Solubility of Liquid Organics of Environmental Interest in Subcritical (Hot/Liquid) Water from 298 K to 473 K

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The solubilities of benzene, toluene, *m*-xylene, *p*-cymene, octane, 2,2,4-trimethylpentane (isooctane), tetrachloroethylene, 1,2-dichlorobenzene, and tetraethyltin were determined at temperatures ranging from 298 K to 473 K. Increasing the temperature up to 473 K increased the solubilities by a factor of ∼10−250. For example, increasing the temperature from 298 K to 473 K increased the mole fraction solubility of tetraethyltin from $(0.03 \pm 0.002) \times 10^{-7}$ to $(8.8 \pm 0.6) \times 10^{-7}$ but only increased the solubility of benzene from $(4.0 \pm 0.1) \times 10^{-4}$ to $(41 \pm 3) \times 10^{-4}$. Pressure had a minimal effect; for example, increasing the pressure from 65 to 400 bar at either 298 K or 473 K reduced the solubility of benzene by only ∼20%.

Introduction

Recent reports have demonstrated the ability of "subcritical" water (water heated to any temperature up to its critical temperature with enough pressure to maintain its liquid state) to quantitatively remove a variety of polar and nonpolar organics from many matrixes (Basile et al., 1998; Hartonen et al., 1997; Hawthorne et al., 1994; Yang et al., 1995, 1997, 1998). The ability of water to solvate hydrophobic organic compounds is due to the effect of temperature on the polarity of water (measured by its relative permittivity or dielectric constant ϵ). Increasing the temperature of water at constant pressure decreases the dielectric constant from ∼80 at 298 K to ∼35 at 473 K (Haar et al., 1984), which is approximately equal to that of ethanol ($\epsilon = 33$).

In all of the reports cited above, raising the temperature of water (with enough pressure to maintain liquid water) has a marked effect on the extraction of organic compounds. However, extraction behavior is hard to understand, since little solubility data have been reported for organic compounds at elevated temperatures, and most of the solutes studied are solids at ambient conditions. The data which do exist show dramatic increases in solubilities with an increase in water temperature. For example, the solubilities of several polycyclic aromatic hydrocarbons (PAHs) and several pesticides (all of which are solids at ambient conditions) are reported to increase ∼5 orders of magnitude with an increase in temperature from 298 K to 498 K (Rössling and Franck, 1983; Miller and Hawthorne, 1998; Miller et al., 1998).

For organic compounds that are normally liquids, there is a wealth of solubility data in the literature, but nearly all available data are at ambient conditions. For example, in an extensive compilation of solubility data by Kertes (*Solubility Data Series*, Vols. 20, 37, and 38), multiple data are reported for 214 compounds, and only a few data (mostly for benzene) are reported at temperatures above the normal boiling point of water. The present work reports a method for determining the solubility of liquid (at room temperature) hydrophobic organic compounds in water at temperatures from 298 K to 473 K (with sufficient pressure to maintain liquid water at all temperatures). A dynamic method for solids reported by Miller and Hawthorne (1998) was modified to allow solubilities of liquid solutes to be rapidly determined over a wide range of temperatures and pressures.

Experimental Section

All solubility determinations were performed using a dynamic method previously used for solid organics which was modified in the present study for liquid organics. A detailed description of the method for solids has been previously reported (Miller and Hawthorne, 1998). Briefly, a high-pressure saturation cell is filled with the test solute and placed in the oven of an HP 5890 gas chromatograph (Hewlett-Packard, Wilmington, DE) to provide precise temperature control (±0.1 °C, according to manufacturer's specifications). An Isco model 100D syringe pump (Isco, Lincoln, NE) was used in the constant-flow mode to supply water at 0.1 mL/min via a 3-m preheating coil (placed in the GC oven) to the saturation cell. A mixing "tee" was installed in the GC oven between the outlet of the saturation cell and an external cooling coil to allow introduction of methylene chloride as a collection solvent. A second Isco model 100D syringe pump operating in the constant-flow mode was used to deliver methylene chloride at 0.4 mL/min to one leg of the mixing tee. This arrangement allowed the solutes saturated in the hot water to partition into the methylene chloride as the water cooled, preventing deposition in the transfer line upon cooling the water to room temperature. In the present study, the original apparatus was modified to replace the outlet control valve with a miniature back-pressure regulator (Upchurch Scientific, Oak Harbor, WA) adjusted to operate at ∼60 bar to maintain sufficient pressure to ensure that water in the liquid state was present throughout the entire temperature range.

