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Molecular Diffusivity of Polycyclic Aromatic Hydrocarbons in Aqueous Solution

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Measured molecular diffusion coefficients of several polycyclic aromatic hydrocarbons (PAHs) in aqueous solution indicate that available techniques largely overestimate the diffusivities of compounds with three or more aromatic rings. The molecular diffusivities of benzene, toluene, naphthalene, phenanthrene, anthracene, benz[*a*]anthracene, and pyrene were measured in water at temperatures ranging from 4 to 40 °C using a modified open tube elution method. An experiment was conducted to assess the effects and interactions of solute concentration, temperature, and salinity on PAH aqueous molecular diffusivity. Aqueous diffusion coefficients increased with temperature and decreased with molar volume of the diffusing species. No significant effects of solute concentration (12.5–50% saturation) and salinity (0–35 ppt) were observed. The experimental data have been used to formulate a new predictive equation for estimation of aqueous molecular diffusivity of aromatic chemicals as a function of temperature.

Introduction

Knowledge of molecular diffusion is fundamental for describing processes that control the environmental fate and distribution of contaminants such as polycyclic aromatic hydrocarbons (PAHs). Aqueous molecular diffusivities are essential for the accurate determination of chemical fluxes across the air–water interface; diffusion coefficients are also important parameters for describing the dispersion of contaminants in interstitial waters of sediments, aquifers, and unsaturated soils. In environmental systems, factors that influence the molecular diffusivity become important due to a wide variety of conditions encountered. Existing experimental data and subsequent predictive equations (*1–7*) show that the diffusivity of a compound (D) is strongly dependent upon the molar volume (V) of the diffusing species as well as the temperature (T) and viscosity (μ) of the medium through which the compound is diffusing. Measured values of molecular diffusion coefficients for organic contaminants, such as PAHs, in water are virtually nonexistent. In order to model chemical fluxes for PAHs, measured diffusivity data and accurate predictive equations must be established.

This study was undertaken to determine the diffusion coefficients of PAHs in water over the temperature and salinity conditions encountered in the marine environment, and to evaluate equations for predicting the aqueous molecular diffusivities of PAHs. Molecular diffusion coefficients of selected PAHs were measured in water at temperatures ranging from 4 to 40 °C. The PAHs studied were selected to permit an evaluation of diffusivity over an approximately 3-fold range of solute molar volume. The effects and interactions of temperature, salinity, and the concentration of solute on molecular diffusion were determined using phenanthrene as the test compound.

In this paper we present diffusivity data for selected organic solutes (acetone, benzene, toluene, and PAHs) in water, methanol, and 60:40 methanol/water (v/v), at temperatures ranging from 4 to 40 °C. Predictive equations for solute molecular diffusivity in water are evaluated, and a new equation is developed to describe the changes in PAH diffusion coefficients as related to the molar volume of the solute and the viscosity of the aqueous solution, which is a function of temperature and salinity.

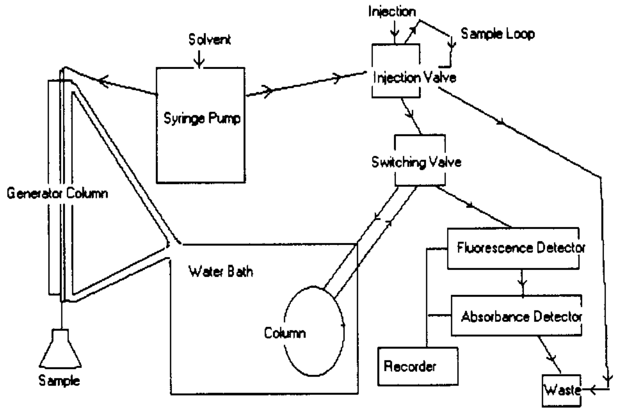

Figure 1. Schematic diagram of the system designed for measuring aqueous molecular diffusion coefficients.

