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Solubility of Polycyclic Aromatic Hydrocarbons in Subcritical Water from 298 K to 498 K

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The solubility of anthracene, pyrene, chrysene, perylene, and carbazole were determined at temperatures ranging from 298 K to 498 K and pressures from 30 bar to 60 bar in subcritical (superheated) water. Increasing temperature up to 498 K increased solubilities by 5 orders of magnitude. For example, increasing the temperature from 298 K to 498 K increased the mole fraction solubility of chrysene from $(0.63 \pm 0.08) \times 10^{-9}$ to $(75\,800 \pm 4000) \times 10^{-9}$. While large increases in pressure result in lower solubilities, over the narrow range of pressures studied, pressure had a minimal effect. Solubilities as a function of temperature were estimated on the basis of simplifying assumptions and empirical correlations based on data presented in this and previously reported work. The method only requires knowledge of ambient temperature solubility. Estimated values generally agree with experimental results within a factor of 4, even over 5 orders of magnitude in solubility changes.

Introduction

Subcritical water (water heated to any temperature up to its critical temperature of 647 K and with enough pressure to maintain its liquid state) has been shown to quantitatively extract a variety of organic compounds from many different matrices. Quantitative extraction of polycyclic aromatic hydrocarbons (PAHs) from railroad bed soil, urban air particulate matter, petroleum waste sludge, and a spent catalyst; phenols from petroleum waste sludge; alkyl benzenes from industrial soil and petroleum waste sludge; anilines from industrial soil (Hawthorne et al., 1994; Yang et al., 1997); and polychlorinated biphenyls (PCBs) from soil and river sediment (Yang et al., 1995; Hartonen et al., 1997) have been reported in the literature. The effectiveness of water as an extraction fluid for hydrophobic organic compounds is due primarily to the effect of temperature on the polarity of water (measured by its dielectric constant, ϵ). Increasing the temperature of water at constant pressure decreases the dielectric constant from ~80 at 298 K to ~27 at 498 K, which falls between those of methanol ($\epsilon = 33$) and ethanol ($\epsilon = 24$). In addition to the extractions listed above, subcritical water has been used for oxidative destruction and for reactions such as the derivatization and extraction of triglycerides from soybean, linseed, and coconut oil (Holliday et al., 1997) and for reverse-phase liquid chromatography (Smith and Burgess, 1996; Miller and Hawthorne, 1997).

It is apparent from the reports cited above that raising the temperature of water (with enough pressure to maintain the liquid state) has a dramatic effect on the solubility of organic compounds. Although there is a wealth of data available in the literature for the solubility of PAHs in ambient water (at or near 298 K) (Wauchope and Getxen, 1972; Mackay and Shiu, 1977; Schwarz, 1977; May et al., 1983; Haines and Sandler, 1995), very little data are available at temperatures greater than 298 K. The solubility of naphthalene (Miller and Hawthorne, 1998), anthracene (Rössling and Franck, 1983; Wauchope and Getzen, 1972), pyrene (Wauchope and Getzen, 1972), benzo[*e*]pyrene (Sanders, 1986), benzo[*a*]pyrene, propazine, chlorothalonil, and endosulfan II (Miller and Hawthorne, 1998) at temperatures ranging from 298 K to 498 K have shown dramatic increases in solubility with increasing temperature. The present work reports the solubility of anthracene, pyrene, chrysene, perylene, and carbazole at temperatures between 298 K and 498 K with sufficient pressure to maintain liquid water at all temperatures. Solubility determinations were performed with a dynamic method (Miller and Hawthorne, 1998) that allows solubilities to be rapidly determined over a wide range of temperatures and pressures.

Experimental Section

All solubility experiments were performed using a dynamic method. A detailed description of the performance and validation of this method has been previously reported (Miller and Hawthorne, 1998). Briefly, a high-pressure saturation cell (either 0.83 mL, 50 mm × 4.6 mm i.d. or 1.67 mL, 100 mm × 4.6 mm i.d. “SFE” cells, Keystone Scientific, Bellefonte, PA) was filled with a 10 mass % mixture of the test solute with clean sea sand. The saturation cell was placed in the oven of a HP model 5890 gas chromatograph (GC) (Hewlett-Packard, Wilmington, DE) to provide precise temperature control (±0.1 °C according to manufacturer's specifications) during the solubility determination. 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 the external cooling coil to allow

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introduction of the collection solvent. In the present study, toluene was used for solute collection to eliminate the need for the glass-lined tubing required when chloroform was used as the collection solvent (Miller and Hawthorne, 1998). An Isco model 260D syringe pump operating in the constant flow mode was used to supply toluene 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 toluene as the water cooled, thereby preventing deposition in the transfer line upon cooling the water to room temperature.

