Aqueous Solubilities and Infinite Dilution Activity Coefficients of Several Polycyclic Aromatic Hydrocarbons

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Determining the aqueous solubilities and infinite dilution activity coefficients of polycyclic aromatic hydrocarbons (PAHs) is important for environmental reasons. However, common methods for the measurement of infinite dilution activity coefficients, such as ebulliometry or gas chromatography, cannot be used for solutes that are only very slightly soluble in water and have very low vapor pressures, such as the PAHs. Here we report values of the aqueous infinite dilution activity coefficients of four polycyclic aromatic hydrocarbons obtained by measuring their very low aqueous solubilities and their enthalpies of fusion. The values of the infinite dilution activity coefficients we obtain range from 4.2×10^5 for acenaphthene to 3.7×10^8 for benzo[a]pyrene, with an average error of ±12.5%.

Introduction

Determining the aqueous solubilities and infinite dilution activity coefficients of polycyclic aromatic hydrocarbons and other EPA priority water pollutant chemicals is important for the cost-effective remediation of these chemicals in the environment, and the development of process designs to reduce their release into the biosphere. However, common methods of measurement of infinite dilution activity coefficients based on colligative properties such as changes in boiling or freezing points fail for solutes that both are only very slightly soluble in water and have very low vapor pressures (*1,2*). Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) are examples of such solutes. Here we report values of the aqueous infinite dilution activity coefficients of four polycyclic aromatic hydrocarbons obtained from measured values of their enthalpies of fusion and very low aqueous solubilities. The values of the aqueous infinite dilution activity coefficients we obtain range from 4.2×10^5 for acenaphthene to 3.7×10^8 for benzo[a]pyrene.

Theory

For a sparingly soluble solid dissolved in a liquid, the equation relating the infinite dilution activity coefficient to the aqueous solubility, the molar enthalpy of fusion, and the melting point temperature is (*3*)

$$\gamma_i^{\infty} = \frac{1}{x_i} \exp\left[-\left\{\frac{\Delta_{fus}H(T_m)}{RT}\right\}\left[1 - \frac{T}{T_m}\right] + \frac{\Delta C_p}{R}\left\{1 - \frac{T_m}{T} + \ln\left(\frac{T_m}{T}\right)\right\}\right] \quad (1)$$

where T_m is the melting point temperature, $\Delta_{fus}H(T_m)$ is the molar enthalpy of fusion at T_m, R is the gas constant, x_i is the aqueous solubility (in mole fraction), ΔC_p is the difference in heat capacities between the liquid and solid phases, and T is the system temperature (298 K). Because of the small temperature ranges involved, the small magnitude of ΔC_p, and the lack of the necessary heat capacity data, the last term in eq 1 will be neglected. Consequently, we see that, from the measured melting temperature, enthalpy of fusion, and aqueous solubility of a component, we can compute its infinite dilution activity coefficient in water; this is what we do here.

In particular, we have developed a protocol for the measurement of aqueous solubilities of PAHs and similar compounds based on the saturated flask technique (*4, 5*). The molar enthalpies of fusion also needed were either taken from the literature (*4, 6*) or measured here using a differential scanning calorimeter (DSC). The melting points of the compounds we have studied were given by the supplier.

Materials

The polycyclic aromatic hydrocarbons of this study were obtained from Aldrich and used as received. They are acenaphthene (99% purity by mass), anthracene (99%), benz[a]anthracene (99%), and benzo[a]pyrene (98%). Other chemicals used, also purchased from Aldrich, were HPLC grade acetonitrile for the mobile phase and hexane (99.9%) as an eluent in the solid phase extraction process described below. Deionized (DI) water was obtained from a Barnstead/ Thermolyne Nanopure purification system.

