

# A Fluorescence Method for the Measurement of the Partition Coefficients of Naphthalene, 1-Methylnaphthalene, and 1-Ethylnaphthalene in Water

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**A method is described for the determination of the partition coefficients of aromatic hydrocarbons in water by fluorescence measurements. The partition coefficients of water solutions of naphthalene, 1-methylnaphthalene, and 1-ethylnaphthalene between 8 and 31 °C were determined by this method. The solubilities of naphthalene in water over this temperature range were calculated from its partition coefficients.**

An important removal mechanism for the aromatic hydrocarbon components of oil spills dissolved in the ocean is partitioning with the air (5). This mechanism can be expressed as a partition coefficient which is the ratio of the equilibrium concentration of a component in water to its equilibrium concentration in the vapor state at a given temperature.

Literature values of the partition coefficients of aqueous aromatic hydrocarbon solutions are available only for the benzene homologues (3). If the solubilities and vapor pressures of the aromatic hydrocarbons were known, the partition coefficient can be calculated by assuming that Henry's law holds to saturation. The solubilities of some of the aromatic hydrocarbons in water have been measured by McAuliffe (11) at room temperature. Wauchope and Getzen (16) have determined the solubilities of some of the polycyclic aromatic hydrocarbons between 30 and 75 °C. Vapor pressure data for the polycyclic aromatic hydrocarbons are available for only a few compounds at ambient temperatures.

In this paper an in situ method for the measurement of partition coefficients as a function of temperature is described. The concentrations of solutions which are allowed to equilibrate with the solute vapor at controlled temperatures are measured by fluorimetry. Relative changes in the concentration prior and subsequent to thermal equilibration of the solution are related to the partition coefficient. To demonstrate the capability of the method, it was applied to aqueous solutions of naphthalene, 1-methylnaphthalene, and 1-ethylnaphthalene. These compounds are important in oil spill studies because of their relatively high water solubilities and toxic properties (2). They are harmful to marine life at the  $10^{-5}$  wt % level.

## Experimental Section

**Materials.** The purities of naphthalene, 1-methylnaphthalene, and 1-ethylnaphthalene were determined by gas chromatography to be greater than 99.9 mole %. They were obtained from Chemical Samples Co., Columbus, Ohio. The water was purified by distillation from a potassium permanganate solution and passage through a Sephadex column (7). The absolute ethanol was from Phicker Industries Inc. and used without any further purification.

**Solutions.** Saturated solutions of the naphthalene homologues were prepared by slowly stirring an excess of the solute in water for several days in sealed flasks. These solutions were allowed to stand for 1 week before use. Dissolved oxygen, which quenches the fluorescence signal, was removed by purging the solutions with argon. Subsequent manipulations of the solutions were performed in an argon atmosphere.

For the partition coefficient measurements portions of the saturated solutions were diluted and allowed to stand for 4 days.

To confirm that these dilute solutions did not contain any of the excess solute, their concentrations were monitored by absorption and fluorescence measurements during the 4 days. The diluted solutions were on the order of  $10^{-6}$  M.

For the solubility measurements, portions of the saturated solutions were diluted with equal volumes of ethanol and similarly checked. These saturated solutions had been equilibrated at controlled temperatures for several days.

**Partition Coefficient Measurements.** The partition cell used in the partition coefficient measurements is shown in Figure 1. Fluorescence measurements of the solution were made on the lower portion of the partition cell, which was a  $1 \times 1$  cm suprasil fluorescence cell. The upper, larger cylindrical portion of the partition cell made up the head space volume.

