1993

Molecular Diffusion Coefficients for Polycyclic Aromatic Hydrocarbons in Air and Water

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Recommended Citation

Gustafson, Kurt E., "Molecular Diffusion Coefficients for Polycyclic Aromatic Hydrocarbons in Air and Water" (1993). *Dissertations, Theses, and Masters Projects.* Paper 1539617664.
https://dx.doi.org/doi:10.25773/v5-pd77-fe86

MOLECULAR DIFFUSION COEFFICIENTS FOR POLYCYCLIC AROMATIC HYDROCARBONS IN AIR AND WATER

A Thesis
Presented to
The Faculty of the School of Marine Science
The College of William and Mary in Virginia

In Partial Fulfillment
Of the Requirements for the Degree of
Master of Arts

by
Kurt E. Gustafson
1993

APPROVAL SHEET

This thesis is submitted in partial fulfillment of the requirements for the degree of

Master of Arts

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ACKNOWLEDGEMENTS

I would like to thank my major advisor Rebecca Dickhut for her guidance and financial support as well as the opportunity to work on this project. I would also like to thank my advisory committee: Drs. Schaffner, VanVeld, Hale, and MacIntyre as well as Dr. Greaves for helpful discussions. I would like to thank Libby MacDonald for her help as well as other students in the lab and friends that have given me advice and support during this project.

I must also thank my Parents and Grandmother for their support. I would like to thank Dr. J. Morgan Wells and John Machen for encouraging me to attend VIMS.

This work is a result of research sponsored by NOAA Office of Sea Grant, U.S. Department of Commerce, under federal Grant No. NA90AA-D-SG803, to the Virginia Graduate Marine Science Consortium and the Virginia Sea Grant College Program.

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ABSTRACT

The molecular diffusivities of benzene, toluene, naphthalene, phenanthrene, anthracene, and benzo(a)anthracene were measured in water at temperatures ranging from 4°C to 40°C using a slightly modified open-tube elution method. A 2^3 factorial design experiment was conducted to assess the main effects and interactions of solute concentration, temperature, and salinity on molecular diffusivity of phenanthrene in water. Aqueous molecular diffusivities for all compounds studied decreased exponentially with solvent viscosity and molecular size. However, no measurable effect of salinity or solute concentration on diffusivity was observed. Predictive equations for determining aqueous molecular diffusivities were found to significantly overestimate the diffusivity of the polycyclic aromatic hydrocarbons (PAHs) in water. Consequently, experimental data have been used to formulate a predictive equation for the accurate estimation of aqueous diffusivity of aromatic chemicals as a function of temperature and salinity. Furthermore, it is proposed that the 3 and 4 ring PAHs may interact in aqueous solution to form dimers and trimers, thereby increasing their effective molar volume.

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

MOLECULAR DIFFUSION COEFFICIENTS FOR POLYCYCLIC AROMATIC HYDROCARBONS IN AIR AND WATER

CHAPTER 1: INTRODUCTION

It has been suggested that persistent, semivolatile pollutants, such as chlorinated hydrocarbons, are transferred throughout the world via successive deposition and reemission- a "grasshopper" scenario (Ottar, 1981). As described by Mackay et al. (1986), semivolatile pollutants, e.g. polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and organochlorine pesticides may cycle between air and water with periods of net upward flux during dry weather followed by periods of intense downward flux during rainfall; a fact recently demonstrated by Baker and Eisenreich (1990) for PCBs in Lake Superior.

There is an apparent contradiction in the proposed "grasshopper" scenario in that hydrophobic organic compounds are usually of high molecular weight and low vapor pressure, and thus evaporation should be slow. However, a factor which is often overlooked is the remarkably large activity coefficients of these compounds in water which cause unexpectedly high equilibrium vapor partial pressures and, thus, high rates of evaporation and short half-lives in waterbodies (Mackay and Wolkoff, 1973). Consequently, the physical-chemical properties of many trace organic contaminants indicate that these chemicals will be long-lived in the environment, cycling between the atmosphere and water (Mackay et al., 1986). This will increase their effective residence times in the total environment. The original substances and their transformation products eventually will be deposited to the Earth's surface and impinge on communities or ecosystems that may be hundreds or even thousands of kilometers removed from the original point of release (Schroeder and Lane, 1988).

It is now clear, that for many chemicals, air-water transfer is an important environmental pathway influencing the concentrations, and hence, exposure levels in both phases. The importance of quantifying air-water exchange processes is evident. For example, a substance which is very evaporable, or more specifically, has a high Henry's law constant, may volatilize quite rapidly if emitted into an aquatic system. For such a chemical, the exposure to biota residing in the water will, to a large extent, be controlled by the balance between absorption and volatilization rates.

Air-water transfer processes for chemicals include volatilization, absorption, dry deposition with particles, wet deposition by rain or snow, i.e. particle and vapor "washout", spray transfer, and bubble scavenging (Mackay et al. 1986). Advective transport processes such as rain dissolution and particle washout are dependent upon rainfall intensity and the vapor-particle partitioning of the chemical which is controlled by the chemical's vapor pressure as well as the size, surface area, organic content, and concentration of total suspended particles. Additionally, rain dissolution is dependent upon the compound's Henry's law constant, an air-water partition coefficient, which is a function of the compounds vapor pressure and solubility in water. Dry deposition is a function of the deposition surface, particle size distribution, and windspeed. Diffusive air-water transfer of gaseous chemicals is driven by the concentration gradient between equilibrium concentrations at the interface and bulk reservoirs. The rate of diffusive mass transfer is a dependent upon windspeed and the molecular diffusion coefficient of the compound in air and water. Mackay et al. (1986) have illustrated that both diffusive and advective transfer of chemicals need to be considered when determining the net exchange of semi-volatile organic chemicals between the atmosphere and a water body.

Gas exchange is the dominant process governing air-water transfer of chemicals during calm conditions while advective transfer mechanisms control chemical transport under turbulent conditions. In the range of environmental wind speeds (0 - 17 m/s) there are three regimes where different physical processes appear to be controlling gas exchange. The smooth surface regime covers windspeeds of 5 ± 3 m/s with the value of the solute mass transfer coefficient in water increasing only very gradually. At wind speeds of 5 - 10 m/s capillary waves are formed and the transfer velocity increases considerably. Above wind speeds of 10 m/s, gas transfer is further increased by bubbles formed by breaking waves (Achman et al. 1993).

Quantification of the evaporation rate or volatile transport of chemicals across the air-water interface relies primarily on the two layer (film) model presented by Liss and Slater (1974). The basic assumption of this model is that the two fluid phases are separated by stagnant layers, a liquid film and a gaseous film, through which transport occurs via molecular diffusion driven by the concentration (or fugacity) gradient of the chemical between the bulk reservoirs (Figure 1-1). This framework was extended by Mackay and Leinonen (1975), wherein they presented calculations for the transport of low solubility compounds including selected saturated and aromatic hydrocarbons, pesticides, and PCBs expressed in terms of mass transfer coefficients instead of diffusion coefficients and boundary layer thicknesses. Transport by molecular diffusion across two boundary layers has also been adopted by Doskey and Andren (1981), and Bopp (1983), in separate PCB air-water transfer models, and by Eisenreich et al. (1981), in modeling organic contaminants in the Great Lakes ecosystem.

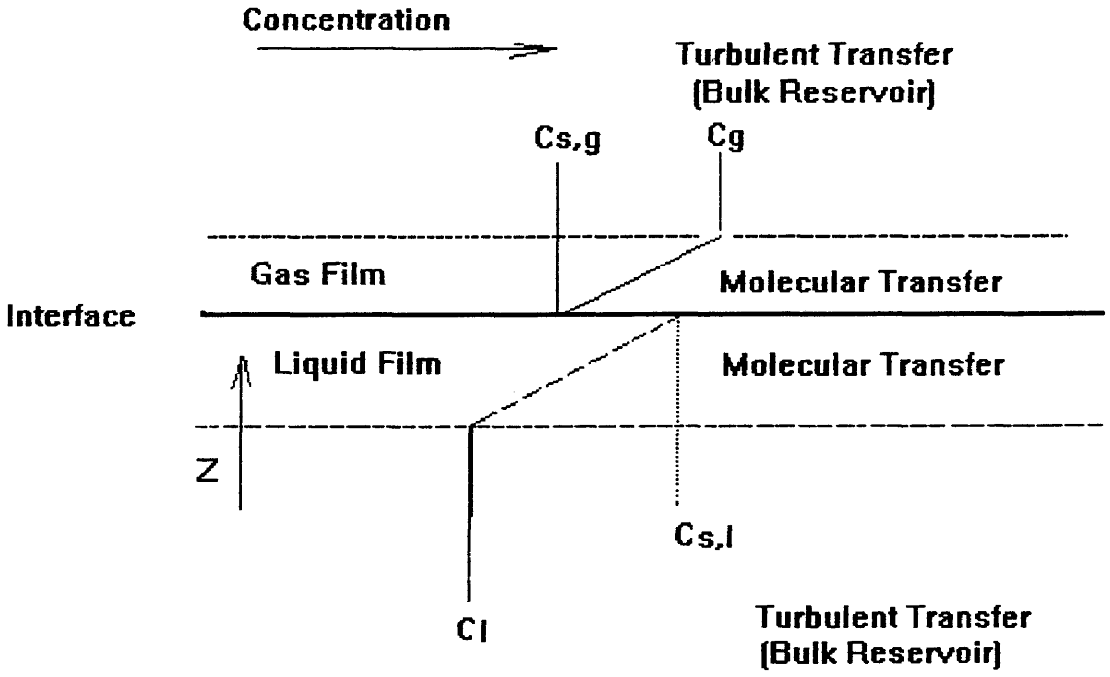


FIGURE 1-1: Liss and Slater Two-fim Model of the Air/Water Interface

The volatile flux (F_{vol}) is described by Eisenreich, et al. (1981) as:

$$F_{vol} = K_{ol}(C_{fw} - p/H) \tag{1.1}$$

where $1/K_{ol} = 1/K_w + RT/HK_a$, C_{fw} is the concentration of freely dissolved chemical in the water, p is the chemicals' partial pressure in the atmosphere, H is the compound specific Henry's law constant, K_{ol}, K_w, and K_a are the overall, water, and air mass transfer coefficients, respectively, R is the gas constant and T is temperature (K). The mass transfer coefficients control the rate of passive transport across environmental interfaces and have been related to the Schmidt number (Sc) and wind speed at a reference height of 10 meters (U_{10}) by Mackay and Yeun (1983):

$$K_a = 0.001 + 0.462(U^*)(Sc_a)^{-0.67} \tag{1.2}$$

$$K_w = 1.0(10)^{-6} + 34.1(10)^{-4}(U^*)(Sc_w)^{-0.5} \tag{1.3}$$

$$K_w = 1.0(10)^{-6} + 144(10)^{-4}(U^*)^{2.2}(Sc_w)^{-0.5} \tag{1.4}$$

where equation (1.3) applies for $U^* > 0.3$, equation (1.4) applies for $U^* < 0.3$, and $U^* = U_{10}(6.1 + 0.63U_{10})^{0.5}(10)^{-2}$. The air and water mass transfer coefficients (K_a and K_w) are related to molecular diffusion via the Schmidt numbers of a chemical in water (Sc_w) and air (Sc_a) (Bird et al. 1960):

$$Sc_w = \mu_w/\rho_w D_{sw} \tag{1.5}$$

$$Sc_a = \mu_a/\rho_a D_{sa} \tag{1.6}$$

where D_{sa} and D_{sw} are the molecular diffusivities of a chemical solute in air and water, respectively, and ρ's and

μ's are the densities and viscosities of the bulk phases, respectively. Consequently, the volatile flux of a chemical contaminant between air and water can be quantitatively predicted from the water concentration, atmospheric partial pressure, Henry's law constant and molecular diffusivities of a chemical in air and water.

Serious deficiencies exist in our ability to model chemical fluxes across the air-water interface. These deficiencies are largely due to a considerable lack of data regarding the basic physical-chemical properties of organic chemical contaminants (Baker and Eisenreich, 1990). Water concentrations and atmospheric partial pressures of organic pollutants are readily measured, and Henry's law constants are becoming more abundant. However, measured values of molecular diffusivities for toxic organic chemicals in air and water are virtually nonexistent.

The following research provides experimentally determined molecular diffusivities of selected PAHs in air and water. Additionally, the influence of temperature and salinity on molecular diffusion are evaluated. Empirical constants for predictive correlations are updated via fitting the measured molecular diffusivity data of selected PAHs. This results in improved accuracy in predicting molecular diffusion coefficients of other such PAHs. The molecular diffusivities determined in this study provide valuable information necessary for developing models for the transfer of toxic organic chemicals between the atmosphere and an aquatic system, such as Chesapeake Bay.

BACKGROUND\LITERATURE REVIEW

The basis for utilizing molecular diffusion coefficients when modeling air-water transfer processes was first formulated by Liss and Slater (1974). Liss and Slater developed the two-phase (film) model to estimate the flux of gases across the air-sea interface proposing molecular diffusion through stagnant films at the interface (see Figure 1-1). Subsequently, Mackay and Leinonen (1975) extended the use of diffusion coefficients and boundary layer thicknesses to mass transfer coefficients for modeling volatile chemical flux across air-water interfaces.

Based on an examination of the literature, the most accurate and commonly used technique for measuring molecular diffusivities in gaseous systems is the arrested elution method. The arrested flow elution method for measuring gaseous diffusion coefficients was first introduced by Knox and McLaren (1964). This method consists of injecting a narrow band of solute into an open tubular column. When the solute is part way through the column, the flow is arrested and the band is allowed to spread by molecular diffusion alone. The band is then eluted and the concentration profile determined by a suitable gas chromatographic (GC) detector. Under these conditions peak width is directly related to molecular diffusion in the gas phase (D_{sa}) via:

$$d\sigma^2_t/dt = 2D_{sa}/v^2 \qquad (1.7)$$

where σ^2 is the peak variance equivalent to 1/16 the peak width, t is the retention time and v is the average linear velocity of the carrier gas. The diffusion coefficient is determined from the slope of a plot of peak variance versus time of residence in the column. Results with a standard deviation of about 2% have been reported by this method.

Cloete et al. (1976) expanded on the arrested flow method of Knox and McLaren by statistically analyzing and optimizing peak parameters, as well as reducing experimental and instrumental errors, to yield results with experimental deviations in the range of 0.5 to 1%. The arrested elution method was also chosen by Choudhary and Parande (1977) for the GC study of binary diffusion of nitrobenzene and aniline in hydrogen. Pathak et al. (1980, 1981) also used the arrested elution method for the determination of binary diffusion of gases and the binary diffusion coefficients of selected organic vapors including benzene and toluene in hydrogen, nitrogen, and argon. The Pathak et al. study was the first to report gaseous diffusion coefficients of organic vapors in the literature.

Predictive correlations for determining gaseous diffusion coefficients can be traced to the hard sphere model given by Chapman:

$$D_{sa} = 3/32n\theta^2_{sa}[(8kT/\pi)(1/M_s + 1/M_a)]^{1/2} \qquad (1.8)$$

where n is the total concentration of both species (molecules/cc), k is the Boltzman constant, M_s is the molecular weight of the solute, and θ_{sa} is the collision diameter (Fuller et al., 1966). Subsequently, several contributions aimed at overcoming the limitations of the hard sphere model have been introduced, such as a temperature correction and correlating θ_{sa} with the Le Bas molar boiling point volumes. To gain freedom from the physical and mathematical restrictions of the hard sphere model, Fuller et al. (1966) fitted the following generalized equation to the data from a nonlinear least squares regression analysis of 153 different binary systems:

$$D_{sa} = CT^b(1/M_s + 1/M_a)^{1/2}/p[\Sigma_s v_i^{\alpha 1} + (\Sigma_a v_i)^{\alpha 2}]^{\alpha 3} \qquad (1.9)$$

where C is an arbitrary constant, p is pressure, b is a temperature power dependence, v_i is a special diffusion parameter to be summed over atoms, groups, and structural features of the diffusing species, and $\alpha 1$, $\alpha 2$, $\alpha 3$ are arbitrary exponents. Equation (1.9) gave a mean difference of 4.3% between the predicted and observed gas phase diffusivity values (Fuller et al. 1966).

