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Molecular Diffusivity of Polycyclic Aromatic Hydrocarbons in Air

Kurt E. Gustafson* **and Rebecca M. Dickhut**

Department of Physical Sciences, School of Marine Science, The College of William and Mary, Virginia Institute of Marine Science,[†] Gloucester Point, Virginia 23062

The molecular diffusivities of benzene, toluene, naphthalene, acenaphthylene, phenanthrene, anthracene, benz[*a*]anthracene, pyrene, and benzo[*e*]pyrene were measured in air at temperatures ranging from -5 to +40 °C using a modified arrested flow method. Molecular diffusivities in air for all compounds studied decreased with molecular size, and increased logarithmically with temperature. The experimental data have been used to formulate a predictive equation for the estimation of molecular diffusivities of aromatic chemicals in air as a function of temperature and molar volume.

Introduction

Molecular diffusivities in air are essential for the accurate determination of chemical fluxes across the air-water interface. Gas-phase diffusion coefficients are also important parameters for describing the dispersion of contaminants in unsaturated soils. Previous research (*1-9*) shows that the gas-phase diffusion coefficient of a compound (D) is strongly dependent upon the molar volume (V) of the diffusing species as well as the temperature (T), density (ρ), and pressure (p) of the medium through which the compound is diffusing. Measured values of molecular diffusion coefficients of organic contaminants, such as PAHs, in air are virtually nonexistent. Thus, as with the preceding paper (*10*), this research was designed to determine the molecular diffusivities of selected organic pollutants in air under typical environmental conditions and evaluate existing predictive equations for estimating gas-phase diffusivity of PAHs.

In this paper diffusivity data for several aromatic organic chemicals (benzene, toluene, and selected PAHs) in air at temperatures ranging from -5 to +40 °C are presented. The organic compounds studied were selected to permit an evaluation of diffusivity over an approximately 3-fold range of solute molar volume. A new predictive equation has been formulated to describe changes in PAH diffusion coefficients as related to the molar volume of the diffusing species and air temperature.

Experimental Section

Chemicals. The chemicals used in this work had the following purities as reported by the manufacturers: benzene (99.96%), toluene (99%), anthracene (98%), phenanthrene (98%), naphthalene (99%), benz[*a*]anthracene (99%), pyrene (99%), benzo[*e*]pyrene (99.2%), acenaphthylene (99%). Air used in the experiments was Ultra Zero Grade (total hydrocarbons less than 0.1 ppm).

Apparatus. A slightly modified version of the arrested flow elution method (*1-3, 11*) was used for determining molecular diffusivities. The apparatus (Figure 1) consists of a gas chromatograph (GC) (Hewlett Packard 5890 series II) equipped with a flame ionization detector (FID), a six-way switching valve (Rheodyne 7000), a 523.9-cm-long × 1/8-in.-o.d. × 2.1-mm-i.d. stainless steel tube (Supelco, premium grade) coiled into a 1-ft. diameter, a chart recorder (Fisher), a constant-temperature water bath/circulator (Forma Scientific Model 2067), a generator column water jacket (Alltech), and a gas vapor flask.

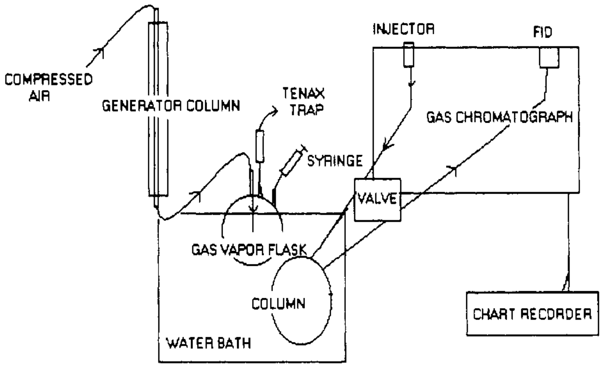

Figure 1. Schematic diagram of the system designed for measuring molecular diffusion coefficients in air.

Preparation of PAH-Saturated Air Vapor. PAH-saturated air vapor was produced using a generator column (see for example ref 12) connected to the gas vapor flask. Acenaphthylene, naphthalene, pyrene, and phenanthrene crystals were packed directly in columns; benz[*a*]anthracene, anthracene, and benzo[*e*]pyrene were coated on Chromosorb W (Chemical Research Supplies) at 1%, 2%, and 1% w/w, respectively. Benzene-saturated air vapor was generated by placing approximately 100 mL of the compound directly into the gas vapor flask (Figure 1). Molecular diffusion coefficients for benzene and toluene were also measured by directly injecting 0.5 μL of the compound and flash evaporating it with a high (200 °C) GC injector temperature.