The empty partition cell was inserted into the fluorimeter and the air was purged out by argon. A measured volume of the diluted solution was quickly introduced into the partition cell through a tube with the end near the bottom of the cell. The opening was closed by a stainless steel tube fitting cap and a fluorescence measurement was taken. A  $1 \times 1 \times 5$  cm suprasil fluorescence cell was completely filled with another portion of the diluted solution and capped with a stainless steel cap. This solution was used as a reference solution and its fluorescence was measured. These initial measurements were performed at 24.0 °C and they were repeated after thermal equilibration at other controlled temperatures between 8.4 and 30.3 °C. Thermal equilibrium within the cell was assumed after rotating the cells at 4 rpm for 24 h in a water bath controlled within  $\pm 0.1$  °C. Longer submersion times did not affect the results. The cell was removed from the bath, quickly wiped dry, and placed in the fluorimeter at room temperature. It was not necessary to thermostat the cell in the fluorimeter because the rate of thermalization of the solution is slow relative to the fluorescence measuring time. This was verified by the observation that the fluorescence measurements did not drift during the measuring time. The measurements at the various temperatures were performed in random temperature order.

The partition coefficient,  $K$ , was calculated from the expression

$$K = \frac{C(T)C'(T)}{C_i/C' - C(T)/C'(T)} (V_g/V_e) \quad (1)$$

where  $C(T)$  is the concentration of the solution in the partition cell at the equilibrium temperature,  $T$ , and  $C'(T)$  is the concentration of the reference solution. The ratio  $C_i/C'$  is the initial concentration of the partition cell solution immediately following its introduction into the partition cell divided by the reference solution concentration at 24 °C. The ratio of the head space to solution volume in the partition cell is  $V_g/V_e$ . The variation of the solution volume over the whole temperature range of 20° is less than 1% so that  $V_g/V_e$  is treated as a constant. The dimension of the partition cell was chosen so that  $V_g/V_e$  was large enough to reduce  $C(T)$  by more than 60% of  $C_i$ . Cells of three different dimensions (cell volume:cell surface area = 1.24, 0.70, and 0.49 cm) were used at 24 °C to compare surface adsorption effects on the coefficient measurements. At the other temperatures from 8.4 to 30.3 °C, the cell with the largest ratio was used.

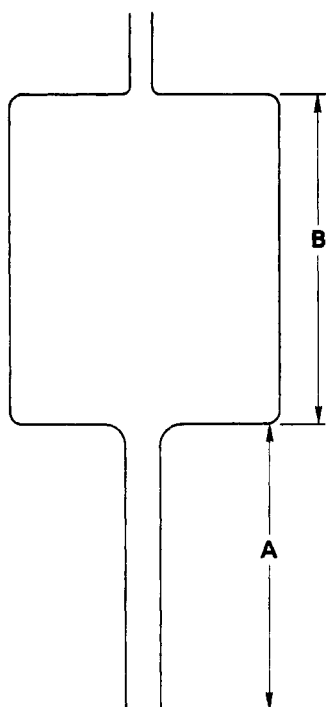


Figure 1. Partition coefficient fluorescence cell: A is a square suprasil fluorescence cell and B is a cylindrical Pyrex vessel.

Table I. Experimental Values of the Partition Coefficients of the Naphthalene Homologues in Water

Naphthalene		1-Methylnaphthalene		1-Ethyl-naphthalene	
$t/^{\circ}\text{C}$	$K$	$t/^{\circ}\text{C}$	$K$	$t/^{\circ}\text{C}$	$K$
21.9	$67 \pm 4$	25.3	$71 \pm 6$	23.1	$60 \pm 4$
25.3	$53 \pm 3$	16.6	$110 \pm 10$	21.9	$67 \pm 5$
16.6	$90 \pm 6$	8.4	$166 \pm 13$	13.2	$99 \pm 8$
8.4	$146 \pm 10$	30.3	$51 \pm 6$	8.4	$134 \pm 9$
10.7	$124 \pm 11$	23.1	$73 \pm 6$	25.3	$53 \pm 3$
18.5	$80 \pm 5$			27.5	$48 \pm 3$
30.3	$39 \pm 2$			30.3	$42 \pm 3$
23.1	$60 \pm 5$				