The arrested elution method is the method of choice for measuring molecular diffusion coefficients in gaseous systems (Knox and McLaren, 1964; Choudhary and Parande, 1977; Pathak et al. 1980, 1981; Cloete et al. 1976). This method yields results with high precision and accuracy because the variance produced by the injector, column connections, detector, and elution along the column are the same for all arrest times and accordingly cancel out. In this work, molecular diffusion coefficients in air for selected organic chemicals, predominantly PAHs, have been determined by the arrested flow method using a GC equipped with a flame ionization detector and an open tubular column.

Molecular diffusion coefficients in liquid systems were traditionally measured using the diaphragm cell method. However, with the development of new methods for measuring liquid diffusion coefficients, the diaphragm cell method has fallen from favor due to inconvenience and inaccuracy when compared to various other methods (Ratcliff and Reid, 1961; Ouano, 1972).

The first report in the literature of liquid phase molecular diffusivities measured by a method other than the diaphragm cell technique was by Ratcliff and Reid (1961). They utilized mass transfer from spherical films to measure the diffusivity of benzene in water with a reported accuracy of 2-5%. However, a major problem with the spherical film method is that it requires a relatively large number of involved mathematical equations, compared to later methods.

Bonoli and Witherspoon (1968) measured the diffusion of aromatic and cycloparaffin hydrocarbons in water from 2°C to 60°C using a modified capillary cell method with a reported uncertainty of 3% in their results. Since liquid hydrocarbons may form dispersions, rather than true solutions in water, care had to be taken to avoid oversaturated solutions. Consequently, Bonoli and Witherspoon relied on reported solubility data for mixing their solutions. Furthermore, they investigated the effects of concentration on diffusion and found that, for a 30 to 40 fold decrease in concentration, the diffusion coefficient decreased by 10% which is not substantially larger than the uncertainty for the modified capillary cell method.

A method for measuring molecular diffusion coefficients in liquid systems based on the hydrodynamic continuity equation for laminar flow was devised by Ouano (1972), based on early work by Taylor (1953) and Biesenberger and Ouano (1970). This flowing medium diffusion cell method relies on measuring the retention volume distribution of the peak (V_r) and peak width (W) at different flow rates (Q). The aqueous diffusion coefficient (D_{sw}) is determined from the following equation:

$$D = 0.212(Q/L)(V_r/W)^2 \qquad (1.10)$$

where L is the column length. However, equation (1.10) is valid only if the assumption that $Q/D_{sw}L << 1$ or $Q/D_{sw}L \dashrightarrow 0$ holds true. Consequently, by plotting the experimentally determined diffusivities versus the dimensionless ratio of the flow rate divided by the molecular diffusivity and the length of the column (D vs Q/DL) a limiting diffusion coefficient is obtained from the intercept. By this method, aqueous diffusion coefficients can be measured within practical limits of flow rate and column length.

Various correlations for predicting diffusion coefficients of dissolved substances in water, based on the Stokes-Einstein equation have been developed. These include the Othmer and Thakar equation:

$$D_{sw} = 14.0(10^{-5})/\mu_w^{1.1}V_s^{0.6} \qquad (1.11)$$

the Scheibel equation for $V_s<V_w$:

$$D_{sw} = 25.2(10^{-8})T/\mu_w V_s^{1/3} \qquad (1.12)$$

and for $V_s > V_w$:

$$D_{sw} = 8.2(10^{-8})[1 + (3V_w/V_s)^{2/3}]T/\mu_w V_s^{1/3} \qquad (1.13)$$

and the Wilke-Chang equation:

$$D_{sw} = 7.4(10^{-8})(2.6M_w)^{0.5}T/\mu_w V_s^{0.6} \qquad (1.14)$$

where V_s and V_w are the molar volumes of the solute and water, respectively, M_w is the molecular weight of water, and the coefficient of 2.6 in equation (1.14) is designated as an association parameter for water (Hayduk and Laudie, 1974). These correlations were developed from data largely obtained prior to 1950 and have subsequently been updated by Hayduk and Laudie (1974) who have derived new constants for the Othmer-Thakar equation based upon a compilation of data obtained from the literature:

$$D_{sw} = 13.26(10^{-5})/\mu_w^{1.14}V_s^{.589} \qquad (1.15)$$

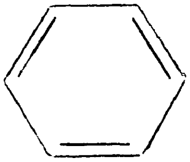
Molecular diffusion coefficients in liquid systems are on the order of 10^{-5}cm^2/s, approximately three orders of magnitude less than gaseous diffusion coefficients. Therefore, it was found to be impracticable to use the arrested flow elution method for measurement of diffusion in water. The open tube elution method as developed by Ouano (1972) and based on the hydrodynamic continuity equation was modified slightly and used to measure the diffusion coefficients of selected aromatic hydrocarbons in water.

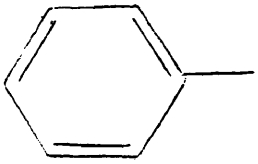
HYPOTHESES/OBJECTIVES

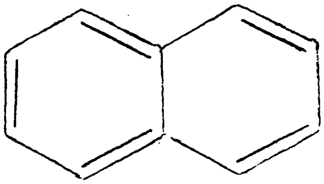
Molecular diffusion of a solute in water is a function of solvent viscosity, temperature, solute molecular size, and the degree of association of the solvent. Likewise, the diffusivity of a solute in air is a function of atmospheric pressure, temperature, and solute and air molecular size (i.e. molecular mass and collision diameter). Consequently, it is hypothesized that molecular diffusivities of PAHs in the marine environment will be influenced by salinity as it affects solvent viscosity, temperature, and solute molecular size; whereas the degree of association of water, atmospheric pressure and molecular size remain relatively constant and will not significantly effect PAH diffusivity. Furthermore, it is proposed molecular diffusion coefficients for PAHs in the marine environment will be accurately predicted through calibration of existing predictive equations with experimental diffusivity data measured at appropriate environmental conditions.

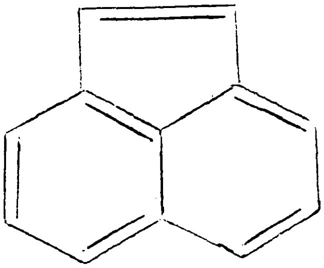
In this study molecular diffusion coefficients for selected aromatic organic chemicals, particularly PAHs, in water and air were measured at various environmental conditions. Selected aromatic organic chemicals include benzene, toluene, and PAHs: naphthalene, phenanthrene, anthracene, acenaphthylene, pyrene, benzo(e)pyrene, and benzo(a)anthracene (Figure 1-2). The selected aromatic organic chemicals allow for evaluation of the effect of solute molecular size (Table 1.1) on diffusivity and provide data necessary for modeling gas exchange of target species being examined as part of the Chesapeake Bay Atmospheric Deposition (CBAD) study. Molecular diffusivities in water were measured as a function of temperature between 4°C and 40°C, and salinity, between 0 ppt and 35 ppt. A factorial experimental design was used to determine if any interactive effects of temperature and salinity on D_{sw} exist. The effect of the aromatic organic chemical concentration on D_{sw} was also evaluated. Additionally, molecular diffusivities in air were measured as a function of temperature between -5°C and 40°C. Finally, the measured molecular diffusivity data were used to calibrate equations for predicting D_{sa} and D_{sw} of high molecular weight aromatic chemicals.

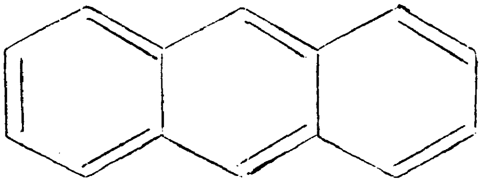
FIGURE 1-2: Molecular structure of selected PAHs

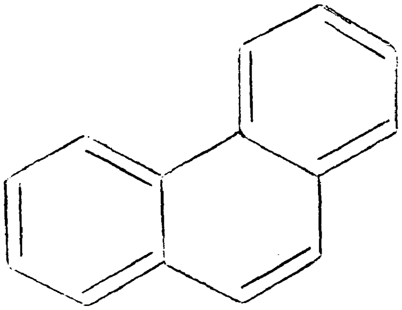

benzene

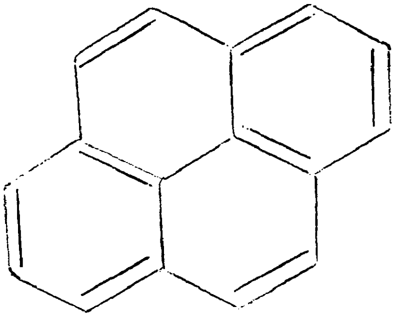

toluene

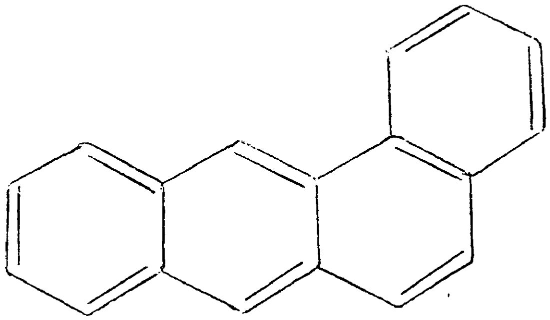

naphthalene


acenaphthylene

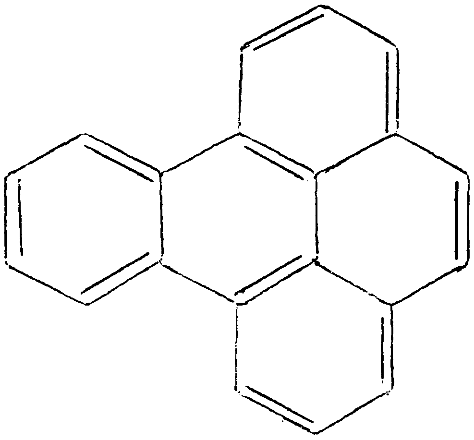

anthracene


phenanthrene


pyrene



benzo(a)anthracene



benzo(e)pyrene

TABLE 1.1: Molar volumes of selected aromatic compounds and constants necessary for their calculation

Physical properties of air

M_A	28.97 g/mol
V_A	20.1 cm^3/mol
e/k	78.6 K
o_A	3.711 A

Atomic and structural diffusion volume increments (V_b)

	(cm^3/mol)
C	16.5
H	1.98
Aromatic and Heterocyclic rings	-20.2

Additive Volume Increments for Calculating LeBas Molar Volumes (V_b')

	(cm^3/mol)
C	14.8
H	3.7
Ring	
5-membered	-11.5
6-membered	-15.0
naphthalene	-30.0
anthracene	-47.5

SOURCE: Lyman, W.J. et al. 1982.

	V_b'	V_b
benzene	96.0	90.68
toluene	118.2	107.18
naphthalene	147.6	140.44
acenaphthylene	165.7	153.24
anthracene	196.7	190.2
phenanthrene	199.2	190.2
pyrene	213.8	203
benzo(a)anthracene	248.3	239.96
benzo(e)pyrene	265.4	252

NOTE:

V_b' used in predictive equations of this work, Wilke-Lee, Hayduk-Laudie, Othmer-Thakar, Wilke-Chang, Scheibel.

V_b used in the FSG predictive equation.

CHAPTER 2: MOLECULAR DIFFUSION IN AQUEOUS SOLUTION

Introduction

Knowledge of molecular diffusion is fundamental for describing processes that control the environmental fate and distribution of contaminants such as 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 (Bonoli et al. 1968; Hayduk et al. 1974; Knox et al. 1983; Othmer et al. 1953; Ratcliff et al. 1961; Scheibel, 1954; Wilke et al. 1955) 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 toxic organic compounds, 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 characterize the diffusion of PAHs in water as related to the differing environmental factors of temperature and salinity encountered in the marine environment. Molecular diffusion coefficients of selected PAHs were measured in water at temperatures ranging from 4°C to 40°C. The PAHs studied were selected to permit an evaluation of diffusivity over an approximately three-fold range of solute molar volume. Additionally, a factorial design experiment using phenanthrene as the test compound was initially conducted to determine the effects and interactions of temperature, salinity, and the concentration of solute on molecular diffusion (Appendix 1).

In this chapter 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°C to 40°C are presented. Predictive equations for solute molecular diffusivity in water are evaluated and updated to describe the changes in PAH diffusion coefficients as related to the molar volume of the solute and the viscosity of the aqueous solution as affected by temperature and salinity.

EXPERIMENTAL SECTION

Chemicals. The chemicals used in this work had the following purities: acetone(99.78%), benzene(99.96%), toluene(99%), methanol(99.99%), anthracene(98%), phenanthrene(98%), naphthalene(99%), 1,2-benzanthracene(99%), pyrene(99%), as reported by their manufacturers. Water used in the experiments was pretreated by distillation and passage 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 as indicated by manufacturer specifications and the salinity was verified with a refractometer.

Apparatus. A slightly modified version of the open tube elution method (Ouano, 1972) was used for determining molecular diffusivities. The apparatus (Figure 2-1) used for measuring aqueous diffusion coefficients consists of a high precision syringe pump (Isco LC-5000), sample injection valve (Rheodyne 7010), a 100 ft. long x 1/16 in. O.D. x 0.03 in. I.D. stainless steel tube (Supelco) coiled into a 1 ft. diameter, U.V. (Isco 228 with type 6 optical unit), and fluorescence detectors (Isco FL-2), a chart recorder, and a constant temperature waterbath/circulator (Forma Scientific Model 2067).

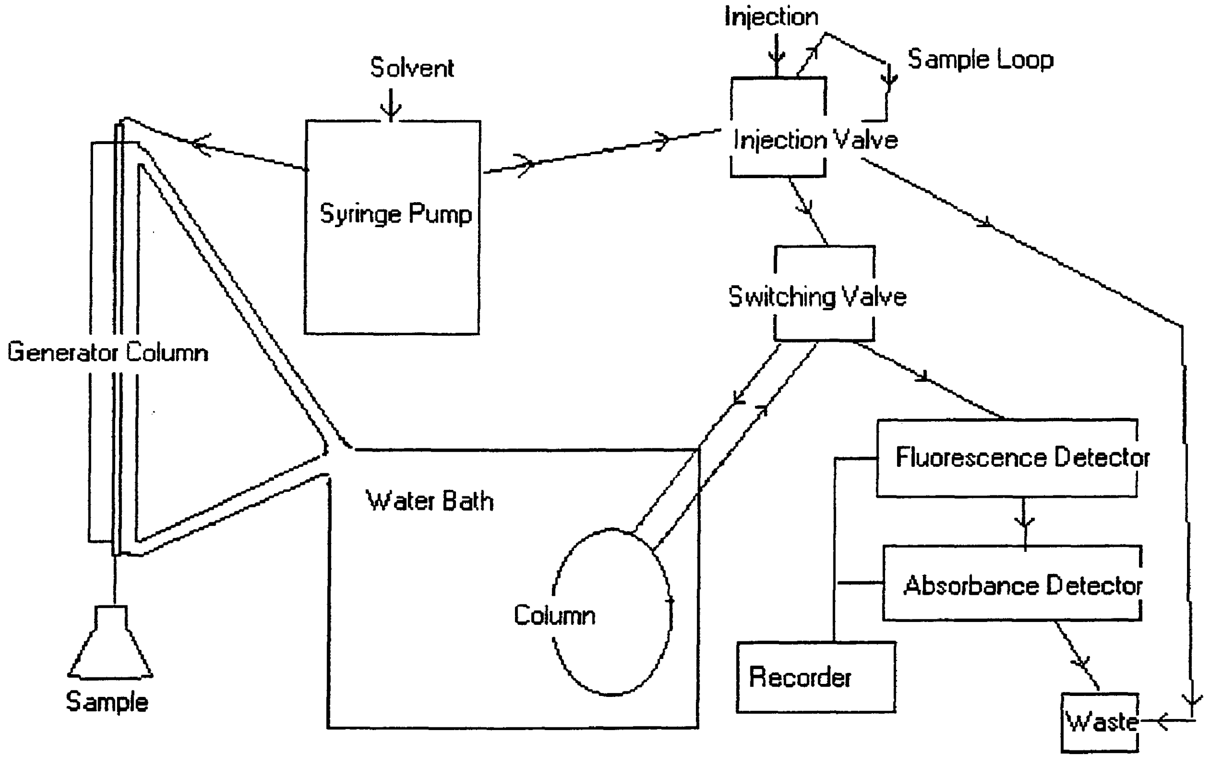


FIGURE 2-1 : Schematic Diagram of the System Designed for Measuring Aqueous Molecular Diffusivities

Preparation of saturated solutions. Saturated aqueous solutions of PAHs were produced using a generator column (Dickhut et al. 1986). Naphthalene, pyrene, and phenanthrene crystals were packed directly in columns; benzo(a)anthracene, and anthracene were coated on Chromosorb W (Chemical Research Supplies) 1% and 2% w/w, respectively. Saturated solutions of benzene and toluene in water 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 at room temperature. Saturated solutions were drawn from the aqueous layer as needed. Aqueous sample 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 as part of a factorial design experiment. Solutions of acetone, benzene, and naphthalene in methanol and 60:40 methanol:water were made on a weight per volume basis as indicated in Table 2.1.