An additional improvement to our earlier report was the use of a miniature back-pressure regulator (Upchurch Scientific, Oak Harbor, WA) adjusted to operate at ~50 bar to maintain sufficient pressure to ensure that water in the liquid state was present throughout the entire temperature range. After a 30-min equilibration period at the desired temperature, 5 to 10 fractions were collected for 3 min each in autosampler vials, the appropriate internal standard was added, the water phase was removed with a pipet, and the vials were capped for analysis by gas chromatograph/mass spectrometry (GC/MS). The temperature of the saturation cell was then raised to the next temperature and the cycle repeated. The final temperature in each solubility suite was near but below the normal melting point of the test solute.

Ten mass percent mixtures of either anthracene, pyrene, chrysene, perylene, carbazole (Aldrich Chemical, Milwaukee, WI), or anthracene-d_{10} (Cambridge Isotope Laboratories, Andover, MA) with washed sea sand were used to fill the saturation cell for each determination. A 10 mass % mixture of anthracene, carbazole, and chrysene with washed sea sand was used to fill the saturation cell for the mixed solubility determination. All compounds were of the highest purity available (>98%, confirmed by GC analysis). Solubility determinations were performed between 298 and 498 K and 30 to 60 bar.

All analyses were performed using a HP model 5972 or 5973 GC/MS. Chromatographic separations were accomplished with a 30-m HP-5MS (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 PAHs that eluted near the solute PAH of interest and included fluorene for anthracene, anthracene for pyrene and carbazole, pyrene for chrysene, and chrysene for perylene. Solubilities were calculated on the basis of the quantity of test compound in the toluene collection solvent versus the quantity of water used to obtain each fraction.

Results and Discussion

Effect of Temperature on PAH Solubilities. The solubilities of anthracene ($M_W = 178$, normal melting point = 490 K), anthracene-d_{10} ($M_W = 188$, normal melting point = 492 K), pyrene ($M_W = 202$, normal melting point = 423 K), chrysene ($M_W = 228$, normal melting point = 526 K), perylene ($M_W = 252$, normal melting point = 552 K), and carbazole ($M_W = 167$, normal melting point = 517 K) are shown in Tables 1−5.

Table 1. Solubility of Anthracene and Anthracene-d_{10} in Water

		$10^9(x_2 \pm \mathrm{SD}^a)$			
		anthracene			
T/K	P/bar	exptl	eq 1	eq 2	anthracene-d_{10} exptl
		Literature[b]			
298	1	7.4 ± 0.5			
		This Work			
298	49	8.1 ± 0.7	8.1	8.1	*c*
323	50	17 ± 2	34	35	12 ± 1
373	45	320 ± 50	343	435	260 ± 20
423	47	9200 ± 600	2000	6000	10400 ± 600
473	48	210000 ± 25000	8000	170000	217000 ± 11000

[a] Standard deviations (SD) are based on 10 fractions collected at each condition. [b] Mackay and Shiu, 1977. [c] Not determined.

Table 2. Solubility of Pyrene in Water

		$10^9(x_2 \pm \mathrm{SD}^a)$		
T/K	P/bar	exptl	eq 1	eq 2
		Literature[b]		
298	1	12 ± 0.4		
		This Work		
298	41	10.7 ± 0.5	10.7	10.7
323	42	38 ± 1	44	45
373	40	900 ± 50	428	544
373	200	780 ± 36	428	544
373	400	100 ± 6	428	544

[a] Standard deviations (SD) are based on 10 fractions collected at each condition. [b] Mackay and Shiu, 1977.