Aqueous Solubility Measurement

The equipment used to produce a saturated aqueous solution consisted of an 1800 mL Pyrex flask, a heating/ stirring plate, and a cooling jacket. A glass tube (18 cm × 1 cm id.) and a thermometer sensitive to 0.1 °C were inserted into the flask through a rubber stopper. The glass tube allowed for the sampling of the saturated solution without contamination by crystals present at the liquid–vapor interface. For mixing and equilibration of the solution in the flask, we used a porcelain top stirring hot plate. The cooling jacket was connected to a Model RTE-4 Neslab Endocal refrigerated recirculating bath that maintained the temperature at (25 ± 0.1) °C. Saturation of the aqueous solutions was achieved by adding 50 mg of the solute (PAH) to about 1800 mL of distilled and deionized water. To minimize or eliminate the adsorption of the very hydrophobic chemicals studied onto the walls of the equipment used, and especially onto organic matter that could be present on the walls, all surfaces and equipment were thoroughly acid washed before use (*2*). Also excess solute was used to ensure that the solution was saturated. The solute and water were mixed continuously at a temperature

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Table 1. Operation Specifications for the HPLC

mobile phase	wavelength	time constant
CH_3CN/H_2O 50/50 (v/v)	254 nm	5.0 s

flow rate:	1.5 mL/min (15 cm column) 0.9 mL/min (7.5 cm column)
column temperature:	(30.0 ± 0.1) °C
pressure drop(at specified flow rates):	500−600 psig (7.5 cm column) 1500−1600 psig (15 cm column)

of 30 °C for at least 4 days. The temperature was then lowered to 25 °C, and the solution was allowed to equilibrate for another 2 days. After one measurement of the concentration in the manner described below, the solution was mixed for an additional 2 days and the concentration measured again to assure that equilibration had been achieved. All glassware coming in contact with the saturated aqueous solution was prepared by acid washing, and thorough rinsing with the saturated solution in order to minimize the loss of solute due to adsorption.

A high-performance liquid chromatograph (HPLC) was used for the analysis of solute compositions. The unit consisted of a multisolvent delivery system (model 600), multiwavelength ultraviolet (UV) detector (model 490), Nova-Pa C_{18} column (both 7.5 cm and 15 cm × 3.9 mm columns were used), temperature control module, and systems interface module, all manufactured by Waters, Associates. An IBM-AT personal computer with Waters Maxima 820 software (version 3.30) was used for data acquisition and peak integration. The HPLC operating parameters are listed in Table 1.

The concentrations of acenaphthene, anthracene, and benz[*a*]anthracene at saturation were sufficiently high to allow HPLC analysis by direct injection of the saturated solution. This was done as follows. After equilibration of the solutions at 25 °C, the stirring was stopped and the glass sampling tube inserted into the flask to a point just below the surface of the liquid. A slow stream of air was passed through the tube to eliminate deposition of the solute on the interior of tube, and to expedite the settling of solid particles from solution. After all of the solute crystals had settled, the air stream was slowly turned off and a prepared pipet was used to sample the aqueous phase at a position approximately 3 cm from the end of the tube, and 4−5 cm from the bottom of the flask. Approximately 3 mL of saturated solution was withdrawn from the flask with this pipet and placed in a prepared sample vial. Before injection into the HPLC, the solution was examined with a microscope to ensure that there were no suspended crystals.

Filtration was necessary for solutions of anthracene and benz[*a*]anthracene since these chemicals formed small solute aggregates that would not settle out of solution. The smallest particle size found in these solutions was microscopically found to be about 0.3 μm, and a hydrophilic 0.2 μm Supor-200 47 mm membrane filter from Gelman Sciences in a Kontes vacuum filter holder was used for the removal of these particles from aqueous solution. The filtering apparatus was first prepared by passing 100 mL of the saturated aqueous solution through it to reduce the initial loss of solute onto the filter. An aspirator was used to produce the slight vacuum used in the filtration; this vacuum did not result in vaporization of either the water or the solute. After preparation, approximately 250 mL of the solution was filtered, collected in a prepared flask, and then analyzed directly on the HPLC.