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 was 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 (ml/s), was measured as the time in seconds to fill a 10 ml volumetric flask.

Molecular diffusivity calculations. Measurement 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 (Ouano, 1972):

$$dc/dt + U[1-(r/R)^2]dc/dx - D[d^2c/dx^2 + dc/rdr + d^2c/dr^2] = 0 \qquad (2.1)$$

where c is the concentration of the solute, r is the distance from the axis of the tube, R is the radius of the tube, t is time, and x is the distance along the tube measured on a coordinate which moves at the average velocity of flow U. Ouano (1972) has shown that this dispersion equation can be simplified to:

$$D = 0.212(Q/L)(V_t/W)^2 \qquad (2.2)$$

in relation to a retention volume distribution if the following conditions, Q/DL <<< 1 or Q/DL --> 0, are 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, equation 2.2 is equivalent to:

$$D = 0.212(Q/L)(t_p/W_t)^2 \qquad (2.3)$$

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

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. Peak width at half height (W_h) was measured and related to base width by:

$$W_t = -4W_h/(8\ln h)^{1/2} \tag{2.4}$$

where h is the fractional height of the peak (Cloete, et al., 1976). 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 to 15 diffusion measurements (ave n = 9) at different flow rates between 7 ml/hr and 24 ml/hr.

RESULTS AND DISCUSSION

Table 2.1 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 error of 6.4%. The measured diffusivities are also compared in Table 2.1 to experimental D values determined in previous studies. Agreement between the values of Knox (1983), Bonoli (1968),

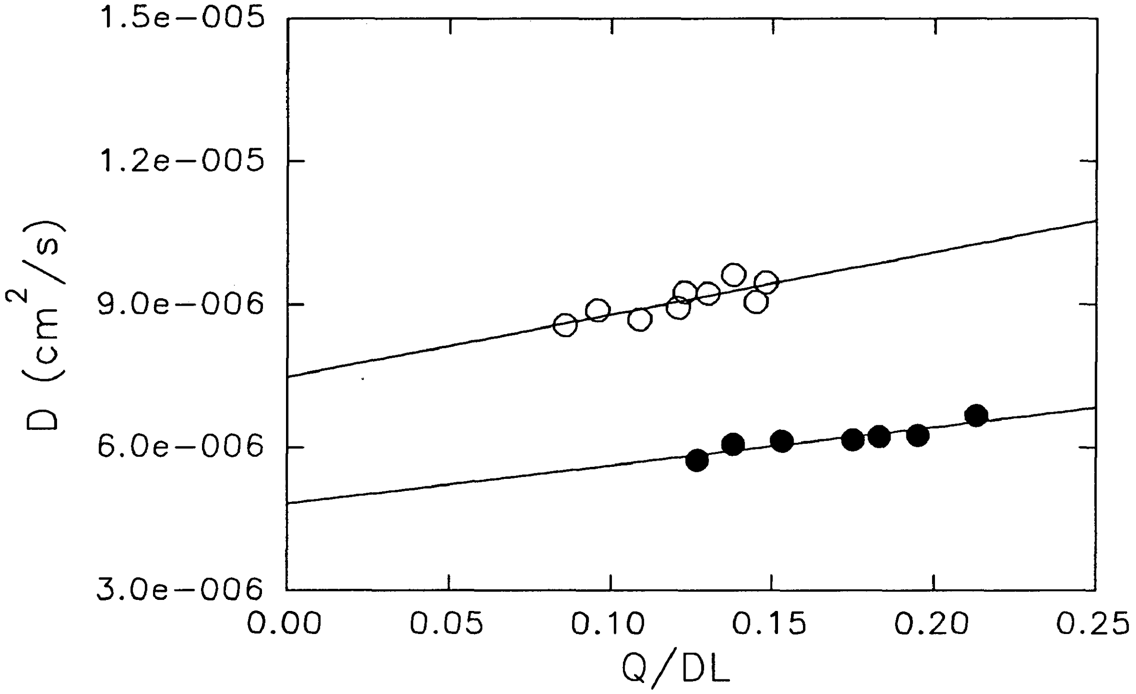


FIGURE 2–2: Diffusivity of naphthalene in water; extrapolation of Q/DL to 0 to obtain the limiting diffusion coefficient: (○) 25°C, (●) 10°C

TABLE 2.1: Molecular Diffusion Coefficients for Selected Organic Chemicals in Water, Methanol, and Methanol/Water Mixtures

SOLUTE	CONC. (mg/l) or (% saturation)	SOLVENT	TEMP. (°C)	DIFFUSION COEFF.[a] (cm^2/s x 10^5)	n[b]	LIT. VALUE (cm^2/s x 10^5)	LIT. REF.	PRECISION[c] (%)	ACCURACY[d] (%)
naphthalene	15.5*	methanol	40	2.127 ± 0.106	11	---	---	5.0	-----
	"		25	1.753 ± 0.083	10	1.83	Knox (1983)	4.7	4.2
	"		10	1.669 ± 0.075	8	---	---	4.5	-----
	4.92*		25	1.715 ± 0.161	11	---	---	9.4	-----
benzene	1730*	methanol	40	2.773 ± 0.203	11	---	---	7.3	-----
	"		25	2.178 ± 0.062	11	---	---	2.8	-----
	"		10	1.741 ± 0.075	11	---	---	4.3	-----
benzene	1766*	60:40	40	1.186 ± 0.038	11	---	---	3.2	-----
	"	methanol:water	25	0.867 ± 0.050	9	---	---	5.8	-----
	"		10	0.574 ± 0.040	10	---	---	7.0	-----
acetone	5300*	60:40	40	1.412 ± 0.053	7	---	---	3.7	-----
	"	methanol:water	25	1.036 ± 0.022	9	1.0	Knox (1983)	2.1	3.6
	"		10	0.754 ± 0.020	8	---	---	2.6	-----
benzene	50	water	40	1.611 ± 0.063	9	1.60	Bonoli (1968)	3.9	0.7
	"		32	1.298 ± 0.049	15	---	---	3.8	-----
	"		25	1.087 ± 0.005	6	1.09	Ratcliff (1961)	0.7	0.3
	"		18	0.951 ± 0.016	10	---	---	1.7	-----
	"		10	0.764 ± 0.008	11	0.75	Bonoli (1968)	1.0	1.8
naphthalene	50	water	40	1.063 ± 0.077	9	---	---	7.2	-----
	"		25	0.749 ± 0.022	13	---	---	2.9	-----
	"		10	0.483 ± 0.013	10	---	---	2.6	-----
	"								
toluene	30	water	40	1.223 ± 0.062	9	1.34	Bonoli (1961)	5.1	9.0
	50		25	0.915 ± 0.016	11	---	---	1.7	-----
	"		10	0.621 ± 0.020	8	0.62	Bonoli (1961)	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	-----
	50	35 ppt salinity	40	0.576 ± 0.039	10	---	---	6.7	-----
	12.5	water	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	-----
	"		25	0.418 ± 0.032	11	---	---	7.7	-----
	"		4	0.303 ± 0.023	9	---	---	7.5	-----
pyrene	50	water	40	0.490 ± 0.089	11	---	---	18.1	-----
benzo(a)anthracene	50	water	40	0.619 ± 0.009	10	---	---	1.4	-----
	"		25	0.335 ± 0.037	9	---	---	11.1	-----
	"		4	0.198 ± 0.015	10	---	---	7.5	-----

---

*concentration (mg/l); all other concentrations as % saturation

[a] mean ± standard deviation

[b] number of experimental measurements

[c] coefficient of variation; relative standard deviation

[d] % deviation between measured and literature values

Ratcliff (1961), 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 study 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 three, and measuring phenanthrene aqueous diffusivity at 50% and 12.5% saturation. Differences between the measured naphthalene diffusivities in methanol were not significant at the 0.01 level of significance. The factorial design experiment using phenanthrene as the test compound further verified the independence of solute concentration on measured aqueous diffusivity (Appendix I) (Figure 2-3). The effect of solute concentration and interactions between variables, temperature, salinity, and solute concentration, were not statistically significant to measurement of phenanthrene diffusivity in aqueous solutions (Appendix I).

The effect of salinity on PAH aqueous diffusivity was also investigated through the phenanthrene factorial design experiment. Within experimental error, the effect of salinity on diffusivity was not significant ($p = 0.05$) (Appendix I) (Figure 2-4). However, the much larger experimental error, up to 24%, of phenanthrene diffusivity measurements in 35 ppt salinity Instant Ocean solutions (Table 2.1) may conceal the effect of salinity on D. The

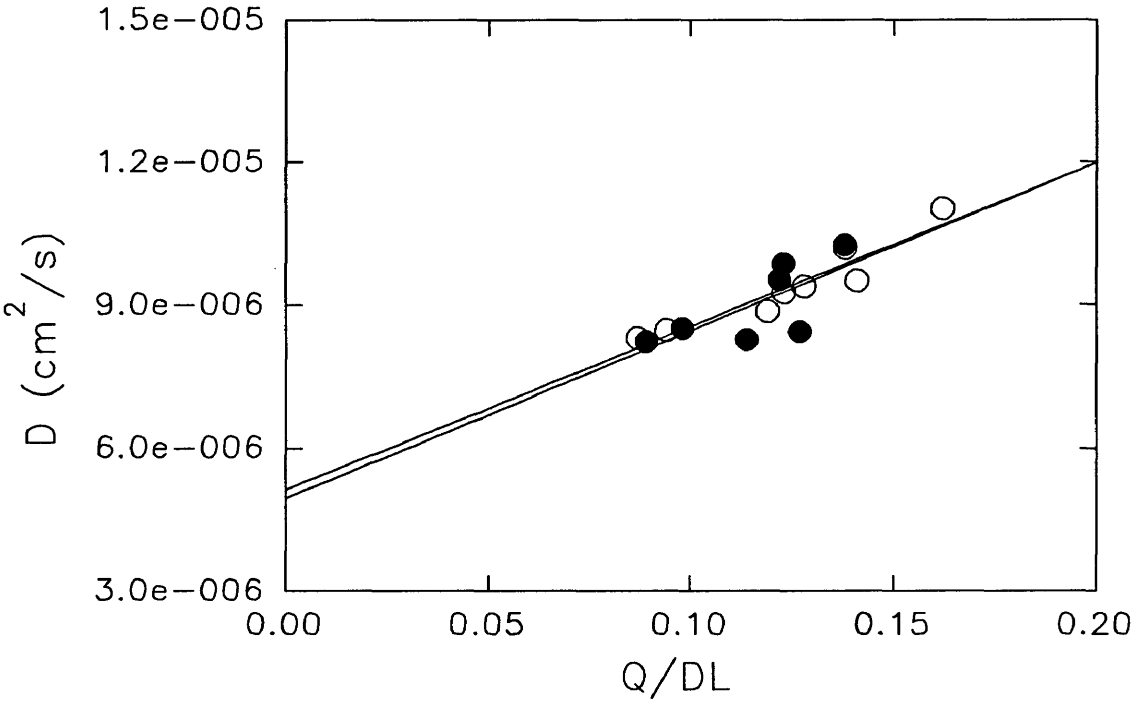


FIGURE 2−3: Effect of concentration on the diffusivity of phenanthrene in aqueous solution at 40^{0}C

(○) 1/2 saturated solubility

(●) 1/8 saturated solubility

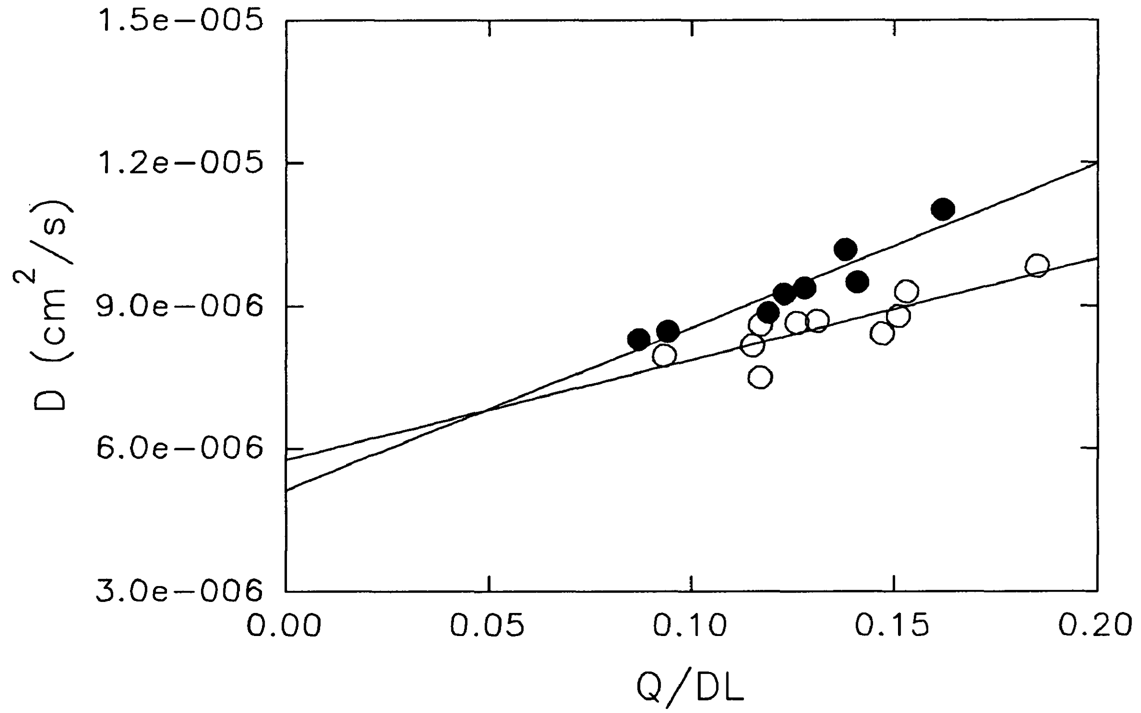


FIGURE 2−4: Effect of salinity on the diffusivity of phenanthrene in aqueous solution at 40°C
(●) 35 ppt salinity
(○) 0 ppt salinity

change in viscosity over the range of 0 to 35 ppt salinity is expected to be 6-8% (Horne, 1969)(Table 2.2), much lower than the experimental error encountered with diffusivity measurements in saline solutions. Large experimental errors for organic chemical diffusivity measurements in saline solutions are likely associated with the high corrosiveness of the solutions which acted to rapidly degrade the stainless steel columns.