Table 3. Solubility of Chrysene in Water

		$10^9(x_2 \pm \mathrm{SD}^a)$		
T/K	P/bar	exptl	eq 1	eq 2
		Literature		
298[b]	1	0.16 ± 0.02		
298[c]	1	0.47		
		This Work		
298	32	0.63 ± 0.08	0.63	0.63
323	36	1 ± 0.3	3.3	3.3
373	38	13 ± 1	45	57
423	43	600 ± 39	330	1 000
473	45	15800 ± 1200	1600	33400
498	62	75800 ± 4000	3130	291000

[a] Standard deviations (SD) are based on 10 fractions collected at each condition. [b] Mackay and Shiu, 1977. [c] Klevens, 1950.

Table 4. Solubility of Perylene in Water

		$10^9(x_2 \pm \mathrm{SD}^a)$		
T/K	P/bar	exptl	eq 1	eq 2
		Literature		
298[b]	1	0.03 ± 0.001		
		This Work		
298		*c*	0.03	0.03
323	50	0.29 ± 0.07	0.19	0.19
373	45	2.10 ± 0.07	3.8	4.8
423	47	120 ± 7	37	113
473	48	5000 ± 300	2280	4750

[a] Standard deviations (SD) are based on 10 fractions collected at each condition. [b] Mackay and Shiu, 1977. [c] Not determined.

Examination of the data in Tables 1−5 shows that the solubility values reported at ambient temperature (298 K) using the method developed in our laboratory are in good agreement with those found in the literature. For example, the ambient mole fraction solubility of anthracene determined using our method is $(8.1 \pm 0.7) \times 10^{-9}$, which compares very well with the literature mole fraction solubility of $(7.4 \pm 0.5) \times 10^{-9}$ (Mackay and Shiu, 1977). Similar results were obtained for the compounds reported in Tables 2−5. The data shown in Tables 1−5 show that increasing the temperature of water (with enough pressure to maintain the liquid state) has a dramatic increase on the solubility of PAHs and carbazole. For example, mole fraction solubility of chrysene (Table 3) increases more than

Table 5. Solubility of Carbazole in Water

T/K	P/bar	$10^9(x_2 \pm \mathrm{SD}^a)$		
		exptl	eq 1	eq 2
		Literature		
298^b	1	130		
		This Work		
298	54	110 ± 4	110	110
323	56	450 ± 11	373	376
373	54	9900 ± 200	2700	3450
423	54	162000 ± 3000	12300	37300
473	52	1900000 ± 28000	41000	850000

[a] Standard deviations (SD) are based on 10 fractions collected at each condition. [b] Pearlman and Yalkowsky, 1984.

120 000-fold from (0.63 ± 0.08) × 10^{-9} to (75 800 ± 4000) × 10^{-9} when the temperature of water is increased from 298 K to 498 K. Similar increases in solubility are shown for anthracene, pyrene, perylene, and carbazole (Tables 1, 2, 4, 5).

The dielectric constant of water at constant temperature increases with increased pressure (Haar et al., 1984), and it would be expected that determinations performed at very high pressures would result in lower solubility values. Rössling and Franck (1983) have shown that the solubility of anthracene at 423 K decreases by nearly an order of magnitude from 5660 × 10^{-9} mole fraction at 60 bar (water dielectric constant of 44) to 608 × 10^{-9} mole fraction at 2850 bar (water dielectric constant of 51). Table 2 shows effect of pressure on the solubility of pyrene at 373 K. At 40 bar, the mole fraction solubility of pyrene is (900 ± 50) × 10^{-9}. Increasing the pressure by a factor of 5 to 200 bar results in ~15% decrease in mole fraction solubility to (780 ± 36) × 10^{-9}. Further increasing the pressure to 400 bar causes an order of magnitude reduction in mole fraction solubility to (100 ± 6) × 10^{-9}, similar to the decrease in solubility previously reported for anthracene (Rössling and Franck, 1983). Even though large pressure increases can result in lower solubility, in general the narrow range of pressures used in this work had little effect on solubility.

Additional experiments were performed to determine whether the presence of other organic solutes affected the solubility of the individual components. A mixture of ~10 mass % each of anthracene, carbazole, and chrysene with clean sea sand was loaded into a 1.67-mL extraction cell and installed in the GC oven. Solubilities were determined for temperatures from 298 K to 473 K, and the results are shown in Table 6. At 298 and 323 K, the mole fraction solubilities obtained from the mixed solutes were virtually identical to those obtained from the individual neat solutes. When the temperature was increased to 323 K, the mole fraction solubilities of anthracene and chrysene determined in the mixed experiment were identical to the individual values but the mole fraction solubility of carbazole decreased slightly. Raising the temperature of the water to 423 K resulted in solubility depression for both anthracene and carbazole, and a small decrease for chrysene compared to the value obtained for neat chrysene. Finally, increasing the temperature to 473 K caused significant solubility depression for all three compounds. At the low temperatures the mixture will behave as three separate solids and the pure compounds will act independently. The results at the lower temperature also indicate that there is little interaction between the three solutes in the water phase. At higher temperatures a liquid mixture of the solutes will be formed that will partition into the water, lowering the amounts in aqueous solution at equilibrium.

