

THE EFFECTS OF TEMPERATURE AND SALINITY ON THE AQUEOUS SOLUBILITY OF POLYNUCLEAR AROMATIC HYDROCARBONS

BRIAN G. WHITEHOUSE*

Department of Oceanography, Dalhousie University, Halifax, Nova Scotia B3H 4J1 (Canada)

(Received July 13, 1983; revision accepted December 20, 1983)

ABSTRACT

Whitehouse, B.G., 1984. The effects of temperature and salinity on the aqueous solubility of polynuclear aromatic hydrocarbons. *Mar. Chem.*, 14: 319–332.

The aqueous solubilities of phenanthrene, anthracene, 2-methylanthracene, 2-ethylanthracene, 1,2-benzanthracene, and benzo(a)pyrene were determined at temperatures ranging from 3.7 to 25.3°C and salinities ranging from 0 to 36.7‰. With the exception of 1,2-benzanthracene, the hydrocarbons experienced salting-out. Their solubilities were insensitive to small changes in salinity and very sensitive to small changes in temperature. On the other hand, 1,2-benzanthracene experienced salting-in, and its solubility was sensitive to small changes in salinity. Potential environmental implications of the data are discussed.

INTRODUCTION

From an environmental standpoint, polynuclear aromatic hydrocarbons (PAH) are of considerable concern. This is mainly due to their relative persistence, carcinogenic and mutagenic potential, and their possible indication of anthropogenic pollution. A considerable amount of research concerning PAH in the marine environment has been published; with a majority of the information concerning PAH in the sediments.

Relatively few of the studies published focus upon PAH dissolved in the water column, with the result that much is still to be learned about the partitioning of PAH in aquatic systems. This statement is supported by the fact that there is a general lack of available information concerning the aqueous solubility of PAH. Numerous factors determine the ultimate distribution of PAH in the aquatic environment, but the compounds' aqueous solubility is a major initial factor. Aqueous solubilities of hydrocarbons have been demonstrated to influence or determine their bioaccumulation (Geyer et al., 1981; Mackay, 1982), biosorption (Steen and Karickhoff, 1981), sorption to minerals and marine sediments (Meyers and Quinn, 1973; Karickhoff et al., 1979; Means et al., 1980; Karickhoff, 1981; Knap and LeB. Williams, 1982), transport in the marine environment (Gearing et al., 1980; Oviatt et al., 1982), fractionation onto glass-fibre filters (Gearing and Gearing, 1982), petroleum exploration (Baker, 1960; Barker, 1979), and carcinogenic potential (Krasnoschekova and Gubergrits, 1976).

* Present address: Institut für Meereskunde, Düsternbrooker Weg 20, D-2300 Kiel, West Germany.

Despite their demonstrated importance, almost all of the PAH solubility data available in the literature are for distilled water at 25°C. There are a few seawater hydrocarbon solubility values available, but these are almost entirely for alkanes and substituted benzene compounds at 35‰ and 25°C. The only PAH seawater solubility data to be located were for naphthalene (Gordon and Thorne, 1967; Eganhouse and Calder, 1976), biphenyl and phenanthrene (Eganhouse and Calder, 1976), and acenaphthene and pyrene (Rossi and Thomas, 1981). All were at 25°C with acenaphthene and pyrene being measured at 35‰ only.

This lack of PAH solubility information is amazing when one considers the amount of research that has been carried out on the presence and toxicity of hydrocarbons in the aquatic environment. Such an environment represents a wide range of temperature and salinity. Attempts to qualitatively understand and quantitatively predict the partitioning of PAH in such an environment will require greater understanding of their solubility under these conditions.

In order to investigate the fundamentals of PAH solubilities under environmental conditions, the aqueous solubility of six PAH was determined at temperatures ranging from 3.7 to 25.3°C and salinities ranging from 0 to 36.7‰.

METHODS

Hydrocarbon solubility determination

There are two commonly accepted methods for determining the aqueous solubility of hydrophobic organic solutes. The first is a mechanical mixing method that is usually referred to as the 'shake-flask' technique. The second is a liquid chromatographic method that is referred to as the "micro-column" or "dynamic coupled column liquid chromatography" (DCCLC) technique. Both techniques are acceptable provided that they are properly employed (Hashimoto et al., 1982).

The DCCLC technique is advantageous as it does not suffer from the supersaturation effects that can result from mechanical mixing. It also avoids the problem of solute adsorption onto the walls of analytical equipment, and it eliminates the problem of sample loss and contamination that may occur during organic extraction and sample cleanup. The DCCLC technique is also faster and facilitates precise temperature control.