The original method was further modified to allow solubility determinations of liquid organic solutes. Rather than mixing the organic solute with sea sand (as reported by the original method for solids), the saturation cell (10.4 mL, 150-mm × 9.4-mm i.d. "SFE" cell, Keystone Scientific,

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Bellefonte, PA) was filled with 3-mm diameter solid glass beads (Fisher Scientific, Pittsburgh, PA). The beads provide a torturous path for the water as it passes through the saturation cell. The direction of the water flow was also changed depending on the density of the organic solute. Flow was from top to bottom when the density of the organic solute was less than that of water, that is, <1 g/mL, and from bottom to top when the density of the organic solute was >1 g/mL. The filling procedure differed, again depending on the density of the organic solute. If the solute was less dense than water, ~0.5 mL of water was pipetted in the bottom of the saturation cell containing the glass beads and the organic solute was then added, filling the remainder of the cell. If the solute was more dense than water, the organic solute was added to the saturation cell first to within ~1 cm of the top of the cell. The remaining void volume was then filled with 0.5 mL of water.

Solubility determinations were begun by starting the flow of both pumps and allowing the system to equilibrate. After a 60-min equilibration period at the initial (ambient) temperature, 10 fractions were collected for 3 min each in autosampler vials, the appropriate internal standard was added, and the vials were capped for analysis. The temperature was then raised to the next temperature, and the cycle was repeated.

The solutes tested in this work were benzene, toluene, *m*-xylene, 2,2,4-trimethylpentane (isooctane), octane, 1,2-dichlorobenzene, tetrachloroethylene, tetraethyltin (Sigma-Aldrich, Milwaukee, WI), and *p*-cymene (Fluka Chemical Corp., Ronkonkoma, NY). All solutes were of the highest purity available (≥99% for all compounds except tetraethyltin, which was 97%, and confirmed by GC analysis). Solubility determinations were preformed between 298 and 473 K and 50 to 65 bar, except for benzene where the pressure was also increased to 400 bar.

All analyses were performed using an HP model 5890 GC with flame ionization detection (FID). Chromatographic separations were accomplished with a 30-m HP-5 (0.25-mm i.d., 0.25-μm film thickness, Hewlett-Packard) fused silica capillary column. Three-point calibration curves were generated for each solute to determine the response with respect to the internal standard. Internal standards were chosen that eluted near and were similar to the solute of interest. Solubilities were calculated on the basis of the quantity of test solute in the methylene chloride collection solvent versus the quantity of water used to obtain each fraction. Representative samples from each temperature range were analyzed by gas chromatography/mass spectrometry (GC/MS, HP 5973) to confirm that no degradation of the organic solute occurred.

Results and Discussion

Effect of Temperature on Solubilities. The solubilities of benzene, toluene, *m*-xylene, *p*-cymene, 2,2,4-trimethylpentane (isooctane), octane, 1,2-dichlorobenzene, tetrachloroethylene, and tetraethyltin are shown in Tables 1−6. The data in Tables 1−5 show that the ambient-temperature (298 K) solubilities determined experimentally in our laboratory are in good agreement with those available in the literature. (No literature value was available for tetraethyltin [Table 6], and therefore, no comparison can be made.) For example, the ambient-temperature mole fraction solubility (298 K, 65 bar) of benzene (Table 1) determined using our method is $(4.0 \pm 0.2) \times 10^{-4}$ and is in good agreement with the mole fraction solubility value of $(4.1 \pm 0.2) \times 10^{-4}$ given by Kertes (1985). Kertes' value is given as the "best value" and is the mean of 19 reported solubility determinations at 298 K which range from 3.97×10^{-4} to 4.29×10^{-4} mole fraction solubility.

Table 1. Solubility of Benzene in Water

T/K	P/bar	$10^4(x_2 \pm \mathrm{SD}^a)$	
		exptl	lit.
298	1	4.0 ± 0.1	4.1 ± 0.2[b]
298	65	4.0 ± 0.2	
298	400	3.3 ± 0.1	
323	65	4.7 ± 0.3	4.8 ± 0.1[b]
373	65	8.9 ± 0.6	9.23,[b] 4.34,[c] 9.49[d]
423	65	22 ± 2	23.1,[b] 13,[c] 24.2[d]
473	65	50 ± 3	69.2,[b] 45.6,[c] 54[d]
473	400	41 ± 3	42[b]

[a] Standard deviations (SDs) are based on 10 fractions collected at each condition. [b] *Solubility Data Series*, Vol. 37. [c] Jaeger, 1923. [d] Tsonopoulos and Wilson, 1983.