Experimental Section

Chemicals. The chemicals used in this study had the following purities as reported by their manufacturers: acetone (99.78%), benzene (99.96%), toluene (99%), methanol (99.99%), anthracene (98%), phenanthrene (98%), naphthalene (99%), benz[*a*]anthracene (99%), pyrene (99%). Water used in the experiments was pretreated by distillation, passed through a Milli-Q water purification system (Millipore Inc.), and subsequently vacuum filtered through a 0.2-μm metricel filter prior to use. Saline solutions, 35 ppt, were made with Instant Ocean (Aquarium Systems) sea salt on a weight per unit volume basis, and the salinity was verified with a refractometer.

Apparatus. A modified version of the open tube elution method (*8*) was used for determining molecular diffusivities. The apparatus (Figure 1) used for measuring liquid diffusion coefficients consists of a high-precision syringe pump (Isco LC-5000), sample injection valve (Rheodyne 7010), 100-ft.-long × 1/16-in.-o.d. × 0.03-in.-i.d. stainless steel tube (Supelco) coiled into 1-ft. diameter UV (Isco 228 with type 6 optical unit) and fluorescence detectors (Isco FL-2), a chart recorder, and a constant-temperature water bath/circulator (Forma Scientific Model 2067).

Preparation of Saturated Solutions. Saturated aqueous solutions of PAHs were produced using a generator column

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Table 1. Molecular Diffusion Coefficients (D) for Selected Organic Chemicals in Water, Methanol, and Methanol/Water Mixtures

solute	concn (% saturation)[a]	solvent	t/°C	$10^6D/(\mathrm{cm^2\,s^{-1}})$[c]	n[d]	10^5D(lit.)/($\mathrm{cm^2\,s^{-1}}$)	lit. ref	$100\sigma(D)/D$[e]	$100\delta(D)/D$[f]
naphthalene	15.5^b	methanol	40	2.13 ± 0.11	11			5.0	
	15.5^b		25	1.75 ± 0.08	10	1.83	Knox (*2*)	4.7	4.2
	15.5^b		10	1.67 ± 0.08	8			4.5	
	4.92^b		25	1.72 ± 0.16	11			9.4	
benzene	1730^b	methanol	40	2.78 ± 0.20	11			7.3	
	1730^b		25	2.18 ± 0.06	11			2.8	
	1730^b		10	1.74 ± 0.08	11			4.3	
benzene	1766^b	60:40 methanol/water	40	1.19 ± 0.04	11			3.2	
	1766^b		25	0.867 ± 0.050	9			5.8	
	1766^b		10	0.574 ± 0.040	10			7.0	
acetone	5300^b	60:40 methanol/water	40	1.41 ± 0.05	7			3.7	
	5300^b		25	1.04 ± 0.02	9	1.0	Knox (*2*)	2.1	3.6
	5300^b		10	0.754 ± 0.020	8			2.6	
benzene	50	water	40	1.61 ± 0.06	9	1.60	Bonoli (*1*)	3.9	0.7
	50		32	1.30 ± 0.05	15			3.8	
	50		25	1.09 ± 0.01	6	1.09	Ratcliff (*3*)	0.7	0.3
	50		18	0.951 ± 0.016	10			1.7	
	50		10	0.764 ± 0.008	11	0.75	Bonoli (*1*)	1.0	1.8
naphthalene	50	water	40	1.06 ± 0.08	9			7.2	
	50		25	0.749 ± 0.022	13			2.9	
	50		10	0.483 ± 0.013	10			2.6	
toluene	30	water	40	1.22 ± 0.06	9	1.34	Bonoli (*1*)	5.1	9.0
	50		25	0.915 ± 0.016	11			1.7	
	50		10	0.621 ± 0.020	8	0.62	Bonoli (*1*)	3.1	0.2
phenanthrene	50	water	40	0.514 ± 0.033	10			6.3	
	12.5		40	0.495 ± 0.064	8			3.0	
	50		4	0.378 ± 0.028	9			7.4	
	12.5		4	0.387 ± 0.026	8			6.8	
	50		25	0.437 ± 0.037	11			8.3	
phenanthrene	50	35 ppt salinity water	40	0.576 ± 0.039	10			6.7	
	12.5		40	0.557 ± 0.129	9			23.0	
	50		4	0.318 ± 0.077	7			24.0	
	12.5		4	0.319 ± 0.037	7			11.6	
anthracene	50	water	40	0.567 ± 0.045	5			8.0	
	50		25	0.418 ± 0.032	11			7.7	
	50		4	0.303 ± 0.023	9			7.5	
pyrene	50	water	40	0.490 ± 0.089	11			18.1	
benz[*a*]anthracene	50	water	40	0.619 ± 0.009	10			1.4	
	50		25	0.335 ± 0.037	9			11.1	
	50		4	0.198 ± 0.015	10			7.5	

