^4 x_2$ at 50 Bars				
298	4.2 ± 0.3	4.2	4.2	0.56
373	8.1 ± 0.9	20	25	7.2
423	17 ± 2	41	130	21
473	46 ± 4	74	15 000	45
Toluene, $10^4 x_2$ at 50 Bars				
298	1.0[a]	1.0	1.0	0.14
373	3.1 ± 0.09[b]	6.4	1.7	2.3
423	8.7 ± 0.26[b]	15	46	7.6
473	25 ± 5[b]	30	630	18
p-Cymene, $10^6 x_2$ at 65 Bars				
298	3.0 ± 0.2[c]	3.0	3.0	0.41
323	4.0 ± 0.4[c]	8.0	8.1	1.7
373	11 ± 1[c]	39	49	14
423	43 ± 2[c]	110	390	64
473	200 ± 20[c]	330	6900	200
Octane, $10^7 x_2$ at 65 Bars				
298	1.4 ± 0.2[c]	1.1	1.1	0.15
323	2.0 ± 0.4[c]	3.8	3.8	0.79
373	7.2 ± 0.2[c]	28	35	10
423	44 ± 2[c]	130	380	62
473	290 ± 10[c]	410	8600	250
2,2,4-Trimethylpentane, $10^7 x_2$ at 65 Bars				
298	4.4 ± 0.5[c]	3.5	3.5	0.47
323	5.2 ± 0.4[c]	11	11	2.3
373	20 ± 1[c]	70	88	25
423	100 ± 3[c]	280	860	140
473	610 ± 30[c]	860	18 000	520
Tetrachloroethylene, $10^5 x_2$ at 65 Bars				
298	2.3 ± 0.2[c]	2.3	2.3	0.31
323	2.7 ± 0.2[c]	5.3	5.3	1.1
373	5.9 ± 0.4[c]	2.0	25	7.1
423	18 ± 1[c]	5.4	160	27
473	59 ± 4[c]	1.2	2500	73
Tetraethyl Tin, $10^9 x_2$ at 65 Bars				
298	3.4 ± 0.2[c]	3.4	3.4	0.46
323	5.4 ± 0.3[c]	15	16	3.2
373	14 ± 2[c]	170	220	62
423	110 ± 4[c]	1100	3300	540
473	880 ± 60[c]	4600	96 000	2800
1,2-Dichlorobenzene, $10^5 x_2$ at 65 Bars				
298	1.7 ± 01[c]	1.8	1.8	0.24
323	2.3 ± 0.1[c]	4.2	4.2	0.87
373	5.5 ± 0.2[c]	16	21	5.8
423	18 ± 1[c]	45	140	23
473	57 ± 3[c]	100	2100	62

[a] Adopted from ref 18. [b] Adopted from ref 14. [c] Adopted from ref 15.

The solubility of the organic analytes at elevated temperatures obtained by this method is given in Table 1. Standard deviations of the measured solubility are also provided in this Table. The variations of temperature and pressure in Table 1 were ±1 K and ±1 bar, respectively. As shown in Table 1, raising the water temperature significantly enhanced the solubility of ethylbenzene. The solubility increased by approximately 100% to 300% for each temperature increase of 50 K. Therefore, the mole fraction (x_2) solubility of ethylbenzene increased from 2.8 $\times 10^{-5}$ to 81 $\times 10^{-5}$ by simply raising the water temperature from 298 K to 473 K. Because the ethylbenzene solubility was only slightly enhanced by increasing the temperature from ambient to 323 K, the solubility of benzene and *m*-xylene was not determined at this temperature.

Table 1 also shows the solubility of *m*-xylene at different temperatures. As with ethylbenzene, the solubility of *m*-xylene was greatly enhanced by increasing the temperature. The solubility of *m*-xylene at elevated temperatures is slightly higher than that of ethylbenzene with the exception of 373 K. At 373 K, the solubility of *m*-xylene is slightly higher than 2 times the ambient solubility, whereas the solubility of ethylbenzene shows a 3-fold solubility increase from 298 K to 373 K.

The solubility of benzene at different temperatures is also given in Table 1. The ambient solubility of benzene is much greater than that of the other two solutes described above. The solubility increase with water temperature for benzene is not as remarkable as the solubility enhancements for ethylbenzene or *m*-xylene. For example, at 473 K benzene's solubility increases 11-fold over the ambient solubility, and ethylbenzene's solubility enhances 29-fold over the same temperature range. This reduced enhancement of solubility for benzene is likely caused by its high solubility in ambient water.