The spectrofluorimeter used in this investigation employs photon counting and is described elsewhere (13, 14). At Napierian absorbances of  $\leq 0.05$ , the fluorescence counts,  $F$ , are proportional to the concentration,  $C$ , as shown,

$$F = AC + B \quad (2)$$

where  $A$  is constant for a solution at fixed UV excitation and fluorescence wavelengths.  $B$  is a background factor due to scattering of the excitation light from the cell and is invariant over the range 300–400 nm. For each concentration measurement, a value for  $B$  was measured at 300 nm, where the solutions do not fluoresce. The fluorescences were excited by 265-nm light and measured at 335 nm. Since the solutions were deaerated, unknown oxygen quenching of the fluorescence signal was eliminated. Furthermore, any quantum yield–temperature variation in  $A$  was taken into account by comparing the fluorescence of the cell with that of the reference solution.

**Solubility Determinations by UV Absorption.** The solubilities of the naphthalene homologues were determined from their absorptivities and Beer's law. Since the concentrations of these compounds in water are too low to determine their extinction coefficients accurately, the absorption measurements were performed on measured volumes of the saturated solutions diluted with equal volumes of ethanol. The extinction coefficients of these 1:1 water–ethanol solutions were determined in the following manner. The absorptivities of the naphthalene

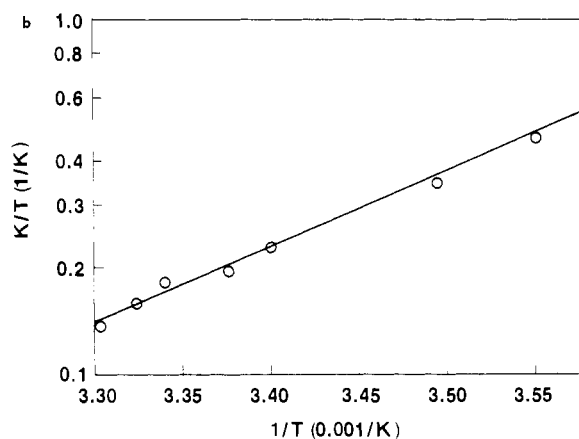
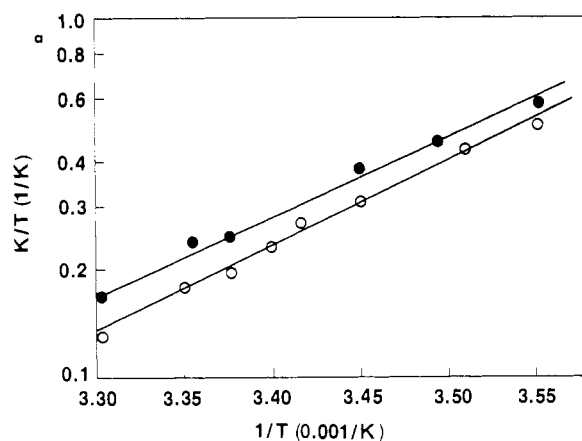


Figure 2. (a) Semilogarithmic plots of  $K/T$  vs.  $1/T$  for naphthalene (O) and 1-methylnaphthalene (●) in water. (b) A semilogarithmic plot of  $K/T$  vs.  $1/T$  for 1-ethylnaphthalene in water.

Table II. Calculated Values<sup>a</sup> of the Partition Coefficients of the Naphthalene Homologues in Water

$t/^{\circ}\text{C}$	Naphthalene	Methylnaphthalene	Ethyl-naphthalene
30.0	41	54	43
28.0	51	65	47
26.0	51	66	52
24.0	57	73	57
22.0	64	81	63
20.0	72	89	70
18.0	81	100	78
16.0	91	111	87
14.0	103	124	97
12.0	117	138	108
10.0	132	155	121
8.0	150	173	135
$\Delta H/R$	$-(5.35 \pm 0.06) \times 10^3$	$-(4.83 \pm 0.16) \times 10^3$	$-(4.76 \pm 0.07) \times 10^3$
$a$	$19.65 \pm 0.02$	$17.67 \pm 0.05$	$17.64 \pm 0.02$