The DCCLC technique was employed in this study. A detailed description and critical evaluation of the technique has been presented by May (1978) and May et al. (1978). May and Wasik (1978) demonstrated its application to PAH in water, and May et al. (1975) employed coupled column liquid chromatography for analyzing hydrocarbons in marine sediments and seawater.

The DCCLC technique is relatively new to the field of marine chemistry, thus a brief description is warranted. Water is pumped through a 60 × 0.6 cm

(0.46-cm I.D.) stainless steel column containing the PAH of interest coated onto 60–80 mesh glass beads. The stainless-steel column (generator column) is temperature controlled to $\pm 0.05^\circ\text{C}$ and has 2- μm stainless steel frits on either end. The PAH saturated solution is then pumped into a Rheodyne six-port valve where the PAH are extracted onto a slurry-packed Rheodyne RP-C18 cartridge (3.0 \times 0.46-cm I.D.). The cartridge and connecting tubing is then rinsed with 6 ml of purified water in order to remove inorganic salts. The PAH are backflushed off the RP-C18 cartridge by switching the six-port valve to the inject position, thus allowing the acetonitrile–water mixture from the high performance liquid chromatograph (HPLC) to flow through the cartridge.

The PAH then flows into a Varian RP-C18 analytical column (30 \times 0.4-cm I.D., 10 μm slurry packed) where it is isocratically separated from impurities. Depending upon the PAH being analyzed, the isocratic mobile phase consisted of 75–90% acetonitrile in water.

Detection was by ultraviolet absorption at 254 nm. Quantification was by peak integration using a Hewlett-Packard 3390A integrator/plotter. This was calibrated with PAH standard injections from a 20- μl loop which could be installed on a four-port valve that was situated between the six-port valve and the RP-C18 analytical column.

May (1978) demonstrated that flow rates between 0.1 and 5.0 ml min^{-1} can be used to generate the saturated solution. After confirming May's observation, this study used a flow rate of $1.0 \pm 0.1 \text{ ml min}^{-1}$. In addition to confirming that the flow rate did not influence the concentration of the solute in the generated solution, Hashimoto et al. (1982) concluded that the solution was particle free at least to 0.3 μm .

By employing two columns in series, May (1978) demonstrated that the process was reversible and that the generated solution was in equilibrium. Hashimoto et al. (1982) also concluded that the generated solution was in equilibrium, as opposed to steady-state.

May (1978) demonstrated that the technique generates an equilibrated, saturated solution with a precision of better than $\pm 3\%$ and a potential accuracy of greater than 98%. May et al. (1978) demonstrated that the extractor cartridge is greater than 99% efficient for PAH solutions of $\leq 25 \text{ ml}$. The extraction volumes employed in this study were always $\leq 5 \text{ ml}$. The reported analytical precision and extraction efficiency were confirmed by this study with solutions of anthracene in purified water.

Materials

The compounds chosen for this study were phenanthrene, anthracene, 2-methylanthracene, 2-ethylanthracene, 1,2-benzanthracene, and benzo(a)pyrene. These PAH span approximately three orders of magnitude in distilled water solubility. They have three, four, or five aromatic rings, and include both linear and nonlinear conformations. They were obtained in

purities of $\geq 97\%$ (Aldrich Chemical Co.). Standards were prepared in HPLC grade acetonitrile (Fisher Scientific Co.).

The PAHs phenanthrene, 2-methylanthracene, and 2-ethylanthracene were also used to construct generator columns. The generator columns for anthracene, 1,2-benzanthracene, and benzo(a)pyrene were obtained commercially (National Bureau of Standards). These commercial columns were supplied with certified distilled water solubility data.

Water was required for HPLC analysis and for diluting various solutions employed in this study. Purified water was obtained as follows: distilled water was passed through a Millipore Super-Q system and then poured into an all-glass distillation apparatus. Prior to condensation and collection, the water vapor passed through an all-quartz tube that was heated to 800°C . The water was prepared no more than 24–36 h prior to use.

Whatman GF/C glass-fibre filters were cleaned by overnight combustion at approximately 450°C . The filters were then rinsed with approximately 100 ml of purified water immediately prior to use.

All glassware employed was cleaned by soaking in chromic acid solution, followed by a purified water rinse and overnight combustion at 450°C .

Sample water collection and preparation

Stock seawater was collected by Niskin bottle hydrocasts in the surface waters of the Scotia Shelf (sample salinity 32.532‰), a Sargasso Sea Warm Core Ring (sample salinity 35.922‰), and the Canadian Central Arctic Ocean (sample salinity 35.607‰).