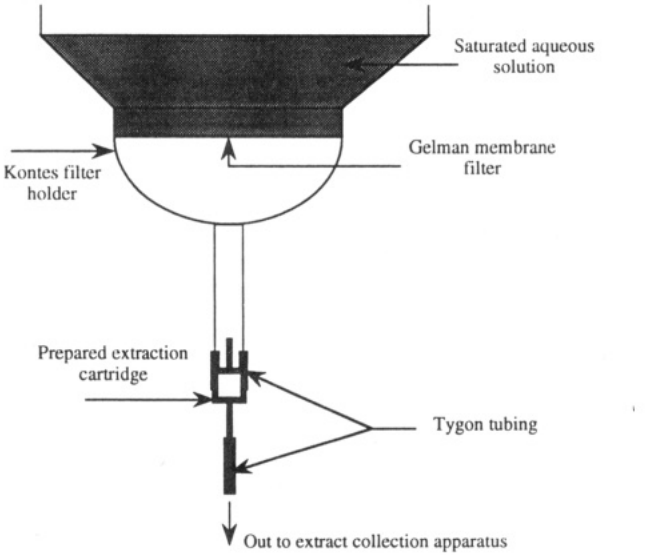

Figure 1. Direct extraction apparatus.

For acenaphthene, anthracene, and benz[*a*]anthracene, injections of 50, 20, and 100 μL, respectively, were made into the HPLC. However, the low aqueous saturation concentration of benzo[*a*]pyrene required raising the concentration (in another solvent) to the quantitatively detectable region. Solid phase extraction (SPE) (*7*, *8*) was used to accomplish this. In solid phase extraction, water is passed through a solid adsorbent and the nonpolar solute is adsorbed. After extraction, the solute is removed from the packing with a nonpolar elution solvent in which it is extremely soluble. For this work, Sep-Pak Classic cartridges packed with octadecyl carbon (C_{18}) bonded to a silica support were used (Waters, Associates) with *n*-hexane as the eluting solvent. Note that the cartridge packing and the column packing we used are similar.

Before use, the cartridge was prepared by wetting the packing with 10 mL of acetonitrile, followed by a rinse with 10 mL of pure, DI water. The preparation was done with luer-tipped syringes with injections of the solvent and DI water made in the same direction as the subsequent flow of the aqueous solution to be extracted. The cartridge was used immediately after preparation, and extraction from the aqueous phase was performed with an in-line apparatus to eliminate unnecessary contact with glassware and solute loss due to adsorption. This equipment consisted of direct extraction (Figure 1) and extract collection equipment (Figure 2). The components included a Sep-Pak cartridge, Kontes filtering apparatus, 500 mL buret, vacuum fitting, 500 mL vacuum trap, aspirator (Venturi ejector), and Tygon tubing.

After preparation of the cartridge and filter, the filter holder was filled with aqueous solution siphoned from the flask used to saturate the solution. Water flow through the Venturi ejector was adjusted to maintain an aqueous solution flow rate through the cartridge of 5 mL/min as this did not result in premature breakthrough of the solute. The breakthrough volume differed for each compound and was related to its retention time on the solid phase used in both the extraction cartridge and the analytical column. The breakthrough volume of acenaphthene was found to be 500 mL with the cartridges we used. As with the preparation step, the eluent was passed through the cartridge with a luer-tipped syringe in the same direction as the flow of aqueous phase. The cartridge was then eluted with *n*-hexane, and the eluent was collected in a calibrated tube to record its exact volume.