Table 2. Solubility of Toluene in Water

T/K	P/bar	$10^4(x_2 \pm \mathrm{SD}^a)$	
		exptl	lit.
298	50	1.07 ± 0.02	1.04 ± 0.04[b]
323	50	1.25 ± 0.04	
373	50	2.7 ± 0.1	3.11 ± 0.09[c]
423	50	6.6 ± 0.3	8.67 ± 0.26,[c] 4.52[d]
473	50	19 ± 1	24.7 ± 4.7,[c] 11.8[d]

[a] Standard deviations (SDs) are based on 10 fractions collected at each condition. [b] *Solubility Data Series*, Vol. 37. [c] Yang et al., 1997. [d] Jaeger, 1923.

Table 3. Solubility of *m*-Xylene and *p*-Cymene in Water

T/K	P/bar	$10^4(x_2 \pm \mathrm{SD}^a)$	
		m-xylene	*p*-cymene
		Literature	
298	1	0.28 ± 0.004[b]	0.03[b]
		This Work	
298	60	0.29 ± 0.01	0.030 ± 0.002
323	60	0.36 ± 0.01	0.040 ± 0.004
373	60	0.85 ± 0.04	0.11 ± 0.01
423	60	2.7 ± 0.1	0.43 ± 0.02
473	60	8.8 ± 0.2	2.0 ± 0.2

[a] Standard deviations (SDs) are based on 10 fractions collected at each condition. [b] *Solubility Data Series*, Vol. 38.

Table 4. Solubility of Octane and 2,2,4-Trimethylpentane in Water

T/K	P/bar	$10^6(x_2 \pm \mathrm{SD}^a)$	
		octane	2,2,4-trimethylpentane
		Literature	
298	1	0.11 ± 0.01[b]	0.35 ± 0.03[b]
		This Work	
298	65	0.14 ± 0.02	0.44 ± 0.05
323	65	0.20 ± 0.04	0.52 ± 0.04
373	65	0.72 ± 0.02	2.0 ± 0.1
423	65	4.4 ± 0.2	10.2 ± 0.3
473	65	29 ± 1	61 ± 3

[a] Standard deviations (SDs) are based on 10 fractions collected at each condition. [b] *Solubility Data Series*, Vol. 38.

As expected, increasing temperature increases the mole fraction solubility of benzene in water. For example, increasing the temperature from 298 K to 473 K increases the mole fraction solubility of benzene more than 10-fold to $(41 \pm 3) \times 10^{-4}$. All of the experimental values reported in Table 1 are in good agreement with those available in the literature. The effect of pressure on solubility is also shown in Table 1. The apparatus as described in the Experimental Section contains a miniature back-pressure

Table 5. Solubility of Tetrachloroethylene and 1,2-Dichlorobenzene in Water

		$10^5(x_2 \pm \mathrm{SD}^a)$	
T/K	P/bar	tetrachloroethylene	1,2-dichlorobenzene
		Literature	
298	1	2.85[b]	1.8[c]
		This Work	
298	65	2.3 ± 0.2	1.7 ± 0.1
323	65	2.7 ± 0.2	2.3 ± 0.1
373	65	5.9 ± 0.4	5.5 ± 0.2
423	65	18 ± 1	18 ± 1
473	65	59 ± 4	57 ± 3

[a] Standard deviations (SDs) are based on 10 fractions collected at each condition. [b] Mackay et al., 1993. [c] *Solubility Data Series*, Vol. 20.