Prior to use in the solubility experiments, the seawater was filtered through a precleaned Whatman GF/C glass-fibre filter and photo-oxidized to remove dissolved organic matter. This involved a 3-h photo-oxidation period with $100\ \mu\text{l}$ of 30% H_2O_2 in each photo-oxidation tube. Solutions of intermediate salinities were prepared by quantitatively diluting this seawater with purified water. Effects of dissolved organic matter on PAH solubility were also investigated, and will be reported at a later date.

RESULTS

The solubility data for the six PAH are presented in Table I. All data are expressed as nmol l^{-1} except for phenanthrene, which is in $\mu\text{mol l}^{-1}$. The solubility data for benzo(a)pyrene at 3.7°C were not obtained due to detection limitations. The data for 1,2-benzanthracene at 36.7‰ and $\leq 12.4^{\circ}\text{C}$ were not obtained due to a shortage of 36.7‰ solution.

The data are presented as the mean \pm the standard deviation of three consecutive solubility measurements. In several cases, the data for 1,2-benzanthracene represent four consecutive solubility measurements.

The resulting standard deviations for phenanthrene, anthracene, 2-methylanthracene, and 2-ethylanthracene are $\leq \pm 3\%$ of the solubility, with 10% of the data having ± 3 –5% standard deviations. The standard deviations of 1,2-benzanthracene and benzo(a)pyrene are $\leq \pm 10\%$ with 1,2-benzanthracene having two points of $\pm 23\%$.

As previously stated, the generator columns for anthracene, 1,2-benzanthracene, and benzo(a)pyrene were obtained from the National Bureau of Standards, along with certified distilled water solubility values from 10 to 30°C at the 99% confidence interval. These certified values are plotted in Fig. 1 along with the corresponding distilled water values obtained in this study. The symbol S_0 refers to distilled water solubility.

There are no literature solubility data for 2-ethylanthracene. The only literature value available for 2-methylanthracene is $157 \pm 46 \text{ nmol l}^{-1}$ in distilled water at 25°C (this value represents the mean and standard deviation of data published by Mackay and Shiu, 1977; May and Wasik, 1978). Table I lists the distilled water, 25.3°C, solubility of 2-methylanthracene as 117 nmol l^{-1} . The literature value for the solubility of phenanthrene in distilled water at 25°C is $6.29 \pm 0.95 \mu\text{mol l}^{-1}$ (Mackay and Shiu, 1977; Eganhouse and Calder, 1976; May and Wasik, 1978). Table I lists the 25.3°C value of phenanthrene in distilled water as $6.16 \mu\text{mol l}^{-1}$.

The only seawater data available in the literature for comparison are those of Eganhouse and Calder (1976) for phenanthrene at 35‰ and 25°C. These authors obtained a value of $3.98 \pm 0.14 \mu\text{mol l}^{-1}$. Table I lists the solubility of this compound as $3.64 \mu\text{mol l}^{-1}$ at 33.1‰ and 21.1°C, and $4.54 \mu\text{mol l}^{-1}$ at 36.5‰ and 25.3°C.

From the above comparisons it is concluded that where literature data are available, the data in Table I are in agreement within the reported precisions.

Discussion

It is easier to visualize the solubility trends by plotting the solubility data of Table I vs. temperature. These plots are presented in Fig. 2. The solubility data for the compounds phenanthrene, anthracene, 2-methylanthracene, and 2-ethylanthracene indicate little or no significant difference in solubility between the distilled water and 4‰ seawater, or between the 33‰ and 36‰ seawater. Benzo(a)pyrene exhibits the same behavior; however, the precision of its solubility data is not as good. In other words, by oceanographic standards, fairly large changes in salinity are required in order to cause significant changes in the solubility of these compounds. This suggests that oceanographers should only have to be concerned about salinity effects upon PAH solubility at interfaces where large changes in salinity occur. Examples of such interfaces would be where terrestrial runoff meets the marine environment, aeolian fallout to the marine surface layer, marine oil spills, urban sewage disposal sites, and offshore production platforms.