Miller et al. determined the solubility of benzene and *m*-xylene in high-temperature water using a very different experimental approach.[15] However, our solubility data for these two solutes are in good agreement with the data reported by Miller et al.[15] The increased solubility of organic compounds in liquid water at high temperature is partially caused by the decreased polarity of subcritical water. Furthermore, the solubility of organics in high-temperature water could also be described by the effect of increased temperature on the solutes. For example, the solubility of organics in supercritical fluids often shows a strong correlation to the vapor pressure of the solute. The solubility shows a rapid rise with increasing pressure at a threshold pressure that is near the vapor pressure of the solute.[17]

Approximation Models. Miller et al.[11] developed an approximation model for the mole fraction solubility of polycyclic aromatic hydrocarbons and pesticides in subcritical water. The approximation for the model assumes that the Gibbs function for the solution does not change over the temperature range and there is no absorption of water by the solute. The assumption for the slight change in the Gibbs function was justified because the enthalpy of the solution for these insoluble molecules does not vary widely with temperature and is much greater than the entropy contribution. The equation for the approximation (eq 1) shows that the mole fraction solubility could be estimated with the knowledge of the mole fraction solubility at ambient temperature (T_0), where the mole fraction solubility at any temperature (T) is $x_2(T)$ and the ambient mole fraction solubility is given by $x_2(T_0)$.

$$\ln x_2(\mathrm{T}) \approx \left(\frac{T_0}{T}\right) \ln x_2(\mathrm{T}_0) \qquad (1)$$

Increasing the temperature shows the higher solvating effect of water on organic compounds as its polarity decreases at higher temperatures. Hence, they achieved approximate fitting adding a cubic equation to the base eq 1. The first approximation for the solubility at T is given by

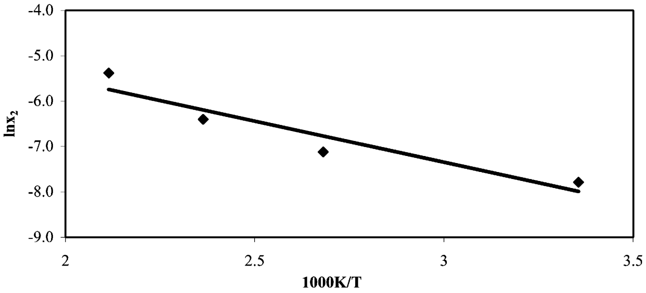

Figure 2. Solubility x_2 of benzene in high-temperature water at different temperatures.

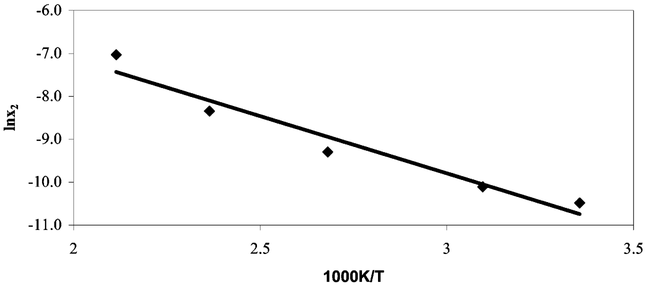

Figure 3. Solubility x_2 of ethylbenzene in high-temperature water at different temperatures.

$$\ln x_2(T) = \left(\frac{T_0}{T}\right) \ln x_2(T_0) + 15\left(\frac{T}{T_0} - 1\right)^3 \qquad (2)$$

However, our solubility data for benzene, ethylbenzene, and *m*-xylene do not support the model described above. Furthermore, our results fitted to the zeroth approximation[11] (Figures 2 and 3) prove it by the straight-line behavior. (A detailed explanation was given in ref 11.)

In this study, we tried to make the second approximation adding to different cubic equation to the base, eq 1, which is $2[((T - T_0)/T) - 1]^3$. And hence the equation becomes

$$\ln x_2(T) = \left(\frac{T_0}{T}\right) \ln x_2(T_0) + 2\left(\frac{T - T_0}{T_0} - 1\right)^3 \qquad (3)$$

A comparison of the results was performed using eqs 1, 2, and 3. The results for the compounds reported in this paper are shown in Table 1. In general, eqs 1 and 3 are slightly better at predicting the mole fraction solubility of solutes reported in this paper at temperatures from 323 K to 473 K, with eq 3 predicted values for almost all solute conditions, except the initial point of 298 K. The predicted values using eq 3 give excellent agreement with the experimental results at 373 K or higher temperature. Because eq 3 is a better predictor for the data presented in this work, this equation was also used to predict values for the solutes reported by Yang et al.[14] and Miller et al.[15] As shown in Table 1, the predicted values using eq 3 generally agree well with experimental results except for the solubility at lower temperatures.

Conclusions

Increasing the temperature of water with enough pressure to keep the liquid state showed a significant increase in the solubility of alkylbenzenes. Our newly developed model (eq 3) based only on the knowledge of solubility at ambient temperature gives reasonable estimates compared to the experimental data for the solubility of liquid organics at temperature of or higher than 373 K. Such estimates are good enough to obtain information for possible experiments or processes in advance.

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