Aqueous molecular diffusivities of the selected organic chemicals were found to decrease with temperature (Table 2.1). The effect of temperature on molecular diffusivity has been previously correlated to the viscosity of the solvent (Hayduk et al. 1974; Othmer et al. 1953; Scheibel, 1954; Wilke et al. 1955). 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 (Appendix II); linear regression coefficients ranged from 0.984 for phenanthrene to 1.0 for naphthalene and toluene. The resultant regression lines for all compounds had an average slope of 0.905 ± 0.316. While the standard deviation for the average slope is large, no relationship was found between the individual slopes and properties of the compounds studied.

Aqueous molecular diffusivities of the selected organic chemicals also decreased with molecular size. The log of the measured diffusion coefficient was found to vary

TABLE 2.2: Viscosity of Water at Various Temperatures and Salinities

Salinity Viscosity	0ppt μ(cp)	30ppt μ(cp)	35ppt μ(cp)	40ppt μ(cp)
Temperature (°C)				
0	1.787	1.887		1.883
4	1.567			
10	1.307	1.380		1.403
15	1.139	1.206		1.229
18	1.053			
20	1.002	1.070		1.092
25	0.8904	0.952	0.902	0.974
30	0.6523	0.860		0.877
32	0.7647			
40	0.6529			

Source: Weast, R.C. 1977.
Horne, R.A. 1969.

linearly with the log of the molar volume (V) for all compounds studied (Figure 2-5). 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.

One of the goals of this work was to evaluate and update equations for predicting the aqueous molecular diffusivities of PAHs. Several equations for predicting molecular diffusion coefficients have been cited in the literature (Hayduk et al. 1974; Othmer et al. 1953; Scheibel 1954; Wilke et al. 1955). The recommended equation for predicting molecular diffusivity in aqueous solutions is the Hayduk-Laudie equation (Lyman et al. 1982). The Hayduk-Laudie equation is a revised form of the Othmer and Thakar equation based on a larger compiled data base (Hayduk et al. 1974). Previously, Bonoli and Witherspoon (1968) 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 2.3). Of these, it was found that the unrevised Othmer-Thakar equation gave the best fit to measured values with an average absolute error of 30.4% (Table 2.3). However, predicted diffusivities for PAHs in

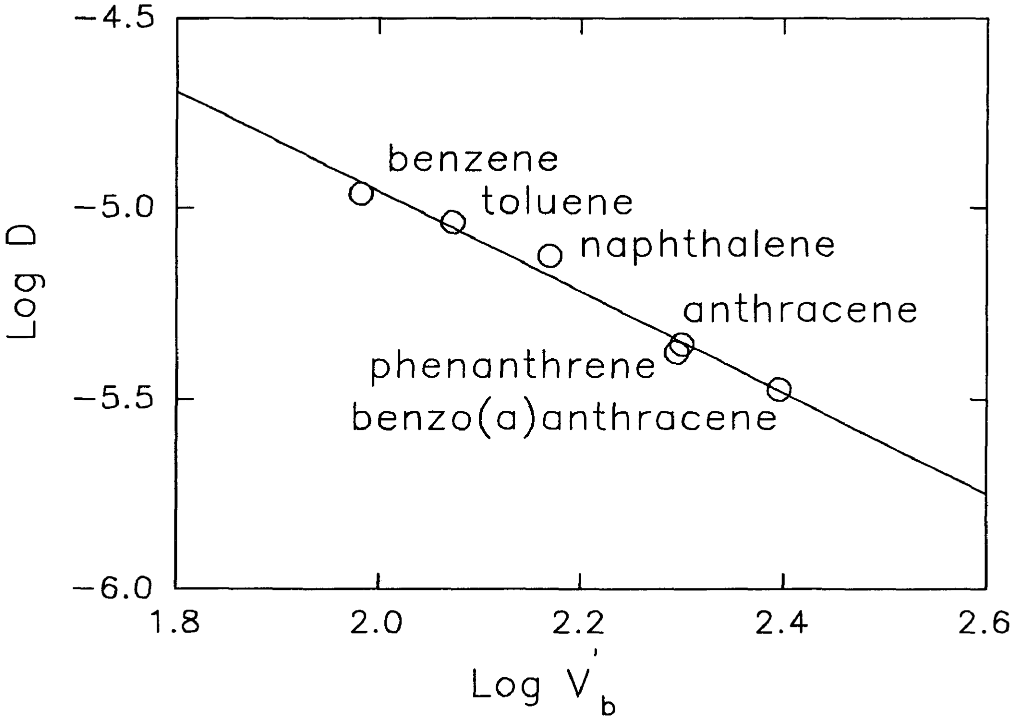


FIGURE 2–5: Relationship between molar volume and aqueous diffusivity at 25°C

TABLE 2.3: Comparison between experimental and predicted diffusivities of selected aromatics in aqueous solution.

				Percent absolute error between experimental and predicted D				
				Predictive equations				
Compound	Temperature (°C)	Experimental D x 10^5(cm^2/s)	Predicted D x 10^5(cm^2/s)	This work	Hayduk-Laudie	Othmer-Thakar	Wilke-Chang	Scheibel
benzene	10	.764	.915	19.8	13.0	11.7	7.1	18.8
	18	.951	1.11	16.9	10.6	10.1	4.9	16.8
	25	1.09	1.29	19.1	5.3	5.4	0.8	11.9
	32	1.30	1.49	14.4	5.7	6.3	0.6	12.1
	40	1.61	1.71	6.4	9.0	10.2	2.6	14.8
toluene	10	.621	.695	11.8	5.4	4.2	0.7	11.5
	25	.915	.983	7.4	0.5	0.8	5.7	7.1
	40	1.22	1.30	6.5	6.0	4.4	13.3	0.4
naphthalene	10	.483	.518	7.2	6.7	7.8	13.3	0.7
	25	.749	.733	2.1	6.7	6.2	13.1	0.5
	40	1.06	.971	8.7	7.0	5.2	14.1	1.4
anthracene	4	.303	.301	0.7	16.9	18.6	24.3	12.8
	25	.418	.501	20.0	61.5	60.1	70.6	54.9
	40	.567	.664	17.0	69.3	65.8	79.9	63.3
phenanthrene	4	.387	.296	23.5	9.1	7.8	3.3	12.2
	4	.378	.296	21.8	7.1	5.8	1.3	10.3
	25	.437	.493	12.8	53.1	51.8	61.8	47.0
	40	.495	.653	32.0	92.8	88.8	105.0	86.1
	40	.514	.653	27.0	85.4	81.6	97.0	79.0
benzo(a) anthracene	4	.198	.221	11.6	55.9	57.7	65.3	53.4
	25	.335	.369	9.9	75.4	73.4	84.8	71.6
	40	.619	.488	21.1	35.3	32.2	43.5	33.2
pyrene	40	.490	.595	21.3	86.5	82.5	98.0	81.1
		Average absolute error		14.7	31.5	30.4	35.3	30.5

water deviate exponentially from measured values with increasing molecular size (Figure 2-6). Therefore, new constants for the Othmer equation are proposed to more accurately predict the molecular diffusivities of PAHs in aqueous solution.

The terms for the revised equation are the slope,the inverse logarithm of the intercept of a plot of log D versus log V, and the mean slope of all regression plots of log D versus log μ (centipoise) for the compounds investigated (Hayduk et al. 1974). The revised equation resulting from this study:

$$D = 4.864(10)^{-3}/(\mu^{.905} * V^{1.322}) \qquad (2.5)$$

resulted in a reduction of the absolute error between predicted and measured molecular diffusivities from 30.4% to 14.7% for the compounds studied (Table 2.3). The error resulting from the modified predictive equation (eq. 2.5) is similar to the accuracy and precision of the measured aqueous diffusivities.

The exponential deviation of PAH aqueous diffusivities from predicted values may potentially be due to hydrophobic interactions. Previously, it has been suggested that benzene associates in dilute aqueous solution to form dimers, due to hydrophobic interactions (Bernal et al. 1986; Rossky et al. 1980; Tucker et al. 1981). The concept of hydrophobic bonding had its origins in observations that nonpolar molecules or molecules with sizeable nonpolar

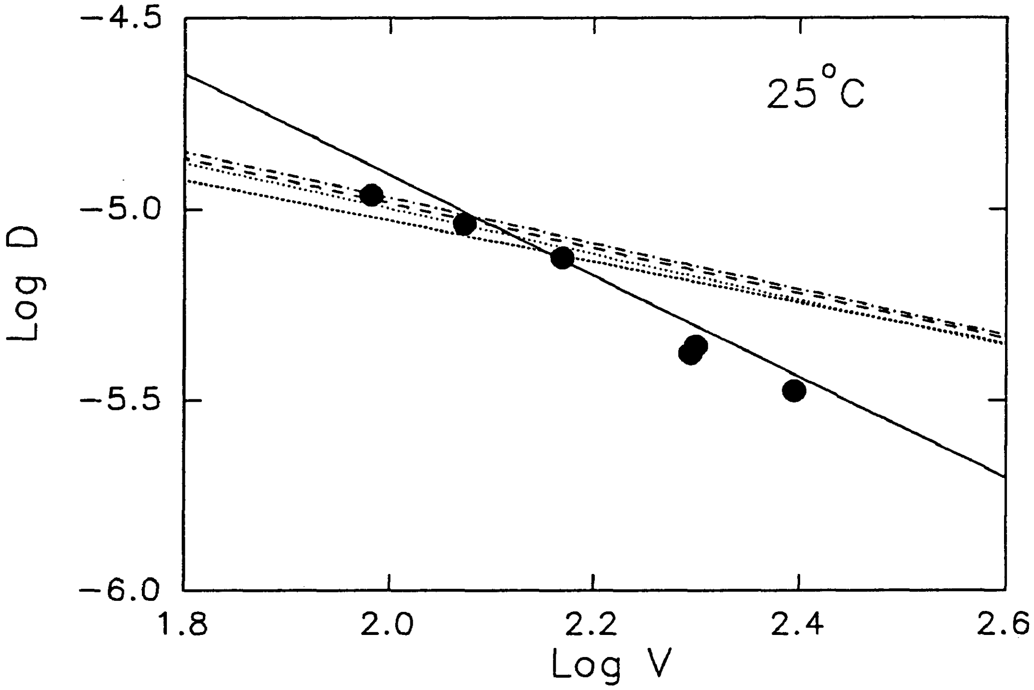


FIGURE 2−6: Comparison of experimental (●) and predicted aqueous molecular diffusivities: (——) this work, (– – –) Hayduk−Laudie, (–·–·–) Wilke−Chang, (-----) Scheibel, and (·······) Othmer−Thakar groups have abnormally large negative entropies of solution in water. These results support the view that water molecules in contact with hydrocarbons are more ordered than those in the bulk. Hydrophobic association occurs between hydrocarbons as a result of the favorable (positive) entropy change that accompanies the loss of part of the ordered region as the nonpolar moieties come into close contact (Tucker et al. 1981).

It is proposed that the larger three and four ring PAHs (phenanthrene, anthracene, and benzo(a)anthracene) may associate sufficiently in aqueous solution to form dimers and trimers thereby increasing their effective molar volume. Figure 2-7 shows that if one assumes a molar volume two times the calculated molar volume for phenanthrene and anthracene, the estimated diffusivity resulting from the Hayduk-Laudie equation lies close to the predicted line. Similarly, if one assumes a value 2.5 times the molar volume of benzo(a)anthracene the predicted diffusivity also lies along the predictive line. Therefore, phenanthrene and anthracene may exist in aqueous solution as dimers and benzo(a)anthracene may exist in solution as a mixture of dimers and trimers.

Furthermore, it should be noted that while updating the molar volume dependence on diffusivity in predictive correlations significantly reduces the error between predicted and experimental diffusivities, updating the

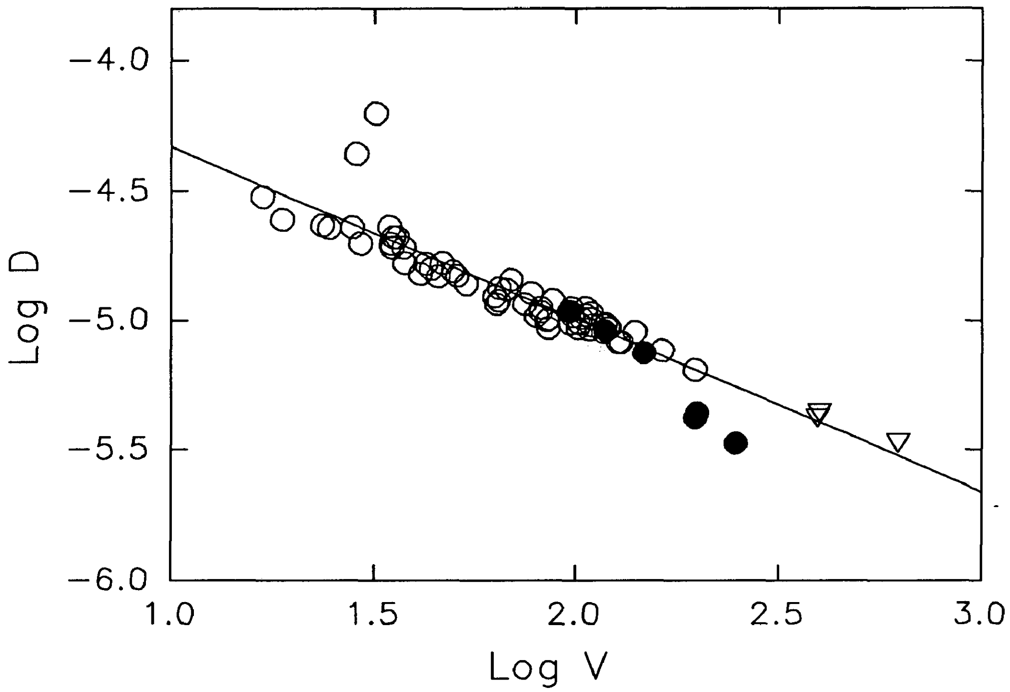


FIGURE 2−7: Proposed hydrophobic interaction:
formation of dimers and trimers
o−data from Hayduk and Laudie (1974)
●−experimental data
▽−proposed dimer/trimer formation

"effective" molar volumes for nonpolar compounds that may associate in aqueous solution due to hydrophobic interactions may be a more accurate method in modeling molecular diffusivity in aqueous solution.

SUMMARY AND CONCLUSIONS

Molecular diffusion coefficients for benzene, toluene, and selected PAHs in aqueous solutions at temperatures ranging from 4°C 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 exponentially 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 (Hayduk et al. 1974; Othmer et al. 1953; Wilke et al. 1955), 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. It is further proposed that the larger three and four ring PAHs may associate in aqueous solution to form dimers and trimers, thereby increasing their effective molar volumes.

CHAPTER 3: MOLECULAR DIFFUSION OF SELECTED AROMATIC ORGANIC CHEMICALS IN AIR

INTRODUCTION

Molecular diffusivities in air are essential for the accurate determination of chemical fluxes across the air-water interface and are important parameters for describing the dispersion of contaminants in unsaturated soils. Existing experimental data and subsequent predictive equations (Choudhary et al. 1977; Cloete et al. 1976; Fuller et al. 1966; Knox et al. 1964; Lugg, 1968; Lyman et al. 1982; Pathak et al. 1980; Skelland, 1985) show that the gas phase diffusion 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. As for aqueous molecular diffusivities (see Chapter 2), measured values of molecular diffusion coefficients for toxic organic compounds, such as PAHs, in air are virtually nonexistent. Consequently, as with the previous work (Chapter 2), this work was undertaken to characterize the diffusion of PAHs in air as related to the molar volume of the diffusing species and temperature.