<sup>a</sup> The equation used was  $\ln K/T = +\Delta H/RT + a$ , where the constants  $\Delta H/R$  and  $a$  were determined from least-squares fits of the experimental  $K$  and  $t + 273.15$  values of Table I.

homologues in ethanol were measured, and from literature values of their molar absorptivities in ethanol,  $5.13 \times 10^3 \text{ L cm}^{-1} \text{ mol}^{-1}$  for naphthalene at 268 nm (4) and for 1-methylnaphthalene at 271 nm (8) and  $5.0 \times 10^3 \text{ L cm}^{-1} \text{ mol}^{-1}$  for 1-ethyl-naphthalene at 271 nm (12), their concentrations were determined by Beer's law. The ethanol solution concentrations were reduced by half upon diluting the solutions with equal volumes of water. From the measured absorptivities of these 1:1 ethanol–water solutions, the extinction coefficients were calculated

Table III. Solubilities of the Naphthalene Homologues in Water

t/°C	Naphthalene (10 <sup>-4</sup> mol L <sup>-1</sup> ) absorption		Lit. values <sup>b</sup>	1-Methylnaphthalene (10 <sup>-4</sup> mol L <sup>-1</sup> ) absorption measurements	1-Ethyl-naphthalene (10 <sup>-5</sup> mol L <sup>-1</sup> ) absorption measurements
	Calcd from K <sup>a</sup>	measurements			
30	2.70				
28	2.66				
26	2.39		2.68		
25	2.31	2.34 ± 0.02		2.1 ± 0.1	6.4 ± 0.1
24	2.25				
22	2.12				
20	1.99			2.0 ± 0.1	6.4 ± 0.1
19	1.92		2.10		
18	1.87	1.90 ± 0.02			
16	1.76		1.84		
15	1.73		1.76		
14	1.64			2.0 ± 0.1	5.2 ± 0.1
12	1.55	1.57 ± 0.02			
10	1.43		1.45	1.6 ± 0.1	5.2 ± 0.2

<sup>a</sup> Calculated from  $K$  and eq 5. <sup>b</sup> Reference 14.

and found to be within experimental error of their values in pure ethanol.

### Results and Discussion

The partition coefficient can be expressed in terms of the solute vapor pressure as shown,

$$K = C^{\circ}RT/P^{\circ} \quad (3)$$

where the concentration,  $C^{\circ}$ , is the solubility in mol L<sup>-1</sup>,  $R$  is the gas constant, and  $P^{\circ}$  is the solute saturate vapor pressure. From thermodynamic theory, the partition coefficient has the following variation with temperature (10),

$$\ln(K/T) = \frac{\Delta H_e}{RT} + a \quad (4)$$

where  $\Delta H_e$  is the differential heat of evaporation of the solute from the solvent and  $a$  is an integration constant.

The partition coefficients of the naphthalene homologues calculated from eq 1 are given in Table I. Plots of the ratios,  $K/T$ , vs.  $1/T$  are presented in Figure 2 for the three naphthalene homologues. The straight lines in Figure 2 are fits of the logarithm of  $K/T$  to linear equations of the form of eq 4. The standard deviations in the slopes,  $\Delta H/R$ , and intercepts,  $a$ , are about 1.0 and 0.1%, respectively, except for the 1-methylnaphthalene values which are three times larger. The smoothed partition coefficients of the naphthalene homologues calculated from eq 4 are presented in Table II at 2 °C intervals from 8 to 30 °C.

The partition coefficients determined in the partition cells with the smaller ratios of volume to surface area agreed within experimental error with the values given in Table II. Surface adsorption effects are thus within the experimental error of the method.