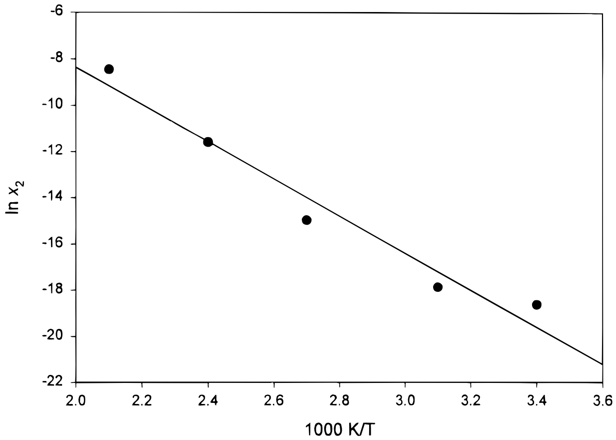

Figure 1. Solubility change of anthracene by temperature in superheated water (40 to 60 bar).

Correlation of the Results

Zeroth Approximation. An approximate equation is first suggested for refinement below, which is as follows.

$$\ln x_2(T) \approx (T_0/T) \ln x_2(T_0) \qquad (1)$$

In this equation, $x_2(T)$ is the solubility, in terms of mole fraction, at any temperature, T, and $x_2(T_0)$ is a known solubility at a temperature, T_0, typically ambient temperature. This equation is based on the assumptions that the solute in equilibrium with the solution does not absorb water and that the Gibbs function for solution does not change greatly over the temperature range. The latter assumption is justified on the basis that the enthalpy of solution of these large insoluble molecules is expected to be greater than the entropy contribution to the Gibbs function change and that the enthalpy change does not vary widely with temperature, as illustrated by the straight line behavior in Figures 1 and 2.

First Approximation. The validity of eq 1 was tested by plotting $\ln x_2(T) - (T_0/T) \ln[x_2(T_0)]$ versus T, as shown in Figure 3. As expected, deviations occur that increase with temperature, demonstrating the higher solvating effect of water on organic compounds as its polarity decreases with higher temperatures. From the limited

Table 6. Solubility of a Mixture of Anthracene/Carbazole/Chrysene in Water

T/K	10^9x_2					
	anthracene		carbazole		chrysene	
	pure	mixed	pure	mixed	pure	mixed
298	8.1	8.7 ± 0.7[a]	110	140 ± 30	0.63	0.47 ± 0.08
323	17	15 ± 1	450	460 ± 20	0.87	1.30 ± 0.08
373	320	260 ± 10	9900	5700 ± 100	13	10 ± 2
423	9200	3600 ± 300	161500	85000 ± 6000	600	460 ± 10
473	210000	120000 ± 5000	1900000	250000 ± 35000	16000	1700 ± 100

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

Table 7. Comparison of Experimental Results for the Solubility of Naphthalene, Benzo[*a*]pyrene, Propazine, Chlorothalonil, and Endosulfan II with Predictive Equation 2

	10^9x_2									
	naphthalene		benzo[*a*]pyrene		propazine		chlorothalonil		endosulfan II	
T/K	exptl	eq 2	exptl	eq 2	exptl	eq 2	exptl	eq 2	exptl	eq 2
298	4780	4780		0.27[a]	493	493	12.2	12.2	11.9	11.9
323	14200	12400			1070	1530	54.4	50.5	48.6	49.5
373			2.9	2.9	8310	11600	1890	609	1330	597
423			430	541	200000	109000	64300	18800	31800	7910
473			4450	19500	2100000	2210000	1580000	460000	199000	213000

[a] Literature value used to calculate predictive value (Mackay and Shiu, 1977).