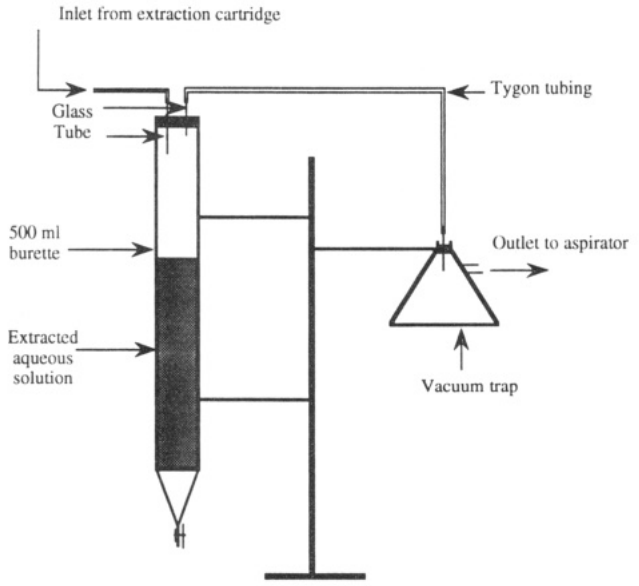

Figure 2. Aqueous extract collection apparatus.

Table 2. Aqueous Solubilities of Anthracene and Benz[*a*]anthracene at 25 °C Obtained by Replicate Direct Measurement

compound	measd solubility (ppm by mass)	lit. value
anthracene	0.0425	0.0446 (*10*)
	0.0435	
benz[*a*]anthracene	0.0144	0.0139 (*9*)
	0.0148	

It was found, by trial and error, that increasing the solvent/solute contact time in the cartridge greatly increased the percent recovery of the retained compound. Therefore, after each 2 mL of eluent passed through the cartridge, we waited 1 min before continuing the elution. Once 10 mL of eluent had passed through the cartridge, the calibrated test tube was capped and well mixed before an injection into the HPLC. The cartridges were then tested for retention of the compounds by additional elution. When no further adsorbed compound was present after additional elution (usually after the first 10 mL), the cartridge was discarded. By tests with acenaphthene, whose solubility we measured both by direct injection and by using solid phase extraction, we found that we could obtain a 99+% recovery using the protocol described above. The PAH concentration ratio in solvent to water is the same as the aqueous solution to eluent volume ratio, which was approximately 27 in the measurements here.

Measured Solubilities

Since the saturation concentration of acenaphthene is above the HPLC detection limit, direct injection of a saturated solution after a settling time of 2 h provided good results. Seven separate aqueous solubility measurements of acenaphthene at 25 °C gave an average value of 3.86 ppm with a reproducibility of 2%, which compares well with the value of 3.88 ppm and 1.8% uncertainty reported by Wauchope et al. (*4*) obtained using a similar saturated flask technique. Average results of two solubility measurements of anthracene and benz[*a*]anthracene, made to check that the solution was saturated, are presented in Table 2. The reproducibilties of the measurements are 2.3% and 2.7% for anthracene and benz[*a*]anthracene, respectively.

The aqueous solubility of benzo[*a*]pyrene was determined with the extraction protocol described above. We extracted benzo[*a*]pyrene from approximately 270 mL of a saturated aqueous solution and then eluted with 10 mL of *n*-hexane,

Table 3. Retention Times on the 7.5 cm HPLC Analytical Column

compound	retention time (min) (with a 0.9 mL/min flow rate)
acenaphthene	8.2
anthracene	11.7
benz[*a*]anthracene	25.6
benzo[*a*]pyrene	42.8

Table 4. Data for Extraction and Solubility Measurement of Benzo[*a*]pyrene

trial	aqueous volume (cm^3)	eluent volume (cm^3)	aqueous solubility (ppm by mass) measd	lit.
1	263	10	4.68×10^{-3}	3.78×10^{-3} (*9*), 3.8×10^{-3} (*5*)
2	269	10	4.77×10^{-3}	

Table 5. Aqueous Solubilities, Enthalpies of Fusion, and Infinite Dilution Activity Coefficients

compound	x_1[a]	$t_{m/°C}$	$\Delta_{fus}H(T_m)$/ (kJ·mol^{-1})	γ_1^∞
acenaphthene	4.53×10^{-7}	94	21.7 (*6*)	$(4.25 \pm 0.55) \times 10^5$
anthracene	4.34×10^{-9}	217	29.0 (*4*)	$(2.35 \pm 0.35) \times 10^7$
benz[*a*]anthracene	1.15×10^{-9}	158	22.3[a]	$(5.41 \pm 0.70) \times 10^7$
benzo[*a*]pyrene	3.37×10^{-10}	178	15. 1[a]	$(3.75 \pm 0.49) \times 10^8$