The solubilities of naphthalene in water calculated from eq 3, using the  $K$  values in Table II and known values of  $P^{\circ}$ , are given in Table III. The vapor pressure of naphthalene was calculated from the expression,

$$\log P^{\circ}, \text{ mmHg} = 10.562 - (3476/T) \quad (5)$$

reported by Karyakin (9) for the temperature range 10–50 °C. The solubilities at 12, 18, and 24 °C were also measured by the UV absorption method. Bohon and Claussen's values for the naphthalene solubilities are also presented in Table III (7).

The solubilities of 1-methylnaphthalene and 1-ethylnaphthalene in water cannot be determined from their partition coefficients since their vapor pressures have not been measured in this temperature range. Therefore, only the solubilities of these compounds determined by the UV absorption method are presented in Table III. The absorption measurements exhibit an

almost constant solubility for 1-methylnaphthalene and 1-ethylnaphthalene between 10 and 25 °C. This behavior is similar to that of other aromatic liquid solutes (e.g., benzene, toluene, and ethylbenzene) in water (3).

The values of the partition coefficient for ethylnaphthalene given in Table II appear to be low since there is a tendency for  $K$  to increase with molecular weight for a homologous series in nonaqueous systems. This apparent inconsistency in the  $K$ , values for 1-ethylnaphthalene may be better understood from the lower solubility of 1-ethylnaphthalene given in Table III. The following equation was derived from eq 3:

$$\frac{K_{\text{men}}C^{\circ}_{\text{etn}}}{C^{\circ}_{\text{men}}K_{\text{etn}}} = \frac{P^{\circ}_{\text{etn}}}{P^{\circ}_{\text{men}}} \quad (6)$$

where the subscripts men and etn refer to 1-methylnaphthalene and 1-ethylnaphthalene, respectively. Substituting  $K$  and  $C^{\circ}$  values in eq 6 yields a value of 0.38 for  $P^{\circ}_{\text{etn}}/P^{\circ}_{\text{men}}$  at 25 °C. An estimate of this ratio at 25 °C may be obtained from extrapolation of the Antoine equations for 1-methylnaphthalene and 1-ethylnaphthalene from 120 to 25 °C (17). The extrapolated value of  $P^{\circ}_{\text{etn}}/P^{\circ}_{\text{men}}$ , 0.37, is in good agreement with 0.38 obtained from eq 6. The solubilities of hydrocarbons in water tend to be dependent on some parameter based on the molecular size of the hydrocarbon such as molar volume (15) or solute surface area (6), whereas there seems to be no direct correlation between  $K$  and solute molecular size.

A value for the enthalpy of solution,  $\Delta H_s$ , was calculated for naphthalene from the slope,  $\Delta H_e/R$ , in eq 4 since

$$\Delta H_e = \Delta H_s - \Delta H_{\text{vap}} \quad (7)$$

where  $\Delta H_{\text{vap}}$  is the enthalpy of vaporization. From  $\Delta H_{\text{vap}}$  of 15.9 kcal mol<sup>-1</sup> for naphthalene (13), an enthalpy of solution of 4.3 kcal mol<sup>-1</sup> was calculated for naphthalene in water. The enthalpies of solution of 1-methylnaphthalene and 1-ethylnaphthalene are nearly zero and the  $\Delta H_e$  values in eq 4 are their enthalpies of vaporization in this short temperature range. The  $\Delta H_{\text{vap}}$  values are 9.7 ± 0.3 kcal mol<sup>-1</sup> for 1-methylnaphthalene and 9.5 ± 0.1 kcal mol<sup>-1</sup> for 1-ethylnaphthalene.

### Conclusion

The fluorescence method for determining partition coefficients of aromatic hydrocarbons in water appears to be a good method based on the results of this investigation. The naphthalene solubilities calculated from the measured partition coefficients are close to those values determined by UV absorption measurements. Relative partition coefficients values of the 1-methylnaphthalene and 1-ethylnaphthalene and their relative solubilities yield a vapor pressure ratio for the two compounds

which agrees with that estimated from their Antoine equations.