Table 6. Solubility of Tetraethyltin in Water

T/K	P/bar	$10^7(x_2 \pm \mathrm{SD}^a)$
298	65	0.034 ± 0.002
323	65	0.054 ± 0.003
373	65	0.14 ± 0.02
423	65	1.09 ± 0.04
473	65	8.8 ± 0.6

[a] Standard deviations (SDs) are based on 10 fractions collected at each condition.

regulator to control the system pressure. This regulator is normally adjusted to operate in the range 50−65 bar. To determine whether this increase in pressure had an effect on solubility, the regulator was removed and replaced with a valve (Model 15-11AF1, High Pressure Equipment Co., Erie, PA) to control the system pressure. For the 1 bar experiment, the valve was fully opened and the only pressure in the system was that required by the pumping system to maintain the desired flows (0.1 mL/min water and 0.4 mL/min methylene chloride); for the 400 bar experiment, the valve was adjusted to obtain the desired pressure. Table 1 shows that the value obtained for the mole fraction solubility of benzene at 298 K and 1 bar ($(4.0 \pm 0.1) \times 10^{-4}$) is identical to that obtained when the system pressure was 65 bar ($(4.0 \pm 0.2) \times 10^{-4}$), and both values agree with the literature value of $(4.1 \pm 0.2) \times 10^{-4}$, indicating that the low system pressure used for these determinations has little effect on the mole fraction solubilities of the solutes studied. If solubility determinations are performed at much higher pressures (~400 bar), significant reductions in solubility occur. Increasing the pressure from 1 bar to 400 bar at 298 K results in a ~20% reduction in the mole fraction solubility of benzene from $(4.0 \pm 0.2) \times 10^{-4}$ to $(3.3 \pm 0.1) \times 10^{-4}$. A reduction of ~20% was also observed when the pressure was raised to 400 bar at 473 K (Table 1).

Table 2 shows the results obtained for the solubility of toluene in water. Good agreement between our results and literature values is achieved at low temperatures. At 298 K, the experimental value of $(1.07 \pm 0.02) \times 10^{-4}$ is nearly identical to the "best value" reported by Kertes (1989) of $(1.04 \pm 0.04) \times 10^{-4}$. At temperatures > 373 K, there is some deviation between the results reported here and those available in the literature. Reported literature values vary by a factor of 2 at 423 K and 473 K, with our data falling approximately midway between. For example, we report a mole fraction solubility for toluene at 473 K of $(19 \pm 1) \times 10^{-4}$, which falls between those reported by Jaeger (1923) (11.8×10^{-4}) and by Yang et al. (1997) $(24.7 \pm 4.7) \times 10^{-4}$.

Similar increases in solubility were obtained for all of the compounds reported in Tables 3−6. For example, raising the temperature of *m*-xylene from 298 K to 474 K results in a 30-fold enhancement in mole fraction solubility from $(0.30 \pm 0.01) \times 10^{-4}$ to $(8.8 \pm 0.2) \times 10^{-4}$ (Table 3). This enhancement with respect to rising temperature is even more dramatic for solutes with very low ambient-temperature solubilities. Table 4 shows the mole fraction solubilities obtained for octane for temperatures from 298 to 473 K. At 298 K, the mole fraction solubility of octane is $(0.14 \pm 0.02) \times 10^{-6}$. Increasing the temperature to 473 K increases the mole fraction solubility to $(29 \pm 1) \times 10^{-6}$, a 200-fold increase. Similar increases were seen for 2,2,4-trimethylpentane (isooctane).

The solubilities of chlorinated hydrocarbons follow the same trend with temperature; that is, increasing temperature increases the mole fraction solubility (Table 5). Raising the temperature from 298 K to 473 K increases the solubilities of tetrachloroethylene and 1,2-dichlorobenzene by factors of 26 and 35, respectively.

Table 6 shows the mole fraction solubility obtained for tetraethyltin at temperatures from 298 K to 473 K. Even though no literature value is available for the ambient solubility of tetraethyltin, the results given in Table 6 indicate that while tetraethyltin is practically insoluble in water at 298 K ($(0.034 \pm 0.002) \times 10^{-7}$ mole fraction), rather dramatic increases in solubility are achieved with elevated temperature. For example, raising the temperature to 473 K increases the mole fraction solubility of tetraethyltin to $(8.8 \pm 0.6) \times 10^{-7}$, a 260-fold enhancement. Several samples from each temperature range obtained during the tetraethyltin/water solubility experiment (as well as samples for all other solutes reported) were analyzed by GC/MS, and no degradation of tetraethyltin, or any of the other solutes reported in Tables 1−5, was found.