[a] Concentration (% saturation) except where indicated. [b] Concentration (mg/L). [c] Mean ± standard deviation. [d] Number of experimental measurements. [e] Coefficient of variation; relative standard deviation: (standard deviation/mean) × 100. [f] δD is the absolute deviation between measured and literature values: (measured − lit. value)/measured × 100.

(*9*). Naphthalene, pyrene, and phenanthrene crystals were packed directly in columns; benz[*a*]anthracene and anthracene were coated on Chromosorb W (Chemical Research Supplies), 1% and 2% w/w, respectively. Saturated aqueous solutions of benzene and toluene were generated by placing approximately 100 mL of organic solvent and 250 mL of water in a 500-mL flask, shaking vigorously, and allowing the solution to equilibrate overnight at room temperature. Saturated solutions were drawn from the aqueous layer as needed using a syringe. Aqueous solutions for all compounds were diluted to 50% saturation for determination of diffusion coefficients. The diffusivity of phenanthrene was also measured using 12.5% saturated aqueous solutions. Solutions of acetone, benzene, and naphthalene in methanol and 60:40 methanol/water (v/v) were made on a weight per volume basis as indicated in Table 1.

Analysis. Each sample solution was loaded into a 200-μL sample loop and injected into the system as a brief pulse. The retention time and distribution of the solute were monitored by either UV absorbance at 254 nm (acetone, benzene, toluene, and naphthalene) or fluorescence (phenanthrene, anthracene, 1,2-benzanthracene, and pyrene) detection with 295-305-nm excitation and 430-470-nm emission filters. The flow rate, Q, was measured as the time in seconds to fill a 10-mL volumetric flask.

Molecular Diffusivity Calculations. Measurements of molecular diffusion coefficients via the open tube elution method is based upon the hydrodynamic continuity equation in cylindrical coordinates for fluids in laminar parabolic (poiseuille) flow (*8*). Ouano (*8*) has shown that the diffusion coefficient is approximated by

$$D = 0.212\,(Q/L)(V_t/W)^2 \tag{1}$$

in relation to a retention volume distribution if one of the following conditions, $Q/DL \ll 1$ or $Q/DL \rightarrow 0$, is met, where V_t and W are the retention volume and volume distribution of the eluted peak, respectively, Q is the volumetric flow rate, and L is the length of the diffusion tube. Using a retention time distribution scale, eq 1 becomes

$$D = 0.212\,(Q/L)(t_r/W_t)^2 \tag{2}$$

where t_r and W_t are the retention time and peak width at the baseline, respectively. Subsequently, a series of measurements of t_r and W_t for different values of Q are used to obtain the limiting diffusion coefficient from a plot of D vs Q/DL by extrapolating to zero as illustrated in Figure 2.