In this chapter diffusivity data for selected organic solutes (benzene, toluene) and PAHs in air at temperatures ranging from -5°C to 40°C are presented, and predictive equations for estimating molecular diffusivity in air were evaluated. The organic compounds studied were selected to permit an evaluation of diffusivity over a three-fold range of molar volumes of the diffusing species. 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: benzene(99.96%), toluene(99%), anthracene(98%), phenanthrene(98%), naphthalene(99%), 1,2-benzanthracene(99%), pyrene(99%), benzo(e)pyrene(99.2%), acenaphthylene(99%) as reported by manufacturers. 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 (Choudhary et al. 1977; Cloete et al. 1976; Pathak et al. 1980,1981) was used for determining molecular diffusivities. The apparatus (Figure 3-1) consists of a gas chromatograph (Hewlett Packard 5890 series II) equipped with a flame ionization detector (FID), 6-way

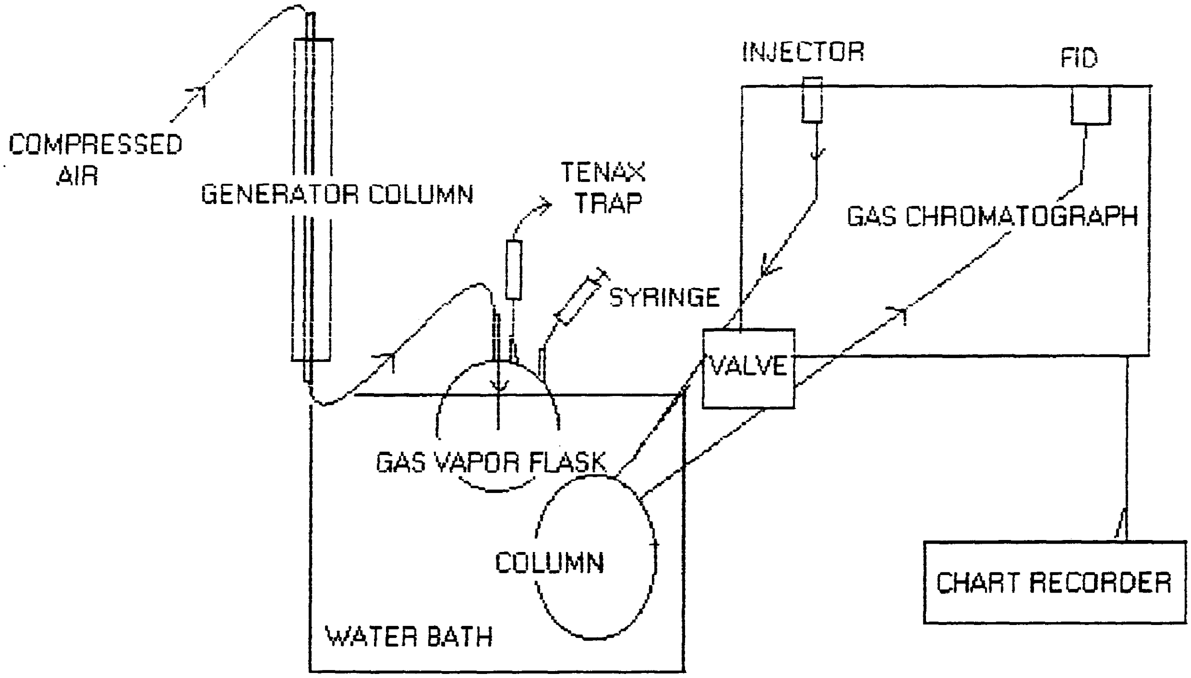


FIGURE 3-1: Schematic Diagram of the System Designed for Measuring Molecular Diffusion Coefficients in Air

switching valve (Rheodyne 7000), a 523.9 cm long x 1/8 in. O.D. x 2.1 mm I.D. stainless steel tube (Supelco, premium grade) coiled into a 1 ft. diameter, chart recorder (Fisher), constant temperature waterbath/circulator (Forma Scientific Model 2067), a generator column with water jacket (Alltech), and gas vapor flask.

Preparation of PAH saturated air vapor. PAH saturated air vapors were produced using a generator column (see Dickhut, et al. 1986) connected to the gas vapor flask. Acenaphthylene, naphthalene, pyrene, and phenanthrene crystals were packed directly in columns; benzo(a)anthracene, anthracene, and benzo(e)pyrene were coated on Chromosorb W (Chemical Research Supplies) 1%, 2%, and 1% w/w, respectively. Benzene saturated air vapor was generated by placing approximately 100 ml of the liquid compound directly into the gas vapor flask (Figure 3-1). 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), or liquid benzene or toluene (0.5 μl) was injected into the system as a narrow band. The compound was eluted half-way through the column, the flow was arrested and the band was then allowed to spread by molecular diffusion. 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. (1964), whereby they have shown 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):

$$d\sigma^2/dt = 2D/u_c \tag{3.1}$$

Cloete et al. (1976) have shown that under laminar flow the diffusion coefficient of an unretained chemical can be determined when equation 3.1 is simplified with experimentally measurable terms:

$$D = (b/2)(u_c/u_p)^2/8\ln r \tag{3.2}$$

where r is the fractional peak height, b is the slope of a plot of peakwidth squared measured at 1/r versus arrest time, u_c is carrier velocity at time of arrest in the column, and u_p is the linear velocity of the chart recorder. Experimentally, u_c (cm/s) 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 (ave n = 8) of peakwidth (at r = 0.5) for different arrest times (0 to 1620 s) are plotted to obtain b. Each of the reported experimental diffusivity values was obtained from equation 3.2 in this manner.

RESULTS AND DISCUSSION

Table 3.1 lists diffusivities for selected organic chemicals in air at temperatures ranging from -5 to 40°C. Standard errors of the diffusivity values varied from 0.8% to 14.5% with a mean error of 3.6%. The diffusivities are also compared to experimental data (Fuller et al. 1966; Lugg, 1968) corrected to experimental temperatures by the following relationship (Choudhary et al. 1977):

$$D_{T2} = D_{T1}(T_2/T_1)^2(P/760) \qquad (3.3)$$

where D_{T2} is the diffusion coefficient of interest at temperature T_2; and D_{T1} and T_1 are the experimentally determined diffusion coefficient and experimental temperature, respectively (Table 3.1). Agreement between the values reported by Lugg (1968), Fuller et al. (1966), and those reported here ranges from 8.9% to 17.8% with an average absolute error of 11.5%.

The arrested-flow elution method described in this manuscript for measuring gas-phase diffusion coefficients was verified to be independent of injection type (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 the injection of air saturated with benzene vapor. Differences between the measured benzene diffusivities by both injection techniques were not found to be statistically significant at the 0.05

TABLE 3.1: Molecular diffusivities for selected aromatic organic chemicals in air

COMPOUND	TEMP. °C	DIFFUSION COEF.^{a} (cm^2/s x 10^2)	n^{b}	LIT. VALUE (cm^2/s x 10^2)	PRECISION^{c} (%)	ACCURACY^{d} (%)
benzene	40	9.57 ± 0.12^{L}	11	10.54^{*e}	1.3	9.2
	25	8.49 ± 0.09^{L}	11	9.32 ± .149^{f}, 9.467^{e}	1.0	8.9, 10.3
	25	8.25 ± 0.34	9		4.1	
	10	7.89 ± 0.10^{L}	11		1.3	
	-5	7.18 ± 0.07^{L}	11		0.9	
toluene	40	8.19 ± 0.24^{L}	11	9.23^{*e}	2.9	11.3
	25	6.98 ± 0.13^{L}	10	8.49 ± .114^{f}	1.9	17.8
	10	5.80 ± 0.24^{L}	10		4.2	
	-5	4.07 ± 0.59^{L}	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	

benzo(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	40	6.99 ± 0.26	7		3.8	
	25	6.28 ± 0.28	7		4.4	
				Ave =	3.6	11.5

[*] corrected by equation (3.3) to experimental temperatures
[L] direct liquid injection into GC
[a] mean ± standard deviation
[b] number of experimental measurements
[c] coefficient of variation; relative standard deviation
[d] % deviation between measured and literature values
[e] data from Fuller, et al., (1966)
[f] data from Lugg (1968)

level of significance (Appendix III).

Molecular diffusivities of the selected organic chemicals in air were found to increase with temperature (Table 3.1, Appendix IV). The logarithms of the measured diffusivities for all compounds investigated in this study were found to vary linearly with temperature. The resultant regression lines for all compounds had an average slope of $3.32(10^{-3}) \pm 1.12(10^{-3})$. The increase in gas-phase diffusivity with temperature is expected from the combination of the ideal gas equation with the kinetic theory of gases which when combined, state that 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 molecular size. The logarithm of the measured diffusion coefficient was found to vary linearly with the logarithm of the molar volume (V) for all compounds studied (Figure 3-2). Plots of log D versus log V for all compounds investigated resulted in linear regression coefficients ranging from 0.614 at 25°C to 0.652 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 (Cloete et

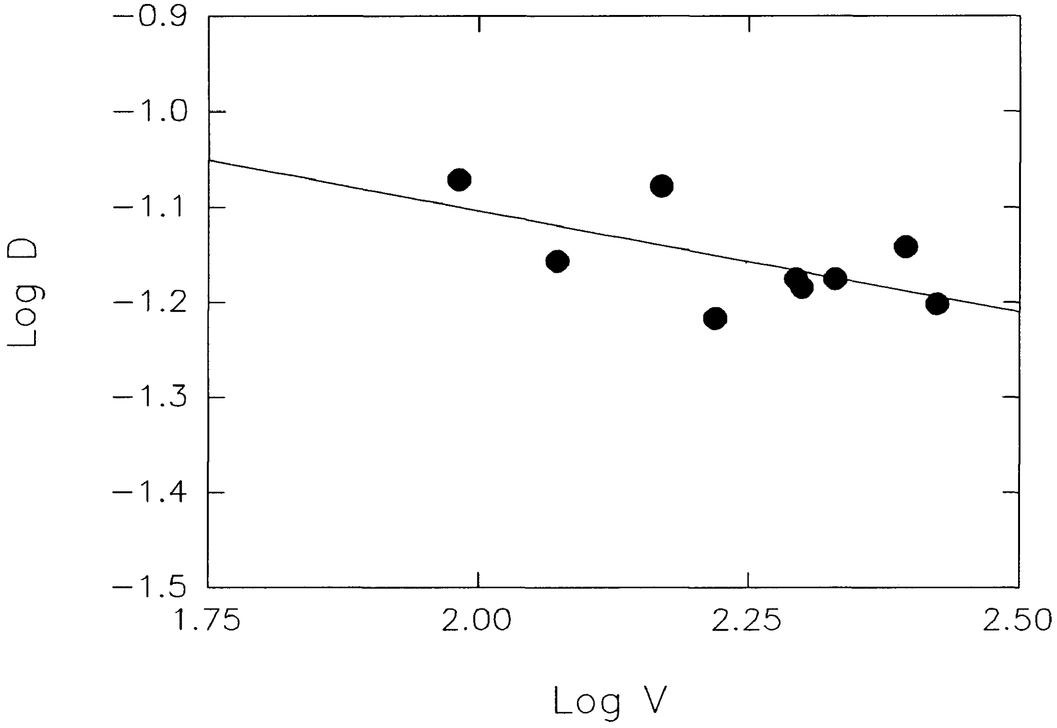


FIGURE 3-2: Relationship between molar volume and diffusivity in air at 25°C

al. 1976; Fuller et al. 1966; Pathak et al. 1981; Skelland, 1985). One of the goals of this work was to evaluate and update equations for predicting the molecular diffusivities of PAHs in air. The recommended equation for predicting molecular diffusivity in air is the Fuller, Schettler, and Giddings (FSG) correlation (Lyman et al. 1983). The FSG correlation is a revised form of the theoretically derived Chapman and Enskong equation on which most predictive equations are based (Fuller et al. 1966).

Measured diffusion coefficients for compounds in this study were compared to predicted values from the FSG correlation and the method of Wilke and Lee (Lyman et al. 1983)(Table 3.2). 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 3.2). However, predicted diffusivities for PAHs in air were found to deviate exponentially from measured values with increasing molecular size (Figure 3-3) and error in estimated gas-phase D values generally increased as temperature decreased (Table 3.2). Therefore, a new equation is proposed to accurately predict the molecular diffusivities of PAHs in air.

The terms for the revised predictive equation are the slope and inverse logarithm of the intercept of a plot of log D versus log V (Hayduk et al. 1974) and the average difference between intercepts of all regression plots of log

TABLE 3.2: Experimental and Predicted Diffusivities of selected Aromatic Chemicals in Air

				Percent absolute error between experimental and predicted D		
Compound	Temperature (°C)	Experimental (cm^2/s)	Predicted this work (cm^2/s)	This Work	FSG	Wilke-Lee
benzene	40	.0957	.0909	5.0	1.8	10.8
	25	.0849	.0796	6.3	5.3	13.9
	10	.0789	.0682	13.5	3.6	11.2
	-5	.0718	.0568	20.8	3.4	10.1
toluene	40	.0819	.0870	6.3	8.6	15.0
	25	.0698	.0761	9.1	16.9	23.0
	10	.0580	.0652	12.5	28.6	34.2
	-5	.0407	.0544	33.5	66.4	72.0
naphthalene	40	.0921	.0830	9.9	15.3	12.3
	25	.0836	.0726	13.1	16.1	13.8
acenaphthylene	40	.0669	.0809	21.0	8.3	8.8
	25	.0607	.0708	16.6	9.5	9.0
anthracene	40	.0804	.0781	2.9	19.1	19.0
	25	.0669	.0683	2.1	10.8	11.4
	10	.0639	.0585	8.3	14.6	16.1
	0	.0591	.0520	11.9	13.3	15.5
phenanthrene	40	.0778	.0778	< 0.1	16.4	16.8
	25	.0654	.0681	4.2	8.8	9.9
	10	.0610	.0584	4.3	10.6	12.7
pyrene	40	.0776	.0767	1.2	14.7	21.2
	25	.0668	.0671	0.5	14.0	16.7
	10	.0697	.0575	17.4	24.6	27.8
	0	.0624	.0511	18.1	21.0	25.0
benzo(a) anthracene	40	.0793	.0743	6.4	28.2	29.5
	25	.0722	.0650	10.0	27.6	29.6
	10	.0718	.0557	22.4	33.4	36.0
benzo(e) pyrene	40	.0699	.0732	4.8	19.9	*
	25	.0628	.0549	2.0	18.2	*
			average	10.1	17.1	20.1

* -boiling point temperatures needed for Wilke-Lee method not available

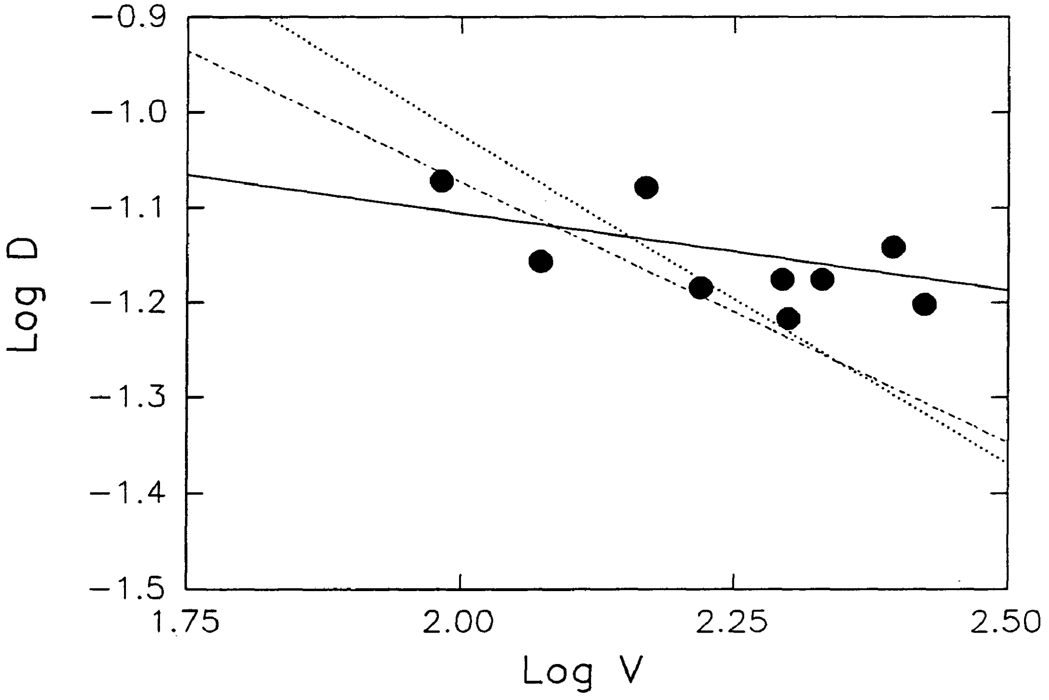


FIGURE 3-3: Relationship between experimental data (●) and predicted diffusivities in air at 25°C. (——) This work, (- - -) FSG, (·····) Wilke-Lee

D vs T for the compounds investigated. The revised equation resulting from this study:

$$D = (0.1603 + (0.002*T))/V^{.213} \qquad (3.6)$$

where T (temperature- °C), resulted in a reduction of the absolute error between predicted and measured molecular diffusivities from 17.1% to 10.1% for the compounds studied (Table 3.2). The mean absolute error for the revised gas-phase diffusivity predictive equation is comparable to the overall accuracy of the data (11.5% - Table 3.1).