[a] Measured here.

which provides a concentration increase of a factor of almost 27. Although the breakthrough volume for benzo[*a*]pyrene is unknown, we do not believe there was any solute breakthrough since the aqueous volume of 270 mL was well below the 500 mL breakthrough volume of acenaphthene, and the retention time (and thus retention volume) of benzo[*a*]pyrene on the HPLC column was much larger than that of acenaphthene (see Table 3). The results of the extraction and the computed aqueous solubility are given in Table 4. Our measured aqueous solubility is slightly larger than the value reported previously in the literature (*5*, *9*). Overall we estimate the accuracy of our solubility measurements to be ±5%.

Differential Scanning Calorimetry (DSC)

The molar enthalpies of fusion for both acenaphthene and anthracene were found in the literature (*4*, *6*), but had to be measured for both benz[*a*]anthracene and benzo[*a*]pyrene. A Du Pont Instruments Model 9900A thermal analyzer equipped with a Model 910 DSC cell was used for this purpose. The DSC was first calibrated with high-purity indium for which the enthalpy of fusion is accurately known. Then a sealed sample containing the compound was placed in one cell and a sealed blank in the other. Both cells with attached thermosensors were then heated in the DSC chamber, and the sensors used to measure temperature so as to adjust the heat input to maintain both cells at the same temperature. The difference in heat input to the cells, $\Delta Q = Q_{blank} - Q_{sample}$, was recorded. At the melting point, ΔQ became negative, representing the endotherm in going from solid to liquid. Once the sample was completely melted, ΔQ increased and then leveled off. The integrated difference in heat input due to melting gives the molar enthalpy of fusion (see Table 5). On the basis of the manufacturer's specifications and our experience, we estimate the accuracy of the enthalpy of fusion measurements to be ±2.5%.

Infinite Dilution Activity Coefficients

From the information in Tables 4 and 5, the values of the infinite dilution activity coefficients were calculated, and the values are given in Table 5. Note that the values

of the infinite dilution activity coefficients we obtain range from 420 000 for acenaphthene to 370 000 000 for benzo-[*a*]pyrene. These are the first reported aqueous infinite dilution activity coefficients for these compounds.

A detailed error analysis based on a 2.5% error in the enthalpy of fusion, 1 K error in reported melting temperatures, 5% error in measured compositions, 0.03 and 0.12 mL errors in measured extract and eluent total volumes, and 0.1 K error in measured temperatures suggests that measured infinite dilution activity coefficients are accurate to ±12.5%. Most of this inaccuracy is equally a result of the errors inherent in the composition and enthalpy of fusion measurements.

Literature Cited

(1) Trampe, D. B.; Eckert, C. A. *AIChE J.* **1993**, *39*, 1045.
(2) Haines, Robert T. S. Masters Thesis, University of Delaware, Newark, DE, Fall 1994.
(3) Sandler, S. I. *Chemical and Engineering Thermodynamics, 2nd ed.*; John Wiley & Sons: New York, 1989; pp 408–479.
(4) Wauchope, R-D.; Getzen, F. W. *J Chem. Eng. Data* **1972**, *17*, 38.
(5) Mackay, D.; Shiu, W. Y. *J Chem. Eng. Data* **1977**, *22*, 399.
(6) Rai, U. S.; Shekhar, H. *Thermochim. Acta* **1991**, *186*, 13 1.
(7) Kicinski, H. G.; Adamek, S.; Kettrup A. *Chromatographia* **1989**, *23*, 354.
(8) Wells, M. J. M.; Michael, J. L. *J Chromatogr. Sci.* **1987**, *25*, 345.
(9) Miller, M; Wasik, S. P. *Environ. Sci. Technol.* **1985**, *19*, 522.
(10) May, W. E.; Wasik, S. P. *Anal. Chem.* **1978**, *50*, 997.

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