These PAH also exhibit what are often considered to be normal solubility

TABLE I
PAH solubility data

	Temperature ($^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$)					
	4.6	8.8	12.9	17.0	21.1	25.3
<i>Phenanthrene</i> ($\mu\text{mol l}^{-1}$)						
0	2.01 ± 0.07	2.45 ± 0.11	3.12 ± 0.13	4.04 ± 0.17	4.94 ± 0.25	6.16 ± 0.28
4.14	1.93 ± 0.02	2.44 ± 0.02	3.12 ± 0.06	3.98 ± 0.06	5.05 ± 0.08	6.25 ± 0.11
8.28	1.74 ± 0.07	2.26 ± 0.02	2.92 ± 0.02	3.72 ± 0.02	4.68 ± 0.02	5.86 ± 0.03
16.6	1.67 ± 0.04	2.16 ± 0.04	2.72 ± 0.05	3.49 ± 0.05	4.35 ± 0.06	5.38 ± 0.06
33.1	1.35 ± 0.01	1.74 ± 0.01	2.23 ± 0.01	2.85 ± 0.03	3.64 ± 0.01	4.48 ± 0.09
36.5	1.36 ± 0.04	1.75 ± 0.04	2.21 ± 0.06	2.81 ± 0.07	3.59 ± 0.10	4.54 ± 0.14
<i>Anthracene</i> (nmol l^{-1})						
0	53.9 ± 0.9	72.4 ± 1.5	99.3 ± 1.3	133 ± 2	181 ± 6	248 ± 4
4.14	52.6 ± 0.7	70.1 ± 1.8	97.6 ± 1.0	130 ± 5	184 ± 5	253 ± 6
8.28	50.5 ± 1.6	68.4 ± 0.4	94.2 ± 0.9	126 ± 3	174 ± 2	236 ± 2
16.6	46.6 ± 2.1	62.8 ± 2.4	84.2 ± 1.2	113 ± 3	153 ± 3	205 ± 5
33.1	38.7 ± 1.0	49.9 ± 1.5	72.4 ± 1.1	96.5 ± 2.6	133 ± 3	180 ± 1
36.5	37.9 ± 0.2	50.7 ± 2.4	68.4 ± 1.0	97.6 ± 1.8	131 ± 4	182 ± 1
<i>2-Methylanthracene</i> (nmol l^{-1})						
0		39.2 ± 1.5	50.4 ± 1.4	63.9 ± 1.7	84.0 ± 2.8	117 ± 2
4.21	22.4 ± 0.8	29.6 ± 0.8	40.4 ± 0.9	55.7 ± 0.6	76.3 ± 0.4	106 ± 1
8.42	20.7 ± 0.2	27.0 ± 0.6	37.0 ± 0.3	50.8 ± 0.9	71.2 ± 0.2	100 ± 1
16.8	19.1 ± 0.2	26.0 ± 0.9	35.7 ± 1.0	47.9 ± 0.7	64.7 ± 0.8	91.2 ± 1.9
33.7	16.4 ± 0.2	20.8 ± 0.1	27.7 ± 0.2	38.1 ± 0.3	53.3 ± 0.8	77.6 ± 0.5
36.5	15.6 ± 0.2	19.5 ± 0.1	26.2 ± 0.3	35.7 ± 0.7	49.4 ± 0.5	70.8 ± 1.7

<i>2-Ethylanthracene</i> (nmol l ⁻¹)									
0	33.8 ± 0.2	40.4 ± 0.2	54.1	68.0 ± 0.3	92.6 ± 1.7	130 ± 2			
4.21	29.4 ± 0.5	38.4 ± 0.4	51.0 ± 0.5	66.9 ± 0.5	88.4 ± 1.1	120 ± 1			
8.42	27.4 ± 0.3	35.7 ± 0.3	47.2 ± 0.2	63.7 ± 0.8	84.5 ± 0.4	113 ± 2			
16.8	25.4 ± 0.3	33.8 ± 0.7	43.8 ± 0.6	57.6 ± 0.5	79.1 ± 0.3	105 ± 0.3			
33.7	20.3 ± 0.1	25.7 ± 0.4	34.4 ± 0.3	46.3 ± 0.4	63.9 ± 1.6	86.9 ± 2.1			
36.5	18.7 ± 0.5	24.5 ± 0.4	32.5 ± 0.4	43.6 ± 0.4	60.9 ± 0.9	79.7 ± 2.6			

Temperature (°C ± 0.1 °C)

3.7	8.0	12.4	16.7	20.9	25.0
<i>1,2-Benzanthracene</i> (nmol l ⁻¹)					
0	21.3 ± 1.7	18.8 ± 1.7	20.6 ± 0.4	27.6 ± 0.7	37.4 ± 1.3
4.20	58.8 ± 2.7	32.3 ± 2.0	25.6 ± 1.4	31.2 ± 0.7	39.6 ± 0.6
8.40	85.0 ± 3.7	44.0 ± 4.8	36.3 ± 1.6	40.6 ± 4.1	46.4 ± 1.8
16.8	91.9 ± 5.1	42.2 ± 1.3	33.4 ± 3.4	38.2 ± 1.2	47.5 ± 2.0
32.1	118 ± 28	57.2 ± 1.6	38.5 ± 2.8	36.7 ± 2.3	40.9 ± 4.3
36.7			44.5 ± 3.3	39.5 ± 3.3	41.6 ± 1.7
<i>Benzo(a)pyrene</i> (nmol l ⁻¹)					
0	2.64 ± 0.24	3.00 ± 0.20	3.74 ± 0.28	4.61 ± 0.18	6.09 ± 0.45
4.03	1.79 ± 0.15	2.26 ± 0.07	3.18 ± 0.06	4.42 ± 0.17	5.12 ± 0.07
8.40	1.60 ± 0.08	2.36 ± 0.12	2.81 ± 0.24	3.93 ± 0.12	5.33 ± 0.12
16.8	1.79 ± 0.10	2.10 ± 0.12	3.02 ± 0.30	4.19 ± 0.18	5.28 ± 0.09
32.1	1.38 ± 0.02	1.99 ± 0.08	2.45 ± 0.18	3.46 ± 0.19	4.88 ± 0.07
36.7	1.40	2.07 ± 0.12	2.50 ± 0.14	3.43 ± 0.45	4.45 ± 0.15