Conclusions

Slight modification of a previously reported method for determining solid organic/water solubilities (Miller and Hawthorne, 1998) allows rapid determination of liquid organic/water solubilities over a wide range of temperatures. Raising the temperature of water from 298 K to 473 K (with enough pressure to maintain the liquid state) typically increased the solubilities of liquid organics by ~2 orders of magnitude, compared to 4 or 5 orders of magnitude for organics such as PAHs and pesticides, which are solids at ambient conditions (Miller and Hawthorne, 1998; Miller et al., 1998). Increases in pressure have only a small depressing effect (~20% for benzene at 400 bar and 298 K or 473 K) on the solubility of organics in water. Over the temperature range of this study, no degradation of any of the solutes occurred (confirmed by GC/MS).

Literature Cited

Basile, A.; Jimenez-Carmona, M. M.; Clifford, A. A. Extraction of Rosemary by Superheated Water. *J. Agric. Food Chem.* **1998**, *46*, 5205−5209.

Haar, L.; Gallagher, J. S.; Kell, G. S. *National Bureau of Standards/National Research Council Steam Tables*; Hemisphere Publishing Corp.: Bristol, PA, 1984.

Hartonen, K.; Inkala, K.; Kangas, M.; Riekkola, M.-L. Extraction of Polychlorinated Biphenyls with Water under Subcritical Conditions. *J. Chromatogr.* **1997**, *785*, 219−226.

Hawthorne, S. B.; Yang, Y.; Miller, D. J. Extraction of Organic Pollutants from Environmental Solids with Sub- and Supercritical Water. *Anal. Chem.* **1994**, *66* (18), 2912−2920.

Jaeger, A. Über die Löslichkeit von flüssigen Kohlenwasserstoffen in überhitzem Wasser. *Brennst.-Chem.* **1923**, *4*, 259.

Mackay, D.; Shiu, W. Y.; Ma, K. C. *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals*; Lewis Publishers/CRC Press: Boca Raton, FL, 1993; Vol. III.

Miller, D. J.; Hawthorne, S. B. Method for Determining the Solubilities of Hydrophobic Organics in Subcritical Water. *Anal. Chem*. **1998**, *70* (8), 1618−1621.

Miller, D. J.; Hawthorne, S. B.; Gizir, A. M.; Clifford, A. A. Solubility of Polycyclic Aromatic Hydrocarbons in Subcritical Water from 298 K to 498 K. *J. Chem. Eng. Data* **1998**, *43*, 1043−1047.

Rössling, G. L.; Franck, E. U. Solubility of Anthracene in Dense Gases and Liquids to 200 °C and 2000 Bar. *Ber. Bunsen-Ges. Phys. Chem*. **1983**, *87*, 882−890.

Solubility Data Series, International Union of Pure and Applied Chemistry; Kertes, A. S., Ed.; Pergamon Press: Oxford, 1985; Vol. 20.

Solubility Data Series, International Union of Pure and Applied Chemistry; Kertes, A. S., Ed.; Pergamon Press: Oxford, 1989a; Vol. 37.

Solubility Data Series, International Union of Pure and Applied Chemistry; Kertes, A. S., Ed.; Pergamon Press: Oxford, 1989b; Vol. 38.

Tsonopoulos, C.; Wilson, G. M. High-Temperature Mutual Solubilities of Hydrocarbons and Water. Part I: Benzene, Cyclohexane and *n*-Hexane. *AIChE J*. **1983**, *29* (6), 990−9.

Yang, Y.; Bowadt, S.; Hawthorne, S. B.; Miller, D. J. Subcritical Water Extraction of Polychlorinated Biphenyls from Soil and Sediment. *Anal. Chem*. **1995**, *67* (24), 4571−4576.

Yang, Y.; Hawthorne, S. B.; Miller, D. J. Class-Selective Extraction of Polar, Moderately Polar, and Nonpolar Organics from Hydrocarbon Wastes Using Subcritical Water. *Environ. Sci. Technol*. **1997a**, *31*, 430−437.

Yang, Y.; Miller, D. J.; Hawthorne, S. B. Toluene Solubility in Water and Organic Partitioning from Gasoline and Diesel Fuel into Water at Elevated Temperatures and Pressures. *J. Chem. Eng. Data*. **1997b**, *42*, 908−913.

Yang, Y.; Belgazi, M.; Lagadec, A.; Miller, D. J.; Hawthorne, S. B. Elution of Organic Solutes from Different Polarity Sorbents using Subcritical Water. *J. Chromatogr*. **1998**, *810*, 149−159.

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