Spectrofluorimetry exhibits the high sensitivity and precision needed for determining the partition coefficients of other aromatic hydrocarbons and even fluorescing pesticides in water. The measurements are performed without removal, handling, or destruction of samples of the solution as is done with gas chromatography (3). The application of this method to determination of the partition coefficients of higher polycyclic aromatic hydrocarbons in water is now in progress.

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## Determination of Temperature Dependence of Solubilities of Polycyclic Aromatic Hydrocarbons in Aqueous Solutions by a Fluorescence Method

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**The fluorescence intensities of saturated aqueous polycyclic aromatic hydrocarbon (PAH) solutions equilibrated at temperatures between 281 and 303 K are proportional to the PAH concentration. The fluorescence measurements are put on an absolute solubility scale by UV absorption measurements at 298.2 K. This method was applied to the determination of the solubilities of naphthalene, 1-methylnaphthalene, 1-ethylnaphthalene, phenanthrene, anthracene, pyrene, and benz[e]pyrene in water and in 0.5 mol L<sup>-1</sup> sodium chloride solution. Ethalpies of solution of the PAH were calculated.**

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Data on the temperature dependence of the aqueous solubilities of the polycyclic aromatic hydrocarbons (PAH) are considerably less than the corresponding data on naphthalene and the benzene derivatives. Bohon and Claussen (1) measured the solubilities of naphthalene and several benzene homologues in water from 0 to 43 °C. Decreases in the naphthalene solubility in water due to the presence of various electrolytes ("salting-out" effect) were investigated by Paul (16) at 25 and 0.1 °C. A temperature dependence of the "salting-out" effect was observed by Morrison (14) for phenol, phenylacetic acid, and benzoic acid in salt solutions. More recently, Wasik and Brown (3) determined the solubilities of benzene, ethylbenzene, and toluene in water and in 0.5 mol L<sup>-1</sup> NaCl solutions from 8 to 40 °C. Wauchope and Getzen (21) have extended these data to larger PAH molecules ranging in size from naphthalene to pyrene. They determined the PAH solubilities in water from 25 to 75 °C.

Previous investigations of the solubility dependence on temperature have been based on extraction and analysis by UV spectrophotometry (1, 16, 21) or by gas chromatography (3). This paper describes a spectrofluorimetric method for the

measurement of the temperature dependence of the solubilities of PAH in aqueous solutions. To demonstrate the capability of the method, it was applied to saturated solutions in water and in 0.5 mol L<sup>-1</sup> NaCl solution of naphthalene, 1-methylnaphthalene, 1-ethylnaphthalene, phenanthrene, anthracene, pyrene, and benz[e]pyrene. These PAH range in size from two to five fused aromatic rings.

#### Experimental Section

**Materials.** The purities of naphthalene, 1-methylnaphthalene, and 1-ethylnaphthalene were determined by gas chromatography and found to be greater than 99.9%. The purities of the phenanthrene, anthracene, pyrene, and benz[e]pyrene crystals were greater than 99 mole %. Measurements of these crystals dissolved in ethanol showed no fluorescing impurities above 0.001 mole %.

The water was distilled over a potassium permanganate-sodium hydroxide solution and passed through a Sephadex column (9). The absolute ethanol, cyclohexane, and sodium chloride were reagent grade.

**Solubility Measurements by Spectrofluorimetry.** Standard 1 × 1 cm quartz fluorescence cells were modified by the addition of a quartz tube to the top of each cell. Each cell could then be sealed by a stainless steel Swagelok cap. The sealed cells contained 5 mL of the aqueous solution and an excess of the PAH. The cells were rotated at 20 rpm for at least 72 h in a water bath at 8.5 ± 0.1 °C. Each cell was removed from the bath, quickly wiped dry, and placed in the fluorimeter. Because the rate of thermalization of the solution was observed to be slow relative to the fluorescence measuring time, it was not necessary to thermostat the cell in the fluorimeter. Upon completion of all the solubility measurements, the water bath temperature was raised several centigrade degrees to the next temperature point