SUMMARY AND CONCLUSIONS

Molecular diffusion coefficients for benzene, toluene, and selected PAHs in air at temperatures ranging from -5°C 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%.

The predictive equations of Wilke and Lee (1955) and Fuller et al. (1966) overestimate the diffusivities of the smaller compounds (log V < 2) and underestimate the diffusivities of the larger 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.

Molecular diffusivities in air for all compounds studied decreased exponentially with molecular size, and increased linearly with temperature. The results illustrate that large differences in diffusivity occur between compounds and with changing environmental conditions (i.e. temperature).

CHAPTER 4: SUMMARY

Molecular diffusion coefficients for benzene, toluene, and selected PAHs in aqueous solutions at temperatures ranging from 4°C to 40°C have been measured using an open-tube elution method; diffusivities in air at temperatures ranging from -5°C to 40°C have been measured using an arrested flow elution method. The experimentally determined diffusivities are in good agreement with literature values.

Aqueous molecular diffusivities for all compounds studied decreased exponentially with solvent viscosity and molecular size; no significant effect of salinity on D_{sw} was observed. Molecular diffusivities in air for all compounds studied decreased exponentially with molecular size, and increased linearly with temperature.

The results illustrate that large differences in molecular diffusivity occur between compounds and with changing environmental conditions (i.e. temperature). As outlined in Chapter 1, volatile/absorptive flux of a chemical across the air-water interface is highly dependent upon temperature sensitive parameters (i.e. diffusivity, Henry's law constant), windspeed, and concentration gradients, all of which vary seasonally and with climate. As temperature increases, the molecular diffusion coefficient and Henry's law constant of a compound increase, the Schmidt number decreases, and the mass transfer coefficients in air and water increase. Therefore, the volatile flux of a compound would be expected to increase. Similarly, as windspeed increases, the mass transfer coefficients in air and water also increase; thus, the volatile flux would also be expected to increase. However, since the volatile flux of a chemical across the air-water interface is a function of temperature, windspeed, and concentration gradients, which vary seasonally, the actual extent, quantitatively, to which volatile fluxes will be affected by molecular diffusion is difficult to predict unless local environmental conditions and solute concentrations in air and water are known.

Nonetheless, the magnitude and direction of air-water vapor transfer would be expected to change with a change in season and climate. For example, as a chemical is transferred to cooler climates, the temperature change lowers both the molecular diffusivity and Henry's law constant of the compound of interest. Therefore, compounds with relatively high Henry's law constants would be expected to volatilize but at a slower rate than that which would occur in warmer climates. Furthermore, the direction of fluxes due to vapor transfer, for compounds with low Henry's law constants, might be expected to switch directions relative to volatile fluxes in warmer climates, and become absorptive fluxes. Together, the combined effects of changing environmental conditions, with both season and climate on the chemical mass transfer coefficient, indicate that the "grasshopper" scenario is not a simple two dimensional process.

Experimental data from this work were used to modify the predictive equation of Othmer and Thakar (1953) to more accurately estimate the molecular diffusion coefficients of PAHs in aqueous solution. Additionally, experimental data generated from this work were used to formulate a predictive equation to accurately estimate the molecular diffusion coefficients for PAHs in air. Experimentally measured PAH molecular diffusivity data and validated predictive equations provide valuable and necessary physical-chemical property data. Through the calibration and formulation of predictive equations, the effects of environmental variables (temperature and salinity) on molecular diffusivity have been quantitatively determined. The updated and validated predictive equations that are a result of this study will allow for modeling behavior characteristics (i.e. mass transfer coefficients) of other related organic compounds under environmentally realistic conditions.

Finally, it is proposed that, due to hydrophobic that PAHs may associate in aqueous solution due to hydrophobic interactions has significant implications for environmental processes. The formation of PAH dimer and trimer complexes magnifies the effective molar volume of these species; many reaction and diffusive transport processes such as microbial degradation, volatilization, sediment pore water exchange, and bioconcentration depend on molecular size. Hence, the rates of many environmental, chemical fate and transport processes may be modified.

The experimentally measured aqueous molecular diffusion coefficients for the larger three and four ring PAHs are slower than predicted values. However, because the measured diffusivities of these proposed complexes are slower, but within a factor of two when compared to predicted values, the net diffusive mass flux on a per mole basis would actually be higher for these compounds if they exist as associated dimer complexes. Furthermore, to an extent, as molecular size increases, the likelihood of association (dimer formation) due to hydrophobic interactions increases. Therefore, it is also possible that the formation of associated complexes (dimers) may influence membrane transport on a size exclusion basis as well as a diffusive mass flux basis.

GLOSSARY

activity coefficient-a factor which when multiplied by the molecular concentration, yields the active mass (a correction factor which makes thermodynamic calculations correct).

bulk reservoir-The well (turbulently) mixed phases on either side of an interface separated by a boundry layer.

dimer-A complex composed of two like structures or molecules (a pair).

entropy- the capacity factor for isothermally unavailable energy. the increase in the entropy of a body during an infinitesimal stage of a reversible process is equal to the infinitesimal amount of heat absorbed divided by the absolute temperature of the body.

entropy of solution (mixing)- After mixing, the difference between the entropy of the solution and the sum of the entropies of the components, of the mixture.

"grasshopper" scenario- refers to the successive deposition and reemission (volatilization) of a semivolatile compound in a polarly direction to cooler climates.

Henry's law constant (H)-A proportionality constant which relates the partial pressure of a substance over a liquid to the solubility of that substance in the liquid.

hydrophobic interaction- the relative tendency of hydrophobic solute particles to aggregate as a result of the increase in entropy and reduction of free energy provided by loss of part of the ordered water structure around the solute particles as the particles come into close contact.

laminar flow-streamline flow of an incompressible, viscous, newtonian fluid; all particles of the fluid move in distinct and separate lines.

molar volume (V)- the volume (cm^3) one mole of a substance occupies at its normal boiling temperature under one atmosphere of pressure

molecular diffusion-The net transport of a molecule in a medium as a result of intermolecular collisions rather than turbulence or bulk transport

molecular diffusion coefficient (D)- a physical chemical property of the solute as well as the medium through which it moves; by Fick's law the molecular diffusion coefficient is equal to the net molal flux of a solute across a hypothetical plane divided by the concentration gradient of the solute at the hypothetical plane.

overall mass transfer coefficient (K_{ol})- kinetic parameter (units of velocity, m/d) quantifies the rate of transfer- dependent upon physical and chemical properties of the compound as well as environmental conditions.

poiseuille flow-the steady flow of an incompressible fluid parallel to the axis of a circular pipe of infinite length produced by a pressure gradient along the pipe (i.e. parabolic laminar flow).

polycyclic aromatic hydrocarbons (PAH) -a class of hydrocarbons containing two or more fused aromatic ring structures

schimdt number (Sc)-ratio of the kinematic viscosity of a fluid to the molecular diffusivity of a substance in that fluid; relates the relative thickness of the diffusive and viscous sublayers which govern mass transfer across a boundry layer at an interface

solvent viscosity (μ)-dynamic or molecular viscosity, a resistance to change of form, an internal friction, dimensions [$ml^{-1}t^{-1}$]

trimer-a complex composed of three like structures (i.e. three PAH molecules)

vapor pressure-the pressure exerted when a solid or liquid is in equilibrium with its own vapor

volatile flux (F_{vol})- the mass flux of a substance from a surface due to volatilization.

APPENDIX I

Phenanthrene Aqueous Diffusivity Experiment

Run#	Temp	Sal	Conc	D(aq)	Yate's Algorithm		
1	-	-	-	3.865e-6	.0000088	.0000176	.00000354
2	+	-	-	4.946e-6	.0000088	.0000179	.00000074
3	-	+	-	3.187e-6	.0000089	.0000035	-4.2e-8
4	+	+	-	5.567e-6	.0000089	.0000039	.00000025
5	-	-	+	3.783e-6	.0000011	-5.7e-8	.00000003
6	+	-	+	5.142e-6	.0000024	1.5e-8	.00000005
7	-	+	+	3.183e-6	.0000014	.0000013	.00000001
8	+	+	+	5.757e-6	.0000026	.0000012	-8.4e-8

ID	Level		Variable
	-	+	
Temp	4°C	40°C	Temperature
Sal	0ppt	35ppt	Salinity
Conc	12%	50%	conc. (%sat)

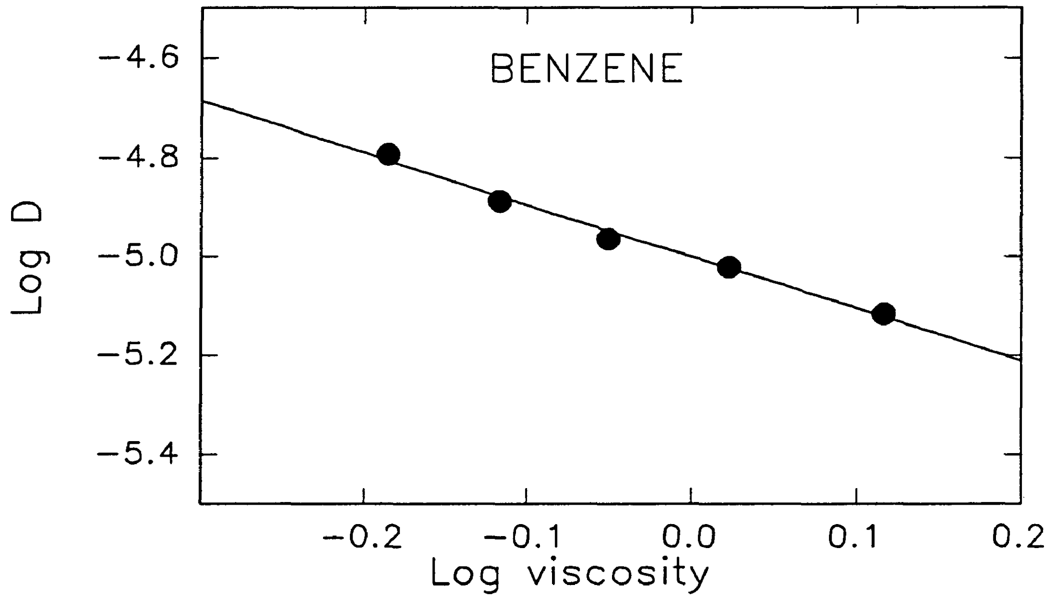
Standard Error of Effects
-calculated from replicate runs and controls

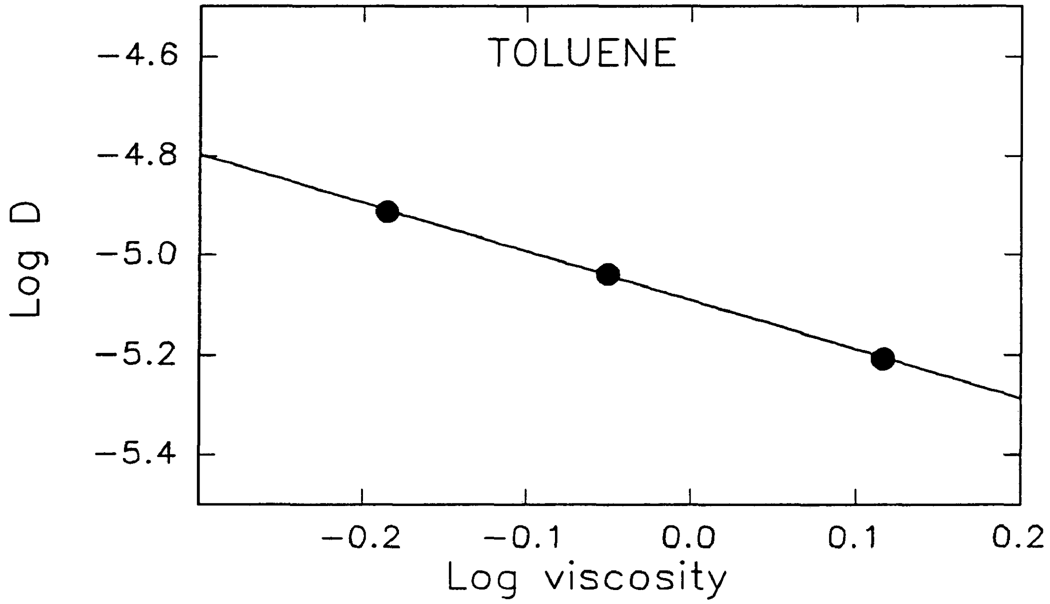
Run#	Variance	Square
1	2.636e-7	6.95e-14
2	6.441e-7	4.15e-13
3	3.691e-7	1.36e-13
4	1.288e-6	1.66e-12
5	2.804e-7	7.86e-14
6	3.252e-7	1.06e-13
7	7.673e-7	5.89e-13
8	3.856e-7	1.49e-13

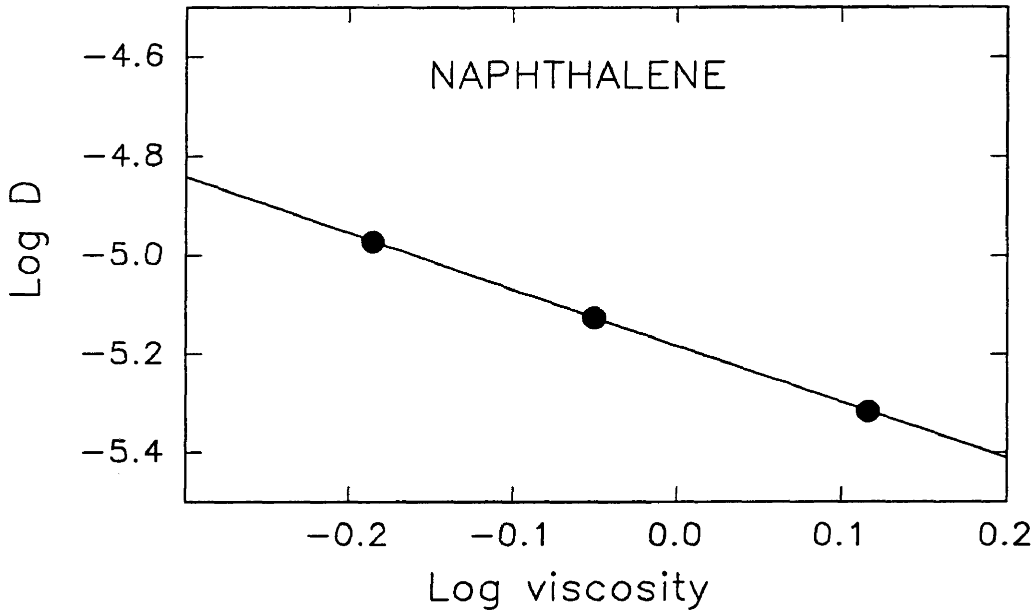
s^2 3.20e-13
V(effect) 8.00e-14
std error 2.829e-7