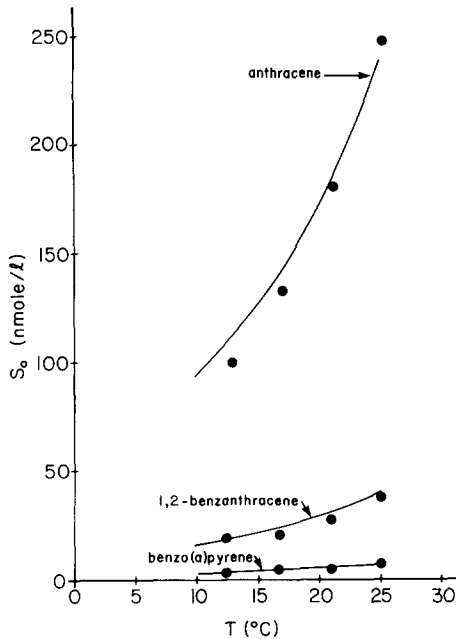


Fig. 1. S_0 vs. T . N.B.S. data (—) and data from Table I (●).

trends. Namely, decreasing solubility with decreasing temperature, and decreasing solubility with increasing salt concentration (salting-out).

On the other hand, salting-in (increased solubility upon the addition of salt) is exhibited by 1,2-benzanthracene. As shown in Fig. 2, the salting-in is much greater at the lower temperatures. Also, unlike the previously discussed five compounds, 1,2-benzanthracene does experience significant differences in solubility upon the addition of small amounts of salt. This only occurs at the lower temperatures and salinities. In fact, the change in solubility at 25.0°C for this compound is of little or no significance at the 95% confidence interval, regardless of the amount of salt added (Whitehouse, 1983). It is only at the temperatures below 25.0°C that salting-in is statistically significant.

This observation of a compound that exhibits salting-in is not unique. What is unusual about the above data is the observation of a class of compounds which experience both salting-out and salting-in for a given salt solution. This has significant theoretical implications and greatly complicates attempts to predict partitioning and transport (Whitehouse, 1983).

Unlike salinity, small decreases in temperature cause significant decreases in the solubility of phenanthrene, anthracene, 2-methylanthracene, and 2-ethylanthracene, especially in the higher temperature range of this study. For example, the anthracene data in Table I and Fig. 2 indicate that a 4°C decrease in temperature causes the same reduction in distilled water solubility