Analysis. Each PAH-saturated air vapor sample (1 mL) and liquid benzene and toluene (0.5 μL) were injected into the system as a narrow band. The compound was eluted halfway through the column, the flow was arrested, and the band was allowed to spread by molecular diffusion alone. The band was then eluted and the concentration profile of the solute determined by GC-FID.

Molecular Diffusivity Calculations. Measurement of molecular diffusion coefficients via the arrested flow elution method is based upon the work of Knox et al. (*4*) who showed that, for diffusional spreading in an empty tube, the diffusion coefficient (D) is related to the variance (σ^2), carrier gas velocity (u_c), and arrest time (t):

$$\mathrm{d}/\mathrm{d}t\sigma^2 = 2D/u_c \tag{1}$$

Cloete et al. (*2*) have shown that under laminar flow in a column the diffusion coefficient of an unretained solute can

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Table 1. Molecular Diffusivities (D) of Selected Aromatic Organic Chemicals in Air

compound	t/°C	$10^2D/(\mathrm{cm^2\,s^{-1}})$[a]	n[c]	$10^2D(\mathrm{lit.})/(\mathrm{cm^2\,s^{-1}})$	$100\sigma(D)/D$[g]	$100\delta(D)/D$[h]
benzene	40	9.57 ± 0.12[b]	11	10.54[d,e]	1.3	9.2
	25	8.49 ± 0.09[b]	11	9.32 ± 0.149,[f] 9.467[e]	1.0	8.9, 10.3
	25	8.25 ± 0.34	9		4.1	
	10	7.89 ± 0.10[b]	11		1.3	
	−5	7.18 ± 0.07[b]	11		0.9	
toluene	40	8.19 ± 0.24[b]	11	9.23[d,e]	2.9	11.3
	25	6.98 ± 0.13[b]	10	8.49 ± 0.114[f]	1.9	17.8
	10	5.80 ± 0.24[b]	10		4.2	
	−5	4.07 ± 0.59[b]	9		14.5	
naphthalene	40	9.02 ± 0.67	8		7.5	
	25	8.36 ± 1.02	8		12.3	
acenaphthylene	40	6.69 ± 0.19	6		2.8	
	25	6.07 ± 0.12	10		1.9	
phenanthrene	40	7.78 ± 0.15	6		1.9	
	25	6.54 ± 0.24	8		3.6	
	10	6.10 ± 0.27	11		4.4	
anthracene	40	8.04 ± 0.22	6		2.7	
	25	6.69 ± 0.06	10		0.9	
	10	6.39 ± 0.16	6		2.6	
	0	5.91 ± 0.09	6		1.5	
pyrene	40	7.76 ± 0.08	6		1.0	
	25	6.68 ± 0.05	6		0.8	
	10	6.97 ± 0.21	6		3.0	
	0	6.24 ± 0.06	6		0.9	
benz[*a*]anthracene	40	7.93 ± 0.12	10		1.5	
	25	7.22 ± 0.49	10		6.8	
	10	7.18 ± 0.60	8		8.4	
benzo[*e*]pyrene	25	6.28 ± 0.28	7		4.4	
				av	3.6	11.5

[a] Mean ± standard deviation. [b] Direct liquid injection into GC. [c] Number of experimental measurements. [d] Data from Fuller et al. (*6*). [e] Corrected by eq 3 to experimental temperatures. [f] Data from Lugg (*7*). [g] Coefficient of variation; relative standard deviation. [h] Percent deviation between measured and literature values.

be determined when eq 1 is simplified with experimentaly measurable terms:

$$D = (b/2)(u_c/u_p)^2/(8 \ln r) \qquad (2)$$

where r is the fractional peak height, b is the slope of a plot of peak width squared at $1/r$ versus arrest time, u_c is the carrier velocity at the time of arrest in the column, and u_p is the linear velocity of the chart recorder. Experimentally, u_c was determined as the time for an unretained peak to be eluted through the column of length 523.9 cm, and u_p was determined from a calibrated chart recorder (cm/s). Subsequently, a series of measurements (av $n = 8$) of the peak width (at $r = 0.5$) for different arrest times (0–1620 s) are plotted to obtain b. Each of the reported experimental diffusivity values was obtained from equation 2 in this manner.