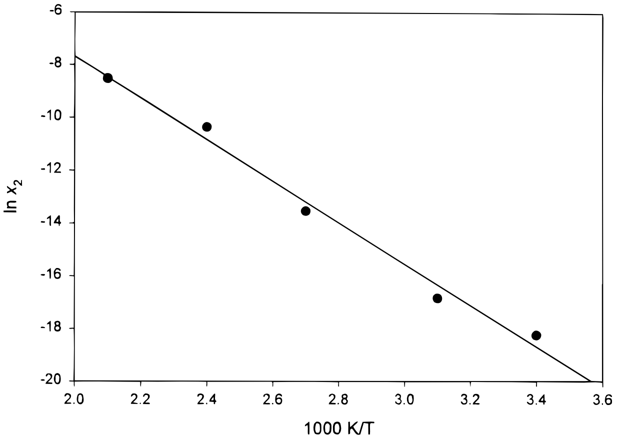

Figure 2. Solubility changes of naphthalene by temperature in superheated water (35 to 50 bar).

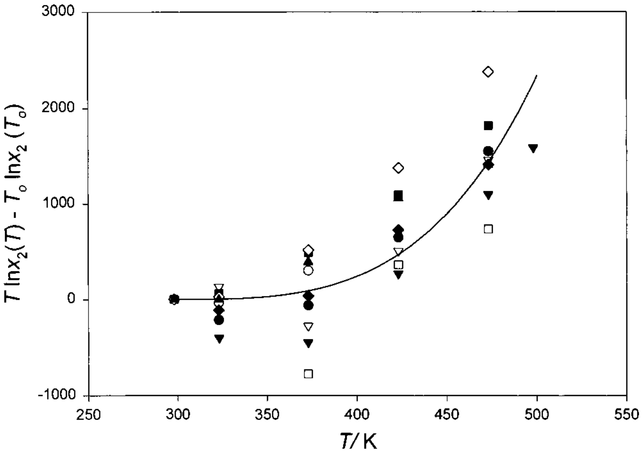

Figure 3. The validity of eq 1 for ●, anthracene; ○, pyrene; ▼, chrysene; ▽, perylene; ■, carbazole; □, benz[*a*]pyrene; ◆, propazine; ◇, chlorothalonil; ▲, endosulfan II, at temperatures from 298 K to 498 K and pressures from 30 bar to 60 bar. Equation 2 fit is indicated by the solid line.

data available, there is not an obvious trend with molecular type, so for a first approximation, a single curve is fitted through all the data presented in Tables 1–5, as well as previously reported solubilities for naphthalene, benzo[*a*]pyrene, propazine, chlorothalonil, and endosulfan II (Miller and Hawthorne, 1998). An approximate fit was achieved with a cubic equation, $(15/2.303)(T/T_0 - 1)^3$, which is shown as the curve in Figure 3. To a first approximation, the solubility at T is given by

$$\ln x_2(T) = (T_0/T)\ln[x_2(T_0)] + 15(T/T_0 - 1)^3 \qquad (2)$$

Comparison of the experimental results was performed using eqs 1 and 2. The results for the compounds reported in this paper are shown in Tables 1–5. In general, eq 1 is slightly better at predicting the mole fraction solubility of the solutes reported in this paper at temperatures from ambient to 373 K, and at temperatures >373 K eq 2 is a much better predictor. With eq 2, predicted values for all solutes and conditions in Tables 1–5 agree with experimental results by a factor of 4 or better, even though solubility changes over 5 orders of magnitude occur. Since eq 2 was the better predictor for the data presented in this work, it was used to predict values for the solutes reported by Miller and Hawthorne (1998). As shown in Table 7, the predicted values agree with experimental results within a factor of 4 except for the highest temperature for benzo[*a*]pyrene.

Conclusions

Raising the temperature of water (with enough pressure to maintain the liquid state) has a dramatic effect on the solubilities of PAHs. Although large increases in pressure have a depressing effect on solubilities over the range of pressures reported in this paper, very little change in the solubility of the compounds tested occurred. Simple predictive equations based only on the knowledge of solubility at ambient temperature give estimates within a factor of 4 compared to experimental results over solubility changes of 5 orders of magnitude. Such accuracy is sufficient for assessing the viability of a possible experiment or process in advance. Refinements to the equations, perhaps including the molecular characteristics of the solute, will be possible when more experimental data become available.

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