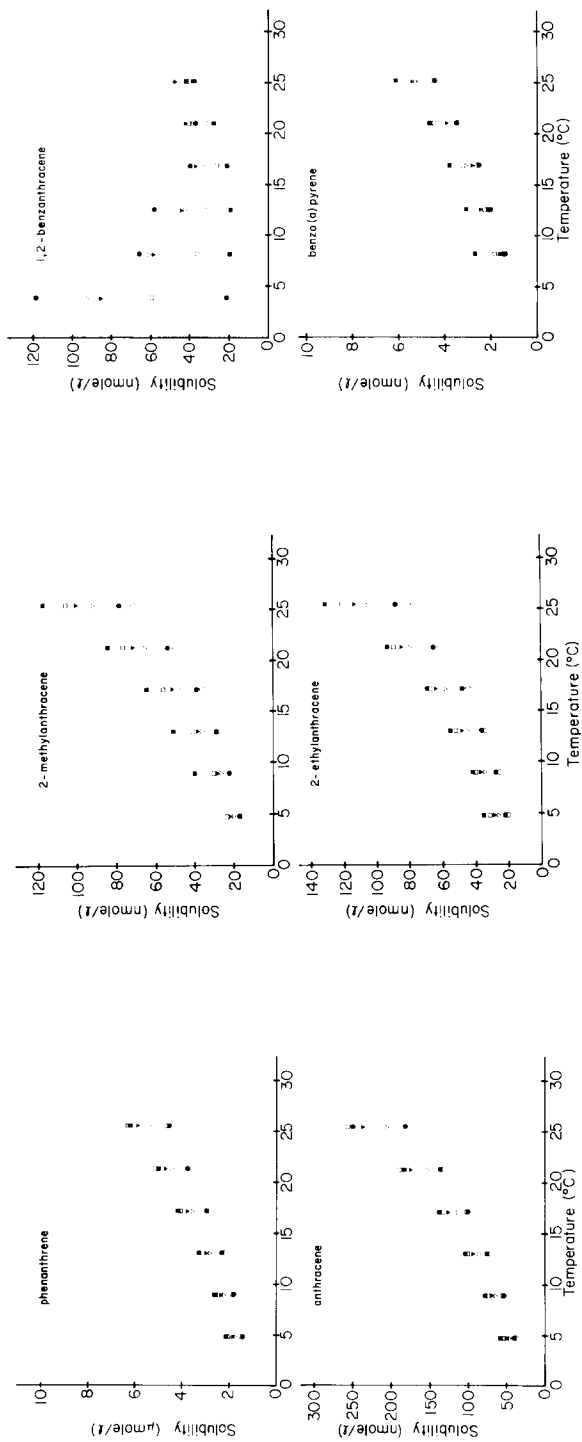


Fig. 2. PAH solubility vs. temperature. Approximate salinity: (■) 0‰; (□) 4‰; (▼) 8‰; (▽) 16‰; (●) 33‰; (○) 36‰. (see Table I for precise salinity data).

as a change from 0 to 33.1‰ salinity. In other words, these compounds are far more sensitive to small changes in temperature than they are to small changes in salinity.

Benzo(a)pyrene exhibits the same trend in temperature as the above four compounds. However, as previously mentioned, the poorer precision for the solubility of this compound makes it difficult to assess the significance of the temperature trend.

Figure 3 is a plot of percentage salting-out at 33‰ vs. temperature. This allows visualization of the magnitude of the salt effect with respect to individual PAH and to temperature. The figure indicates that for a given compound, there is little difference in the percentage salting-out over the temperature range investigated. This statement should not be confused with the previously made statement concerning the sensitivity of absolute solubility to small changes in temperature. The apparent variation in the benzo(a)pyrene data may reflect analytical imprecision.

As indicated in Fig. 3, at 17°C a 33‰ change in salinity would result in an approximately 27% salting-out of anthracene, 29% of phenanthrene, 32% of 2-ethylanthracene, and 40% of 2-methylanthracene. The same conditions at 16.7°C would result in a 34% salting-out of benzo(a)pyrene (and a 87% salting-in of 1,2-benzanthracene). The unexpected observation is not that the compounds experience different percentages of salting-out, but that the amount salted-out does not correspond to the relative differences in the compounds' distilled water solubility. For example, phenanthrene is approximately 25 times more soluble than anthracene, yet exhibits the same percentage salting-out. Also note that benzo(a)pyrene exhibits a percentage salting-out ranging between that of anthracene and 2-methylanthracene, yet it is vastly less soluble than either of these two compounds.

There are reasons for stressing this lack of correlation between a compound's distilled water solubility and its extent of salting-out. First, it will prevent or complicate attempts to predict partitioning in the marine environment simply from a standpoint of the compound's distilled water solubility.

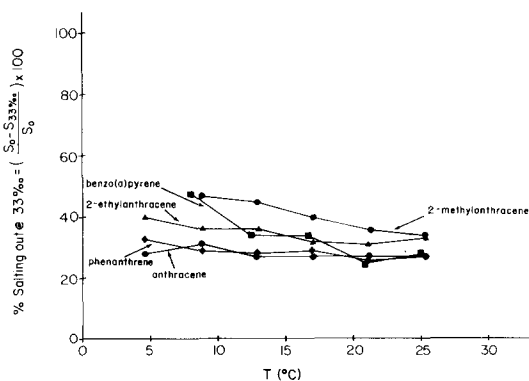


Fig. 3. Percentage salting-out vs. temperature.

Second, it will influence the use of such analytical tools as PAH source determination from alkyl-homolog distributions.

The alkyl-homolog data presented in Table I and Fig. 3 have interesting implications. For example, consider the PAH partitioning between the dissolved phase and particulate matter in the water column in proportion to PAH solubility. This has been observed or suggested in several studies and presentations, as outlined in the introduction. Such a partitioning process would suggest that the less soluble PAH would adsorb onto the particulate matter, and thus eventually be sedimented out of the water column.