Results and Discussion

Table 1 lists diffusivities for selected organic chemicals in air at temperatures ranging from −5 to +40 °C. Standard errors of the experimental diffusivity values varied from 0.8% to 14.5% with a mean error of 3.6%. The diffusivities are also compared to experimental data of others (*5*, *6*) corrected to experimental temperatures by the following relationship (*1*):

$$D_{T_2} = D_{T_1}(T_2/T_1)^2(P/P_{std}) \qquad (3)$$

where D_{T_2} is the diffusion coefficient of interest at temperature T_2, D_{T_1} and T_1 are the experimentally determined diffusion coefficient and experimental temperature, respectively (Table 1), P is the pressure, and P_{std} is the standard atmospheric pressure. Agreement among the values reported by Lugg (*6*) and Fuller (*5*) and those reported here ranges from 8.9% to 17.8% with a mean absolute error of 11.5%.

The arrested flow elution method described in this paper for measuring gas-phase diffusion coefficients was verified to be independent of the injection method (saturated vapor or direct liquid injection) by determining the diffusivity of benzene in air at 25 °C by both the direct injection of liquid benzene and injection of air saturated with benzene vapor. Differences between the measured benzene diffusivities by the two techniques were not statistically significant at the 0.05 level of significance.

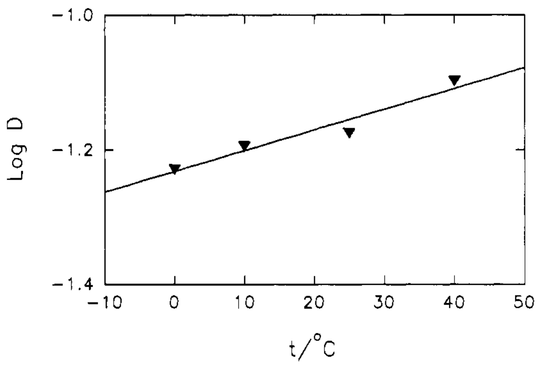

Figure 2. Illustration of the linear relationship between log diffusivity and temperature for anthracene.

Molecular diffusivities of the selected organic chemicals in air increased with temperature (Table 1, Figure 2). The logarithms of the measured diffusivity for all compounds investigated in this study varied linearly with temperature. The resultant regression lines for selected compounds (benzene, anthracene, phenanthrene, and pyrene) had a mean slope of (2.83 ± 0.53) × 10^{-3}. The increase in gas-phase diffusivity with temperature is expected because the mean kinetic energy or mean square velocity of a molecule is proportional to absolute temperature.

Molecular diffusivities of the selected organic chemicals also decreased with increasing molar volume. The logarithm of the measured diffusion coefficient varied linearly with the logarithm of the molar volume (V) for all compounds studied

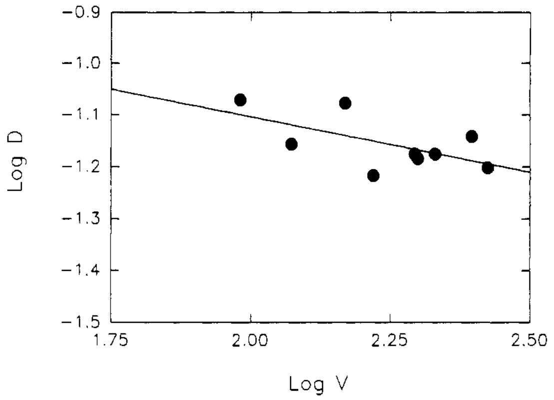

Figure 3. Relationship between diffusivity in air and molar volume for selected aromatic organic chemicals at 25 °C.

(Figure 3). Plots of log D versus log V for all compounds investigated resulted in linear regression coefficients ranging from 0.61 at 25 °C to 0.65 at 40 °C. The low regression coefficient values for the log D–log V relations are likely due to the relatively small range in molar volume for the aromatic organic chemicals investigated in this study.

Several equations for predicting molecular diffusion coefficients have been cited in the literature (*2, 5, 7, 9*). The recommended equation for predicting molecular diffusivity in air is the Fuller, Schettler, and Giddings (FSG) correlation (*8*). The FSG correlation is a revised form of the theoretically derived Chapman and Enskog equation on which most predictive equations are based (*5*). Measured diffusion coefficients for compounds in this study were compared to predicted values from the FSG correlation and the method of Wilke and Lee (*8*) (Table 2). The FSG method gave slightly better estimates of gas-phase D values relative to the Wilke–Lee method, with a mean absolute error of 17.1% (Table 2). However, predicted diffusivities for PAHs in air were found to deviate exponentially with increasing molecular size, and error in estimated gas-phase D values generally increased as temperature decreased (Table 2).