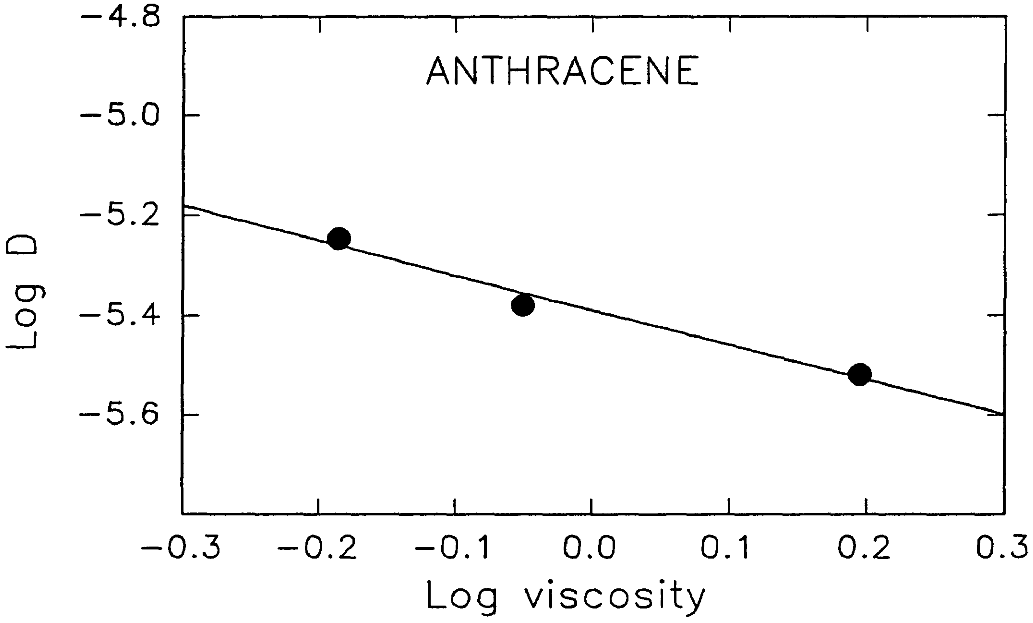
Divisor	Estimate	ID
8	4.429e-6	AVE
4	1.849e-6	Temp
4	-1.05e-8	Sal
4	6.285e-7	TempSal
4	7.5e-8	Conc
4	1.18e-7	TempConc
4	1.8e-8	SalConc
4	-2.1e-8	TSC

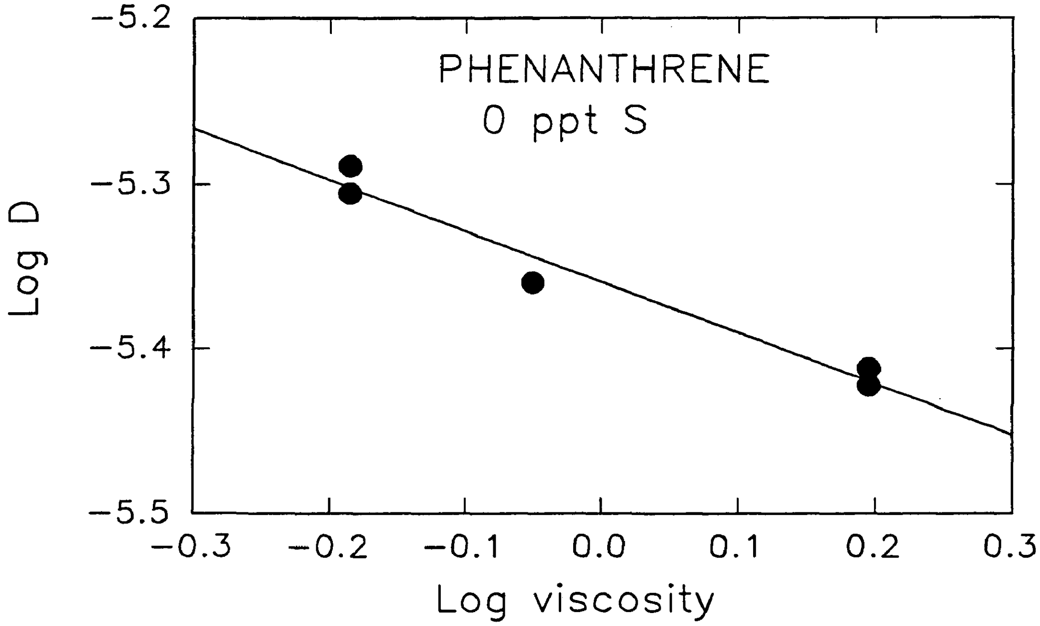
APPENDIX II: Illustration of the direct relationship between solvent viscosity and aqueous diffusivity

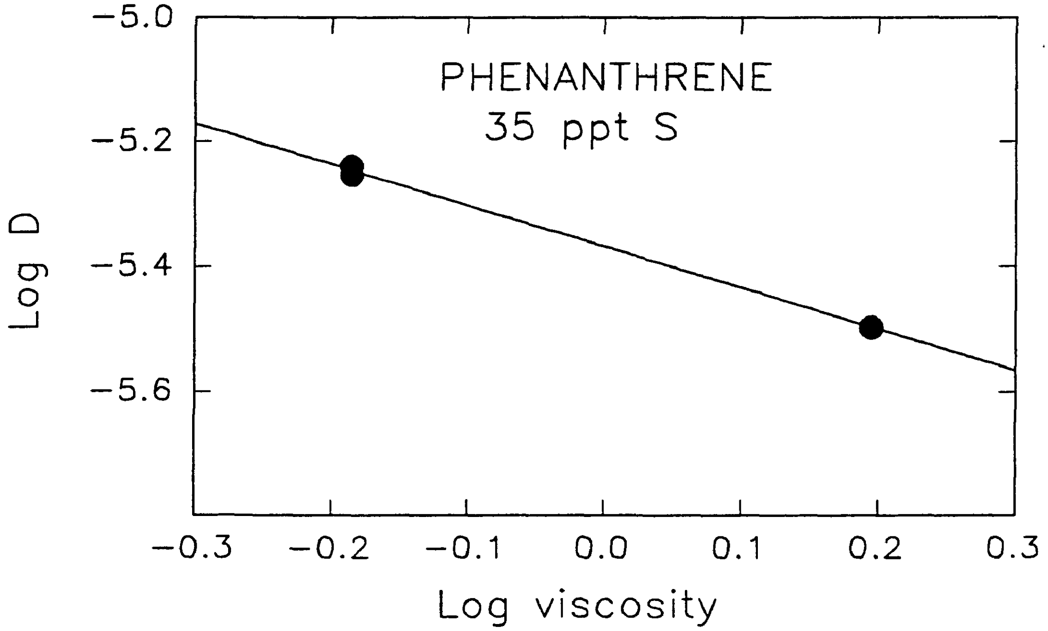


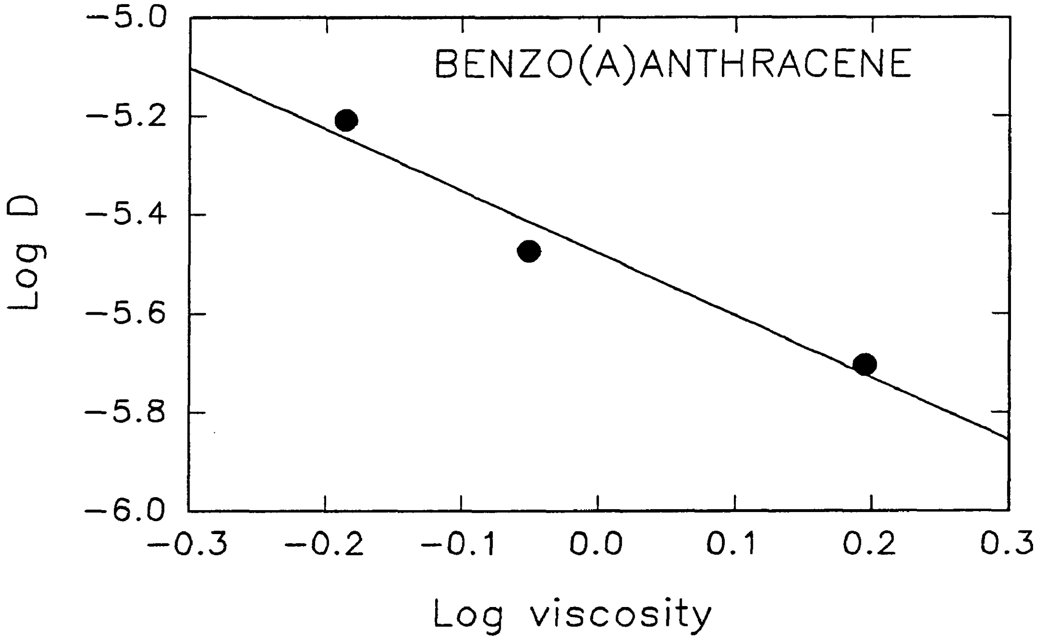



NAPHTHALENE
Log D
−4.6
−4.8
−5.0
−5.2
−5.4
−0.2
−0.1
0.0
0.1
0.2
Log viscosity


ANTHRACENE
Log D
−4.8
−5.0
−5.2
−5.4
−5.6
−0.3
−0.2
−0.1
0.0
0.1
0.2
0.3
Log viscosity


PHENANTHRENE
0 ppt S
Log D
−5.2
−5.3
−5.4
−5.5
−0.3
−0.2
−0.1
0.0
0.1
0.2
0.3
Log viscosity


PHENANTHRENE
35 ppt S
Log D
−5.0
−5.2
−5.4
−5.6
−0.3
−0.2
−0.1
0.0
0.1
0.2
0.3
Log viscosity


BENZO(A)ANTHRACENE
Log D
-5.0
-5.2
-5.4
-5.6
-5.8
-6.0
-0.3
-0.2
-0.1
0.0
0.1
0.2
0.3
Log viscosity

APPENDIX III

Statistical analysis for the determination of independence of injection method on diffusivity measurement in air

$X_1 = 0.0825$ $SS_1 = 0.0034$ $n_1 = 11$ $v_1 = 10$
$X_2 = 0.0849$ $SS_2 = 0.0009$ $n_2 = 9$ $v_2 = 8$

t-Test:

H_o: Determination of diffusivities do not differ among injection methods;

H_a: Determination of diffusivities do differ among methods;

N = 20, = .05, two tailed test

$Sp^2 = (0.0034 + 0.0009)/20 = 2.15(10)^{-4}$

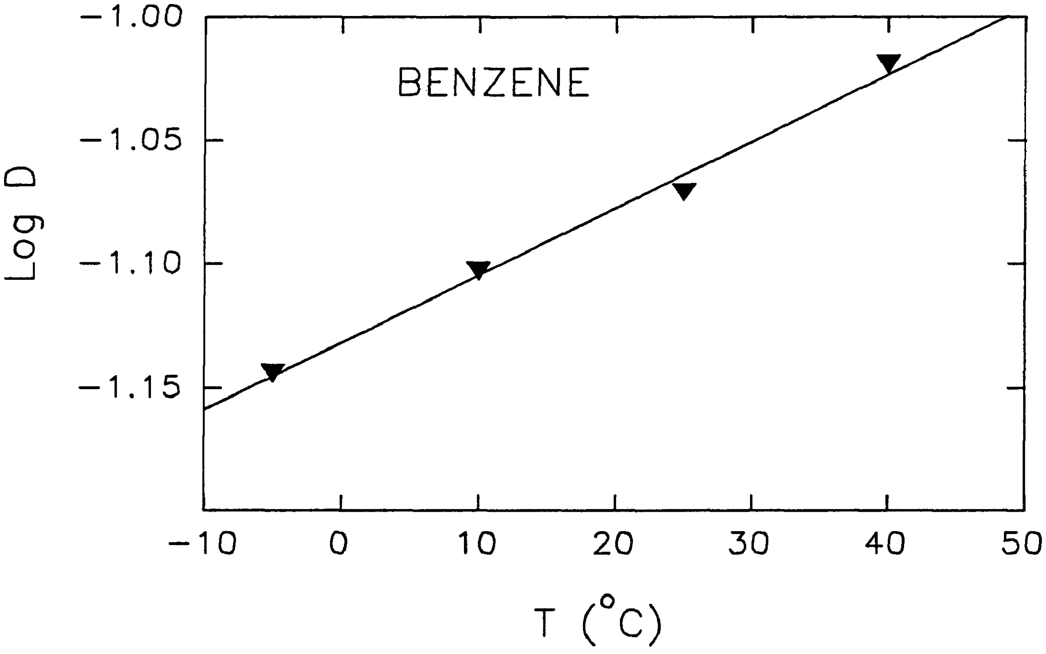
$Sx_1 - x_2 = ((Sp^2/n_1) + (Sp^2/n_2))^{1/2} = 6.59(10)^{-3}$

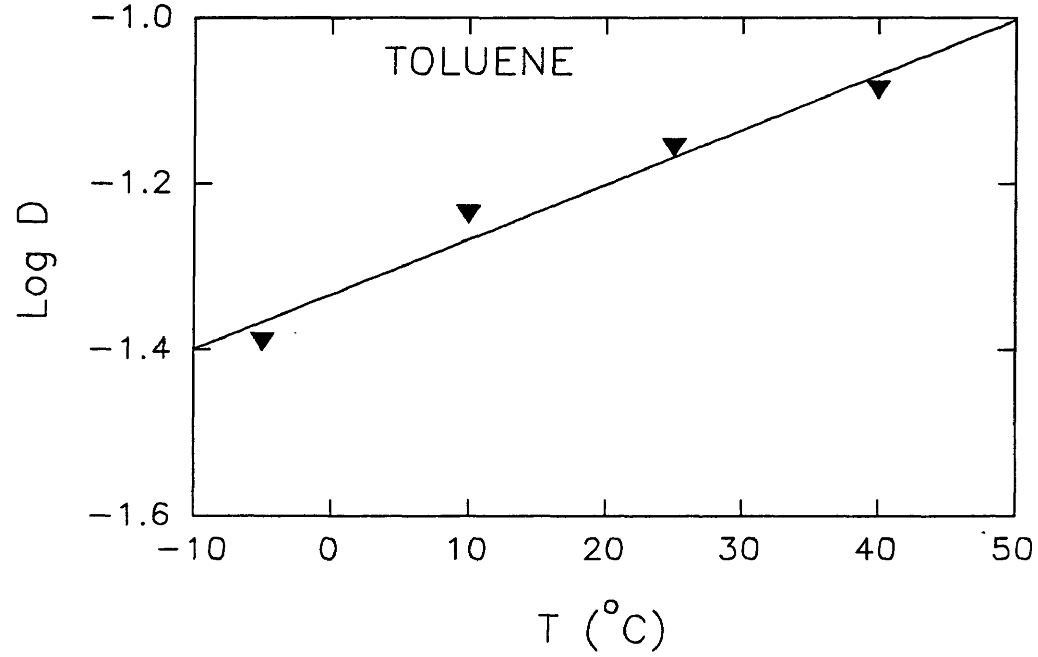
$t = (X_1 - X_2)/Sx_1 - x_2 = 0.364$

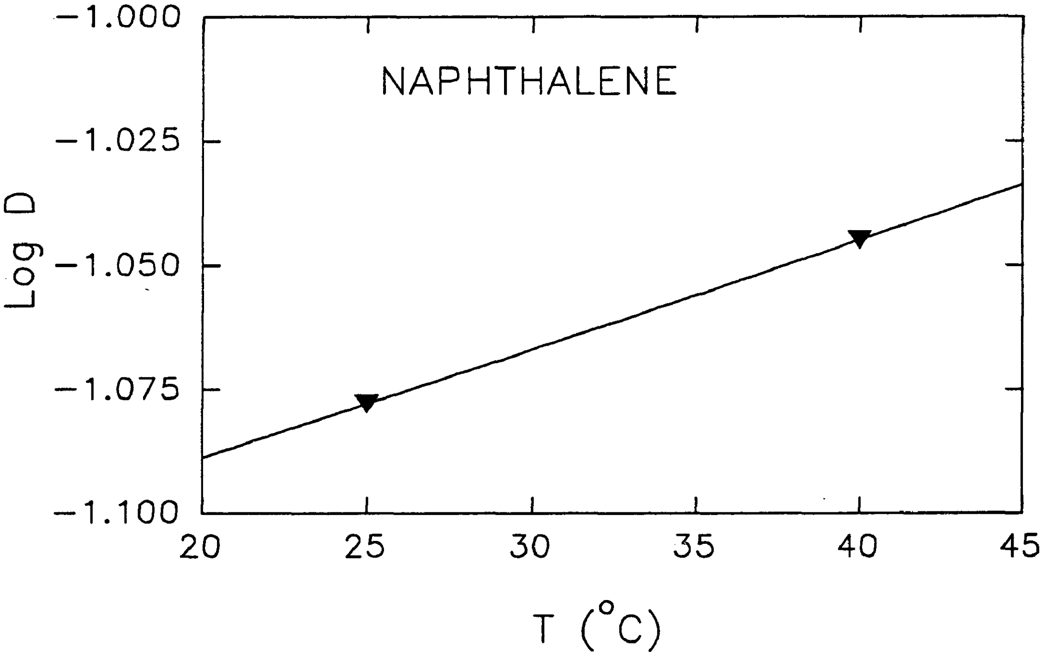
$t_{.05(2),18} = 2.101$

Therefore do not reject H_o. Measurement of molecular diffusion coefficients do not differ among liquid or vapor injection methods unless a type II error was committed.