In this work, the retention time of the solute peak was calculated from the recorder output as the elapsed time between injection and maximum peak height. The peak width at half-height (W_h) was measured and related to the base

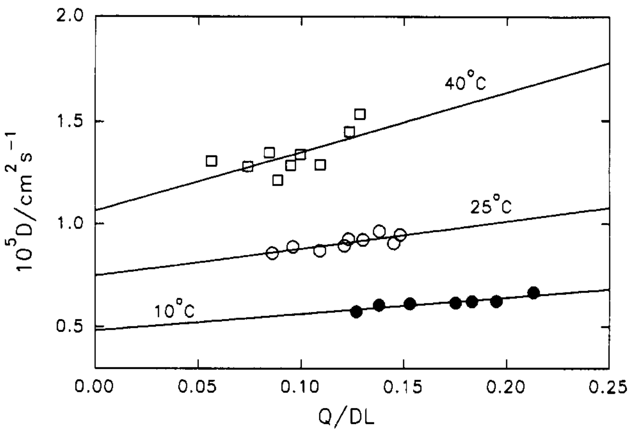

Figure 2. Diffusivity of naphthalene in water. Extrapolation of Q/DL to zero to obtain the limiting diffusion coefficient.

width by

$$W_t = -4W_h/(8 \ln h)^{1/2} \qquad (3)$$

where h is the fractional height of the peak (*10*). Each of the reported experimental diffusivity values is the intercept through the ordinate axis of a regression plot of D vs Q/DL for 6–15 diffusivity measurements (av $n = 9$) at different flow rates between 7 and 24 mL/h.

Results and Discussion

Table 1 lists diffusivities for selected organic chemicals in various solvents at temperatures ranging from 4 to 40 °C. Standard errors of the extrapolated diffusivity values varied from 0.7% to 24% with a mean absolute error of 6.4%. The measured diffusivities are also compared in Table 1 to experimental D values determined in previous studies. Agreement among the values of Knox (*2*), Bonoli (*1*), Ratcliff (*3*), and those reported here ranges from 0.3% to 9% with a mean absolute error of 2.8%.

The open tube elution method described in this paper for measuring liquid-phase diffusion coefficients was independent of solute concentration. This was verified by determining the diffusivity of naphthalene in methanol at two concentrations differing by a factor of 3, and measuring phenanthrene aqueous diffusivity at 50% and 12.5% saturation. Differences between the measured naphthalene diffusivities in methanol and phenanthrene diffusivities in water were not significant at the 0.01 level of significance.

The effect of salinity on the phenanthrene aqueous diffusivity was also not significant ($P = 0.05$). However, the much larger experimental error, up to 24%, of phenanthrene diffusivity measurements in 35 ppt salinity Instant Ocean solutions (Table 1) may conceal the effect of salinity on D. The change in viscosity over the range of 0–35 ppt salinity is expected to be 6–8% (*11*), much lower than the experimental error encountered with diffusivity measurements in saline solutions. Large experimental errors for diffusivity measurements in saline solutions are likely associated with observed corrosion which acted to rapidly degrade the stainless steel columns.

Aqueous molecular diffusivities of the selected organic chemicals were found to decrease with temperature (Table 1, Figure 2). The effect of temperature on molecular diffusivity has been previously correlated to the viscosity of the solvent (*4–7*). The log of the measured diffusivity for all compounds investigated in this study was found to vary linearly with the log of the solvent viscosity; linear regression coefficients ranged from 0.984 for phenanthrene to 1.0 for naphthalene and toluene. The resultant regression lines for all compounds had a mean slope of 0.905 ± 0.316. While the standard deviation for the mean slope is large, no relationship was found between the individual slopes and properties of the compounds studied. The average slope of the plots of log D versus log μ is used to derive coefficients for estimating D, as indicated below.

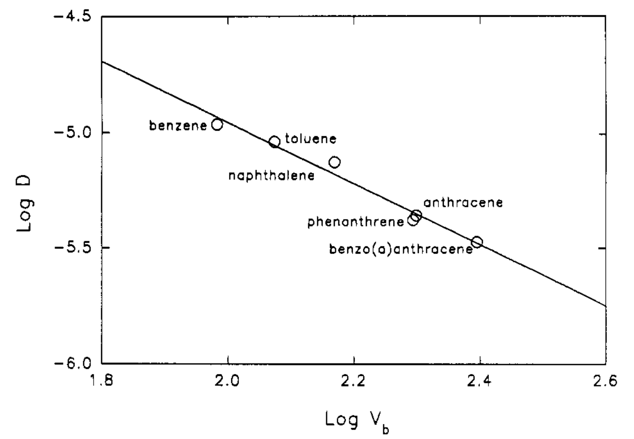

Figure 3. Relationship between molar volume and aromatic organic chemical aqueous diffusivity at 25 °C.