If this is visualized using carbon number (Hites, 1976), or various other pure-component parameters which have been employed when the actual solubility data are unavailable, the end result is significantly different from that obtained by employing the actual solubility data. Specifically, from a standpoint of carbon number 2-ethylanthracene would be less soluble than 2-methylanthracene, and, thus, should experience greater adsorption onto particulate matter and greater enrichment in the sediments. On the other hand, Table I indicates that 2-ethylanthracene is actually comparable to or even slightly more soluble than 2-methylanthracene. In addition, Fig. 3 indicates that 2-ethylanthracene may experience less salting-out than 2-methylanthracene. These facts would indicate that 2-methylanthracene would experience greater adsorption and enrichment in the sediments.

Two homologs of a single PAH is a very limited series. Obviously more studies are required. Equally obvious though, is the conclusion that oceanographers investigating PAH in the marine environment can no longer simply employ distilled water solubility data, or pure component correlations that were determined from other hydrocarbon classes.

Obviously 1,2-benzanthracene is not presented in Fig. 3 as it experiences salting-in instead of salting-out. This further aggravates the implications discussed above.

Due to the complexity of the natural environment, it is not possible to predict PAH partitioning from a standpoint of solubility data alone. However, it is interesting to note that this study supports the observation made by Gearing and Gearing (1982) that the process of oil partitioning into the water column was very sensitive to temperature. Also of relevance is a study reported by Readman et al. (1982) involving the distribution of PAH in the Tamar Estuary. Although their sampling involved salinity ranging from 0 to approximately 30‰, they were unable to observe salting-out effects. This observation supports the statement that field data reflect the complex interaction of many variables, thus, it may not be possible to observe specific chemical effects. The data presented in this study suggests significant effects on solubility by a 30‰ change in salinity. It also indicates a relative insensitivity of PAH solubility to small changes in salinity, which would indicate that the choice of sampling sites would have a significant bearing upon the observation of a solubility-salinity correlation.

CONCLUSIONS

Literature values of aromatic hydrocarbon solubility in seawater have been limited to mono- and di-aromatics, with a single seawater solubility value (35‰) available for phenanthrene and pyrene. This study presents the solubility of six PAH at various temperatures and salinities.

The DCCLC technique is a relatively fast and precise technique for determining the solubility of PAH in aqueous solution. It may become the standard technique for examining the solubility of such compounds. Solubility results presented in this study are in agreement with values obtained by the National Bureau of Standards, and with other values reported in the literature.

All six PAH investigated exhibited decreasing distilled water solubility with decreasing temperature. With the possible exception of benzo(a)pyrene, they were also sensitive to small changes in temperature.

The compounds phenanthrene, anthracene, 2-methylantracene, 2-ethylantracene, and benzo(a)pyrene experienced salting-out in seawater, whereas 1,2-benzanthracene experienced salting-in. To my knowledge, this is the only reported occurrence of a class of compounds experiencing both salting-out and salting-in for a given salt solution. This may reflect the fact that the majority of the reported studies are for single salt solutions that do not have the complexity of seawater (Whitehouse, 1983). It may also reflect the fact that most studies use compounds which are considerably more soluble than 1,2-benzanthracene or benzo(a)pyrene.

Where salting-out was observed, fairly large changes in salinity were required to cause significant changes in solubility. Such was not the case for the compound that exhibited salting-in. However, increasing the salt concentration to greater than approximately 8‰ appeared to have insignificant additional effects upon the solubility of 1,2-benzanthracene.

Different PAH exhibit different percentages of salting-out, but the relative percentages of salting-out do not correspond to the compounds' distilled water solubility. This phenomenon is a potential source of error if we are attempting to estimate PAH partitioning processes in the marine environment from distilled water solubility.

ACKNOWLEDGEMENTS

I thank Dr. P.J. Wangersky for his assistance with this study. The research was funded by Dalhousie University and by grants to Dr. R.C. Cooke from Imperial Oil Ltd. and to Dr. P.J. Wangersky from the Natural Sciences and Engineering Research Council of Canada.

REFERENCES

- Baker, E.G., 1960. A hypothesis concerning the accumulation of sediment hydrocarbons to form crude oil. *Geochim. Cosmochim. Acta*, 19: 309-317.