A new equation has been proposed to predict molecular diffusivities of PAHs in air in a manner analogous to that of Hayduk and Laudie (*13*) for estimation of diffusion coefficients in aqueous solution. The new equation has the form

$$D = 10^{bT} c V^{a} \tag{6}$$

where a is the slope of a plot of log D versus log V for all compounds studied (Figure 2) at 25 °C, b is the mean slope of all compound specific plots of log D versus T (see Figure 1), and c is a curve-fitting parameter calculated from the above equation using measured D values for compounds of known V at experimental temperatures T (°C). The resulting predictive relation

$$D = (0.186 \times 10^{0.002837T})/V^{0.213} \tag{7}$$

reduced the absolute error between estimated and measured molecular diffusivities from 17.1% to 9.1% for the compounds studied (Table 2). The mean absolute error for the revised gas-phase diffusivity predictive equation is comparable to the average accuracy of the data (Table 1).

Summary and Conclusions

Molecular diffusion coefficients for benzene, toluene, and selected PAHs in air at temperatures ranging from −5 to +40 °C have been measured using an arrested flow elution method. The experimentally determined diffusivities are in agreement with literature values; the accuracy of the D values is determined to be within 12%. Molecular diffusivities in air for all compounds studied decreased with molecular size, and increased logarithmically with temperature. The results illustrate that large differences in diffusivity occur between compounds and with changing environmental conditions (i.e., temperature).

Table 2. Predicted Diffusivities (D) of Selected Aromatic Chemicals in Air and Resultant Errors (δD) for Various Gas-Phase Diffusivity Estimation Techniques

compound	t/°C	D/ ($cm^2 s^{-1}$)	D(calcd)/ ($cm^2 s^{-1}$)	$100\delta(D)/D$[a] this work	$100\delta(D)/D$[a] FSG[b]	$100\delta(D)/D$[a] Wilke–Lee[c]
benzene	40	0.0957	0.0913	4.6	1.8	10.8
	25	0.0849	0.0828	2.5	5.3	13.9
	10	0.0789	0.0751	4.1	3.6	11.2
	−5	0.0718	0.0681	5.2	3.4	10.1
toluene	40	0.0819	0.0873	6.7	8.6	15.0
	25	0.0698	0.0792	13.5	16.9	23.0
	10	0.0580	0.0718	23.9	28.6	34.2
	−5	0.0407	0.0651	60.1	66.4	72.0
naphthalene	40	0.0902	0.0833	7.6	15.3	12.3
	25	0.0836	0.0756	9.6	16.1	13.8
acenaphthylene	40	0.0669	0.0813	21.5	8.3	8.8
	25	0.0607	0.0737	21.4	9.5	9.0
anthracene	40	0.0804	0.0784	2.5	19.1	19.0
	25	0.0669	0.0711	6.2	10.8	11.4
	10	0.0639	0.0644	0.9	14.6	16.1
	0	0.0591	0.0604	2.2	13.3	15.5
phenanthrene	40	0.0778	0.0782	0.5	16.4	16.8
	25	0.0654	0.0709	8.4	8.8	9.9
	10	0.0610	0.0643	5.4	10.6	12.7
pyrene	40	0.0776	0.0770	0.8	14.7	21.2
	25	0.0668	0.0698	4.5	14.0	16.7
	10	0.0697	0.0633	9.2	24.6	27.8
	0	0.0624	0.0593	4.9	21.0	25.0
benz[*a*]anthracene	40	0.0793	0.0746	6.0	28.2	29.5
	25	0.0722	0.0676	6.3	27.6	29.6
	10	0.0718	0.0613	14.6	33.4	36.0
benzo[*e*]pyrene	40	0.0699	0.0735	5.2	19.9	*d*
	25	0.0628	0.0667	6.2	18.2	*d*
			av	9.1	17.1	20.1

[a] Percent absolute error between experimental and predicted D values. [b] Reference 6. [c] Reference 10. [d] Boiling point temperatures needed for Wilke–Lee method not available.

The predictive equations of Wilke and Lee (*9*) and Fuller et al. (*5*) overestimate the gas-phase diffusivities of the smaller compounds studied (log $V < 2$) and underestimate the diffusivities of the larger aromatic compounds (log $V > 2.25$) when compared to experimental data. The predictive equation that resulted from this work yields values of D whose deviations from experimental data are comparable to the overall accuracy of that data. Nonetheless, independent measurements of diffusivities for organic contaminants in air are necessary to validate the accuracy of this equation.

Glossary

D = diffusion coefficient
p = pressure
r = fractional peak height
ρ = density
σ^2 = peak variance
t = arrest time
T = temperature
u_c = carrier gas velocity
u_p = linear velocity of the chart recorder
V = molar volume

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