Aqueous molecular diffusivities of the selected organic chemicals also decreased with molecular size. The log of the measured diffusion coefficient was found to vary linearly with the log of the molar volume (V) for all compounds studied (Figure 3). Plots of log D versus log V for all compounds investigated resulted in linear regression coefficients ranging from 0.837 at 4 °C to 0.934 at 40 °C.

Several equations for predicting molecular diffusion coefficients have been cited in the literature (*4–7*). The recommended equation for predicting molecular diffusivity in aqueous solutions is the Hayduk–Laudie equation (*12*). The Hayduk–Laudie equation is a revised form of the Othmer and Thakar equation based on a larger compiled data base (*4*). Previously, Bonoli and Witherspoon (*1*) had measured the diffusivity of aromatic and cycloparaffin hydrocarbons in water and recommended the use of the Wilke–Chang equation for predicting molecular diffusivities of these compounds. Measured diffusion coefficients for compounds in this study were compared to predicted values from the Hayduk–Laudie, Othmer–Thakar, Wilke–Chang, and Scheibel predictive equations (Table 2). Mean absolute errors for predicting aromatic hydrocarbon aqueous diffusivities ranged from 30% to 37% (Table 2). However, predicted diffusivities for PAHs in water deviate exponentially from measured values with increasing molecular size (Figure 4). Therefore, new constants for the Othmer–Thakar equation are proposed to more accurately predict the molecular diffusivities of PAHs in aqueous solution.

The terms for revised equation are the slope, the inverse logarithm of the intercept of a plot of log D versus log V, and the average slope of all regression plots of log D versus log μ for the compounds investigated (*4*). The revised equation from this study

$$D = 4.864 \times 10^{-3}/(\mu^{0.905} V^{1.32}) \qquad (4)$$

resulted in a reduction of the mean absolute error between predicted and measured molecular diffusivities from 30.4% to 14.7% for the compounds studied (Table 2). The error resulting from the modified predictive equation is similar to the accuracy and precision of the measured aqueous diffusivities (Table 1).

The exponential deviation of PAH aqueous diffusivities from predicted values is perhaps due to hydrophobic interactions in dilute aqueous solutions (*13–15*). Assuming the larger three- and four-ring PAHs (phenanthrene, anthracene,

Table 2. Predicted Diffusivities (D) of Selected Aromatic Chemicals in Aqueous Solution and Resultant Errors for Various Aqueous Diffusivity Estimation Techniques

		10^5D/	10^5D(calcd)/	$100\delta(D)/D$[a]				
compound	t/°C	(cm² s⁻¹)	(cm² s⁻¹)	this work	Hayduk–Laudie[b]	Othmer–Thakar[c]	Wilke–Chang[d]	Scheibel[e]
benzene	10	0.764	0.915	19.8	18.8	11.7	7.1	18.8
	18	0.951	1.11	16.9	11.8	10.1	4.9	16.8
	25	1.09	1.29	19.1	2.4	5.4	0.8	11.9
	32	1.30	1.49	14.4	1.1	6.3	0.6	12.1
	40	1.61	1.71	6.4	1.7	10.2	2.6	14.8
toluene	10	0.621	0.695	11.8	11.8	4.2	0.7	11.5
	25	0.915	0.983	7.4	2.5	0.8	5.7	7.1
	40	1.22	1.30	6.5	18.5	4.4	13.3	0.4
naphthalene	10	0.483	0.518	7.2	0.5	7.8	13.3	0.7
	25	0.749	0.733	2.1	10.0	6.2	13.1	0.5
	40	1.06	0.971	8.7	19.6	5.2	14.1	1.4
anthracene	4	0.303	0.301	0.7	4.0	18.6	24.3	12.8
	25	0.418	0.501	20.0	66.4	60.1	70.6	54.9
	40	0.567	0.664	17.0	89.2	65.8	79.9	63.3
phenanthrene	4	0.387	0.296	23.5	19.1	7.8	3.3	12.2
	4	0.378	0.296	21.8	17.3	5.8	1.3	10.3
	25	0.437	0.493	12.8	57.8	51.8	61.8	47.0
	40	0.495	0.653	32.0	115.0	88.8	105.0	86.1
	40	0.514	0.653	27.0	108.0	81.6	97.0	79.0
benz[*a*] anthracene	4	0.198	0.221	11.6	38.7	57.7	65.3	53.4
	25	0.335	0.369	9.9	80.7	73.4	84.8	71.6
	40	0.619	0.488	21.1	51.2	32.2	43.5	33.2
pyrene	40	0.490	0.595	21.3	108.0	82.5	98.0	81.1
av abs error				14.7	37.2	30.4	35.3	30.5