- Barker, C., 1979. Organic Geochemistry In Petroleum Exploration, A.A.P.G. Continuing Education Course Note Series No. 10. American Association of Petroleum Geology, Education Department, U.S.A., 159 pp.
- Eganhouse, R.P. and Calder, J.A., 1976. The solubility of medium molecular weight aromatic hydrocarbons and the effects of hydrocarbon co-solutes and salinity. *Geochim. Cosmochim. Acta*, 40: 555-561.
- Gearing, P.J. and Gearing, J.N., 1982. Behaviour of #2 fuel oil in the water column of controlled ecosystems. *Mar. Environ. Res.*, 6: 115-132.
- Gearing, P.J., Gearing, J.N., Pruell, R.J., Wade, T.L. and Quinn, J.G., 1980. Partitioning of #2 fuel oil in controlled estuarine ecosystems. Sediments and suspended particulate matter. *Environ. Sci. Technol.*, 14: 1129-1136.
- Geyer, H., Viswanathan, R., Freitag, D. and Korte, F., 1981. Relationship between water solubility of organic chemicals and their bioaccumulation by the alga *Chlorella*. *Chemosphere*, 10(11/12): 1307-1313.
- Gordon, J.E. and Thorne, R.L., 1967. Salt effects on nonelectrolyte activity coefficients in mixed aqueous electrolyte solutions. II. artificial and natural seawaters. *Geochim. Cosmochim. Acta*, 31: 2433-2443.
- Hashimoto, Y., Tokura, K., Ozaki, K. and Strachan, W.M.J., 1982. A comparison of water solubilities by the flask and micro-column methods. *Chemosphere*, 11(10): 991-1001.
- Hites, R.A., 1976. Sources of PAH in the aquatic environment. In: Sources, Effects, and Sinks of Hydrocarbons in the Aquatic Environment. Symposium, American University, Washington, DC, pp. 326-332.
- Karickhoff, S., 1981. Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils. *Chemosphere*, 10(8): 833-846.
- Karickhoff, S., Brown, D.S. and Scott, T.A., 1979. Sorption of hydrophobic pollutants on natural sediments. *Water Res.*, 13: 241-248.
- Knap, A.H. and LeB. Williams, P.J., 1982. Experimental studies to determine the rate of petroleum hydrocarbons from refinery effluent on an estuarine system. *Environ. Sci. Technol.*, 16(1): 1-4.
- Krasnoschekova, R. and Gubergrits, M., 1976. The relationship between reactivity and hydrophobicity of polycyclic aromatic hydrocarbons. *Organic React. (U.S.S.R.)*, 13(4): 432-439.
- Mackay, D., 1982. Correlation of bioconcentration factors. *Environ. Sci. Technol.*, 16(5): 274-278.
- Mackay, D. and Shiu, W.Y., 1977. Aqueous solubility of polynuclear aromatic hydrocarbons. *J. Chem. Eng. Data*, 22(4): 399-402.
- May, W.E., 1978. The solubility behavior of polycyclic aromatic hydrocarbons in aqueous systems. In: L. Petrakis and F.T. Weiss (Editors), *Petroleum in the Marine Environment*. American Chemical Society, Washington, DC, pp. 143-192.
- May, W.E. and Wasik, S.P., 1978. Determination of the solubility behavior of some PAH in water. *Anal. Chem.*, 50: 997-1000.
- May, W.E., Chesler, S.N., Cram, S.P., Gump, B.H., Hertz, H.S., Enagonio, D.P. and Dyszel, S.M., 1975. Chromatographic analysis of hydrocarbons in marine sediments and seawater. *J. Chrom. Sci.*, 13: 535-540.
- May, W.E., Wasik, S.P. and Freeman, D.H., 1978. Determination of the aqueous solubility of PAH by a coupled column LC technique. *Anal. Chem.*, 50: 175-179.
- Means, J.C., Wood, S.G., Hassett, J.J. and Banwart, W.L., 1980. Sorption of polynuclear aromatic hydrocarbons by sediments and soils. *Environ. Sci. Technol.*, 14(12): 1524-1528.
- Meyers, P.A. and Quinn, J.G., 1973. Association of hydrocarbons and mineral particles in saline solution. *Nature*, 244: 23-24.
- Oviatt, C., Frithsen, J., Gearing, J. and Gearing, P., 1982. Low chronic additions of #2 fuel oil: chemical behavior, biological impact and recovery in a simulated estuarine environment. *Mar. Ecol. Prog. Ser.*, 9: 121-136.

- Readman, J.W., Mantoura, R.F.C., Rhead, M.M., and Brown, L., 1982. Aquatic distribution and heterotrophic degradation of polycyclic aromatic hydrocarbons (PAH) in the Tamar Estuary. *Estuarine Coastal Shelf Sci.*, 14(4): 369–389.
- Rossi, S.S. and Thomas, W.H., 1981. Solubility behavior of three aromatic hydrocarbons in distilled water and natural seawater. *Environ. Sci. Technol.*, 15(6): 715–716.
- Steen, W.C. and Karickhoff, S.W., 1981. Biosorption of hydrophobic organic pollutants by mixed microbial populations. *Chemosphere*, 10: 27–32.
- Whitehouse, B.G., 1983. The partitioning of polynuclear aromatic hydrocarbons into the dissolved phase of the aquatic environment. Ph.D. Thesis, Dalhousie University, Halifax, N.S., Canada. 153 pp.