APPENDIX IV: Illustration of the direct relationship between temperature and diffusivity in air






NAPHTHALENE
Log D
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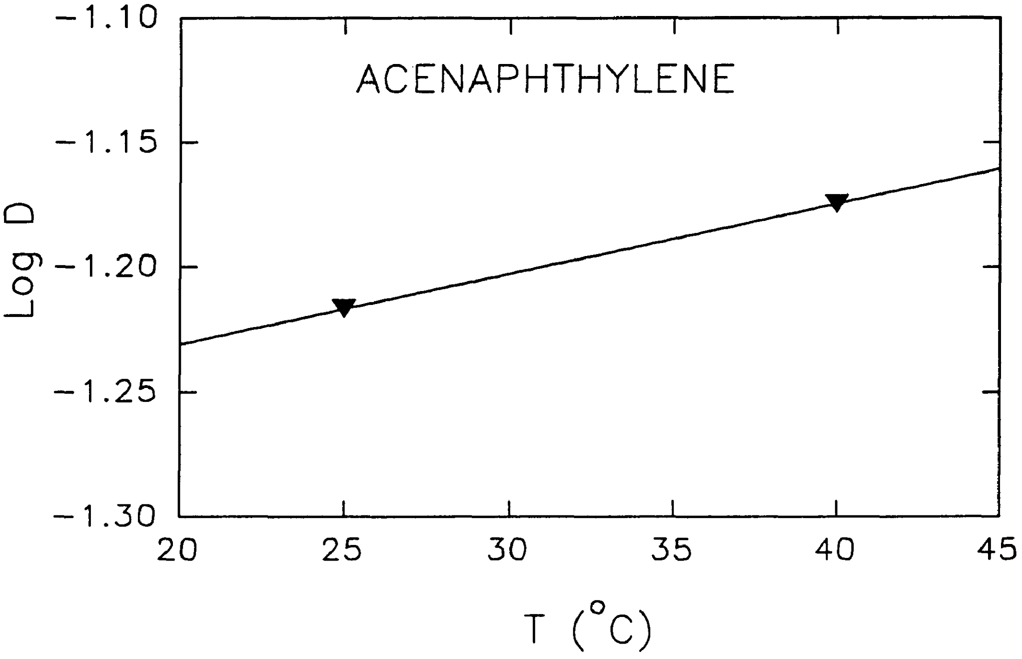
-1.025
-1.050
-1.075
-1.100
20
25
30
35
40
45
T (°C)


ACENAPHTHYLENE
Log D
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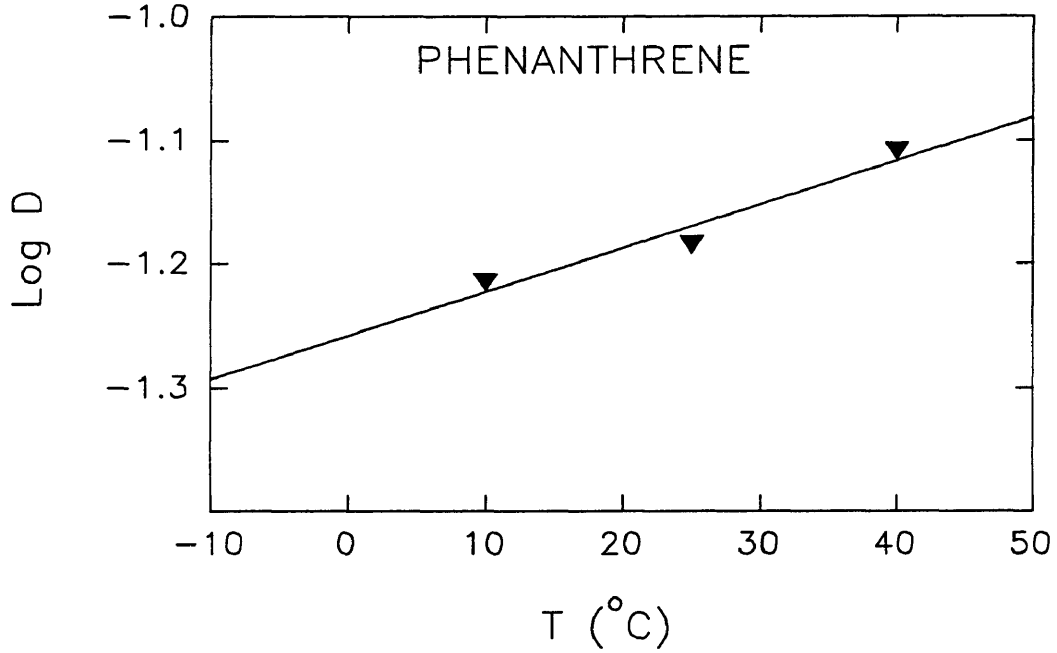
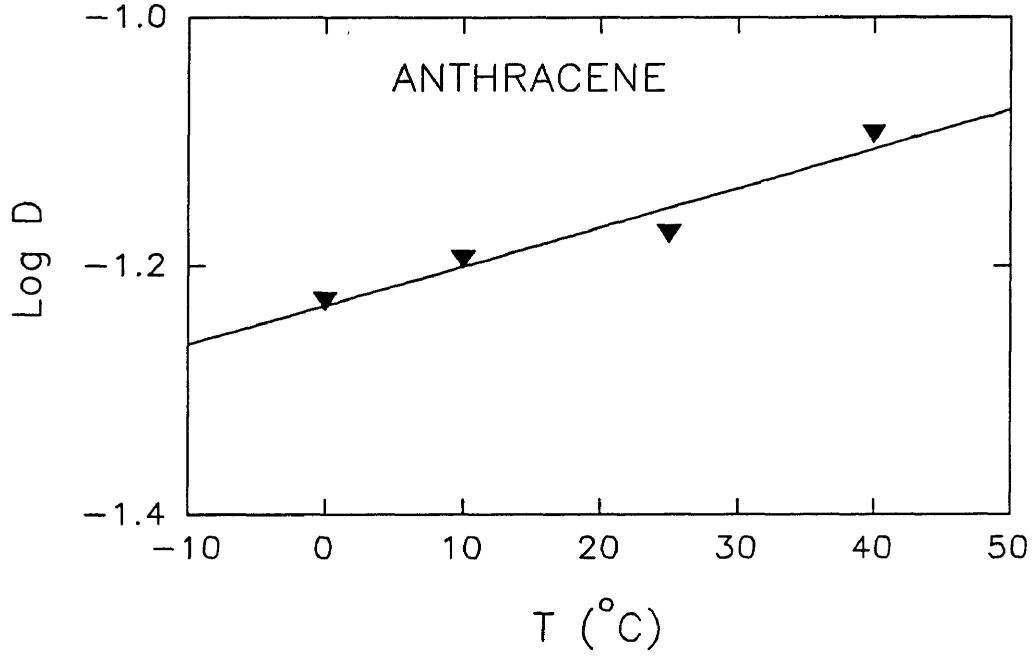
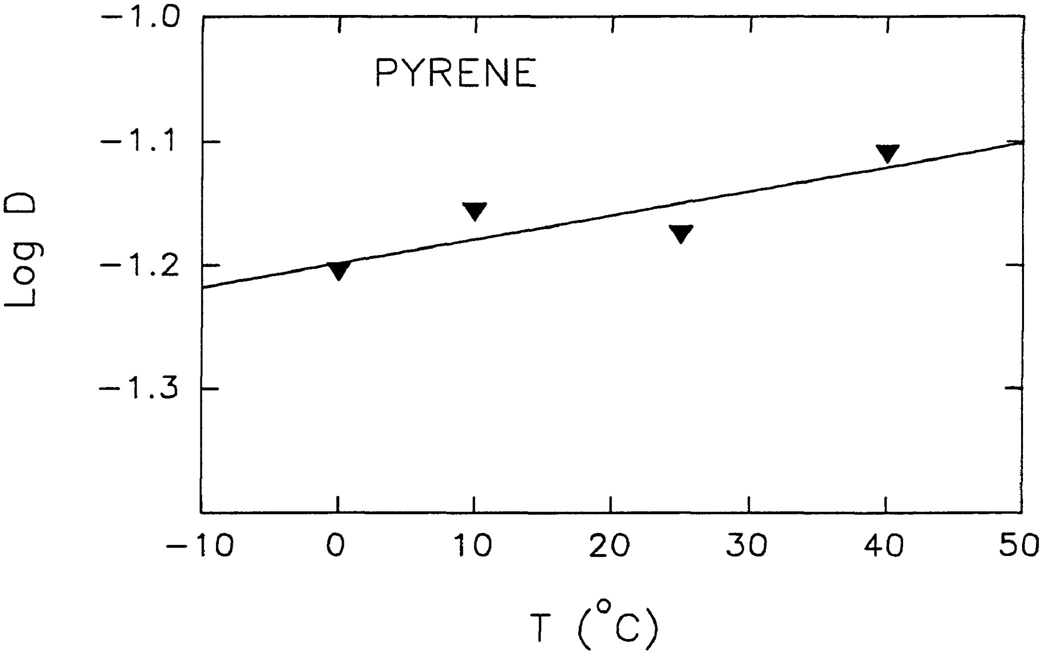
-1.15
-1.20
-1.25
-1.30
20
25
30
35
40
45
T (°C)


PHENANTHRENE
Log D
−1.0
−1.1
−1.2
−1.3
−10
0
10
20
30
40
50
T (°C)


ANTHRACENE
Log D
−1.0
−1.2
−1.4
−10
0
10
20
30
40
50
T (°C)


PYRENE
Log D
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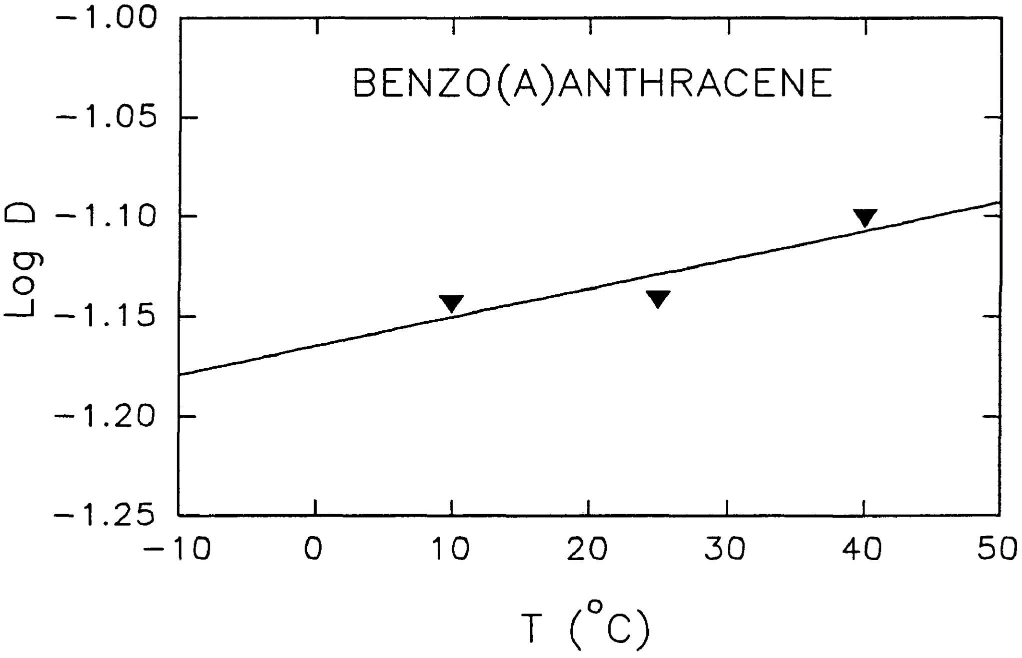
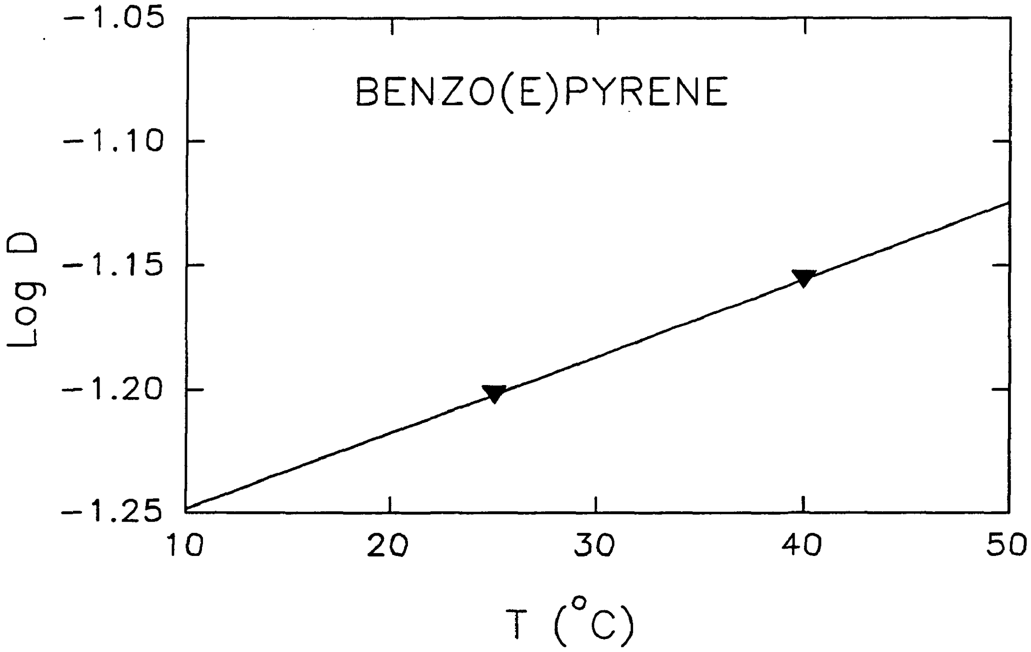
−1.1
−1.2
−1.3
−10
0
10
20
30
40
50
T (°C)


BENZO(A)ANTHRACENE
Log D
−1.00
−1.05
−1.10
−1.15
−1.20
−1.25
−10
0
10
20
30
40
50
T (°C)


BENZO(E)PYRENE
Log D
−1.05
−1.10
−1.15
−1.20
−1.25
10
20
30
40
50
T (°C)

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