[a] δ_D is the absolute error between experimental and predicted values. [b] Reference 4. [c] Reference 5. [d] Reference 7. [e] Reference 6.

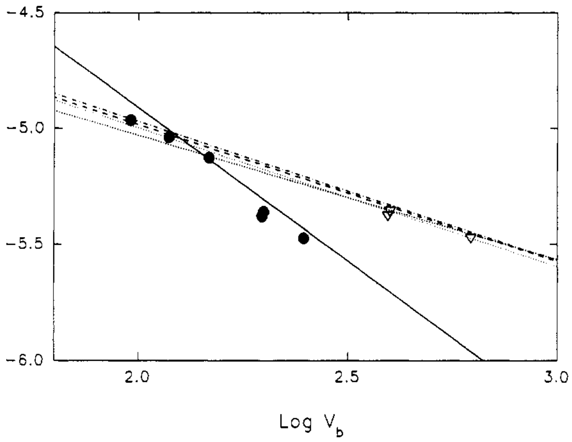

Figure 4. Experimental aqueous diffusivities (●). Predicted values: this work (—), Hayduk–Laudie equation (– – –), Othmer-Thakar equation (···), Wilke-Chang equation (– · –), and Scheibel equation (- - -). Proposed D values for phenanthrene, anthracene, and benz[*a*]anthracene as dimers and trimers.

and benz[*a*]anthracene) form dimers or trimers in aqueous solution, their effective molar volumes will increase. Figure 4 illustrates that, assuming a molar volume of 2 times the calculated value for phenanthrene and anthracene, and 2.5 times the molar volume of benz[*a*]anthracene, the predicted diffusivities resulting from the Hayduk–Laudie equation lie close to the predicted values. Consequently, some phenanthrene and anthracene possibly exist in aqueous solution as dimers, and benz[*a*]anthracene possibly exists as a mixture of dimers and trimers at the concentrations used in this study.

Summary and Conclusions

Molecular diffusion coefficients for benzene, toluene, and selected PAHs in aqueous solutions at temperatures ranging from 4 to 40 °C have been measured using an open tube elution method, and the experimentally determined diffusivities are in good agreement with literature values. Aqueous molecular diffusivities for all compounds studied decreased with solvent viscosity and molecular size. The results illustrate that large differences in diffusivity occur between compounds and with changing environmental conditions (i.e., temperature); however, no measurable effect of salinity on D was observed. Using traditional equations (*4–6*), measured aqueous diffusivities deviate exponentially from predicted D values with increasing molar volume. Consequently, a revised equation for estimating PAH diffusivity in water has been developed; additional independent measurements of aqueous molecular diffusivities for high molecular weight organic chemicals will be required to validate the accuracy of this equation.

Glossary

D = molecular diffusion coefficient
V = molar volume
T = temperature
μ = viscosity
Q = volumetric flow rate
L = column length
V_t = retention volume of the peak
W = retention volume distribution of the peak
t_p = retention time of the peak
W_t = peak width at the baseline
W_h = peak width at fractional height h
h = fractional height of the peak

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