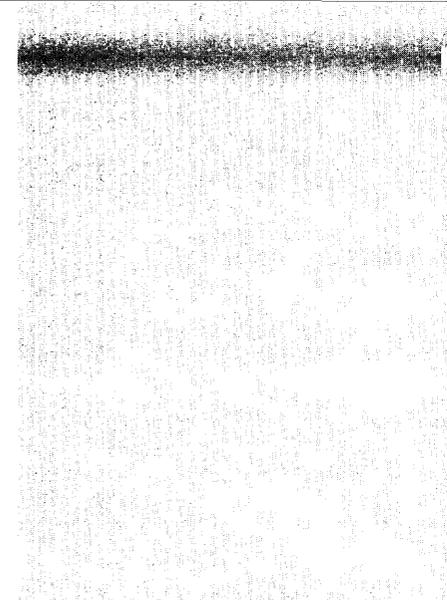


Volatilization of Benzene and Eight Alkyl-Substituted Benzene Compounds from Water



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Volatilization of Benzene and Eight Alkyl-Substituted Benzene Compounds from Water

By R.E. RATHBUN and D.Y. TAI

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CONTENTS

Abstract	1
Introduction	1
Background theory	2
Experimental procedure	3
Results and analysis of the volatilization of benzene compounds from water	5
Experimental ϕ values	5
Evaluation of the ϕ -estimation procedures	6
Molecular-diffusion-coefficient procedure	6
Molecular-weight procedure	8
Analysis of deviations from the estimation procedures	9
Water solubility	10
Deviations of the high-molecular-weight compounds	12
Deviations of the low-molecular-weight compounds	14
Henry's law constants	15
Percentage resistance in the liquid film	17
Discussion	19
Application	20
Summary and conclusions	21
References	22

FIGURES

- 1-11. Graphs showing liquid-film coefficients for the volatilization of specific organic compounds as a function of the liquid-film coefficient for oxygen absorption:
1. Benzene 6
 2. Toluene 6
 3. Ethylbenzene, group 1 experiments 6
 4. Ethylbenzene, group 2 experiments 6
 5. n-Propylbenzene 7
 6. n-Butylbenzene, group 2 experiments 7
 7. n-Butylbenzene, group 3 experiments 7
 8. n-Pentylbenzene 7
 9. n-Hexylbenzene 8
 10. n-Heptylbenzene 8
 11. n-Octylbenzene 8
- 12-21. Graphs showing:
12. ϕ values as a function of molecular-diffusion coefficient 9
 13. ϕ values as a function of molecular weight 10
 14. Water-solubility as a function of molecular surface area for benzene through n-hexylbenzene 11
 15. Water-solubility as a function of molar volume for benzene through n-hexylbenzene 12
 16. Reciprocal values of water solubility as a function of normal boiling temperature for benzene through n-hexylbenzene 12
 17. Values of the factor $k_E A_s / V$ as a function of solubility for n-hexylbenzene, n-heptylbenzene, and n-octylbenzene 14
 18. Vapor pressures at 298.2 K as a function of molecular surface area 16
 19. Vapor pressures at 298.2 K as a function of normal boiling temperature 16
 20. Vapor pressures at 298.2 K as a function of molar volume 17
 21. Henry's law constants as a function of molar volume 17

TABLES

1. ϕ ratios determined by the linear regression of the experimental data and errors of the regressions 9
2. Mean values of water solubility at 298.2 K for benzene through n-hexylbenzene, number of values used to compute the mean values, and coefficients of variation 11
3. Estimated values of water solubility at 298.2 K for n-heptylbenzene and n-octylbenzene, mean values, and coefficients of variation 13
4. ψ ratios, gas-film coefficients, maximum and minimum experimental liquid-film coefficients, and percentage resistances in the liquid film 19
5. Parameters for the calculation of the distance downstream required for 99-percent decrease in concentration of four compounds by volatilization 21

Conversion Factors

The following factors may be used for converting the International System of Units (SI) of measure used in this report to inch-pound units.

Multiply SI unit	By	To obtain inch-pound unit
millimeter (mm)	0.03937	inch
meter (m)	3.281	foot
meter per minute (m/min)	3.281	foot per minute
meter per day (m/d)	3.281	foot per day
kilometer (km)	0.6214	mile
kilometer per day (km/d)	3,281	foot per day
square nanometer (nm ²)	10.76×10^{-18}	square foot
square meter (m ²)	10.76	square foot
square meter per day (m ² /d)	10.76	square foot per day
cubic meter (m ³)	35.31	cubic foot
liter (L)	3.531×10^{-2}	cubic foot
milliliter (mL)	3.531×10^{-5}	cubic foot
milliliter per gram mole (mL/g mol)	1.602×10^{-2}	cubic foot per pound mole
milligram per liter (mg/L)	6.243×10^{-5}	pound per cubic foot
microgram per liter ($\mu\text{g/L}$)	6.243×10^{-8}	pound per cubic foot
gram per gram mole (g/g mol)	1.000	pound per pound mole
gram per milliliter (g/mL)	62.43	pound per cubic foot
microgram per square meter ($\mu\text{g/m}^2$)	2.048×10^{-10}	pound per square foot
kilopascal (kPa)	101.325	standard atmosphere
kilopascal cubic meter per gram mole (kPa m ³ /g mol)	158.1	standard atmosphere cubic foot per pound mole
kilopascal cubic meter per gram mole per kelvin [(kPa m ³ /g mol)/K]	87.83	standard atmosphere cubic foot per pound mole per degree Rankine

Temperature in kelvins (K) may be converted to degrees Celsius ($^{\circ}\text{C}$) as follows:

$$^{\circ}\text{C} = \text{K} - 273.15$$

Temperature in kelvins (K) may be converted to degrees Rankine ($^{\circ}\text{R}$) as follows:

$$^{\circ}\text{R} = (\text{K} - 273.15)(1.8) + 491.7$$

Temperature in kelvins (K) may be converted to degrees Fahrenheit ($^{\circ}\text{F}$) as follows:

$$^{\circ}\text{F} = (\text{K} - 273.15)(1.8) + 32.0$$

SYMBOLS AND DEFINITIONS

A_s	Surface area for sorption, in square meters.
A_v	Surface area for volatilization, in square meters.
a_G	Constant in the equation relating the gas-film coefficient to the molecular-diffusion coefficient in air, in meters to the $(1-2\nu)$ power times days to the $(\nu-1)$ power.
a_L	Constant in the equation relating the liquid-film coefficient to the molecular-diffusion coefficient in water, in meters to the $(1-2\eta)$ power times days to the $(\eta-1)$ power.
b_L	Constant in the equation relating the liquid-film coefficient to the molecular weight, in meters per day times grams per gram mole to the 0.500 power.
C	Concentration of the organic compound or oxygen in the water at time t , in micrograms per liter or milligrams per liter.
C_E	Concentration of the organic compound or oxygen in the water in equilibrium with the concentration of the organic compound or oxygen in the air above the water, in micrograms per liter or milligrams per liter.
C_I	Concentration of the organic compound in the stream at the point of addition, in micrograms per liter.
C_0	Concentration of the organic compound or oxygen in the water at time zero, in micrograms per liter or milligrams per liter.
D	Molecular-diffusion coefficient in water, in square meters per day.
D_{ORG}	Molecular-diffusion coefficient of an organic compound in water, in square meters per day.
D_{OXY}	Molecular-diffusion coefficient of oxygen in water, in square meters per day.
E	Normalized root-mean-square error of prediction for an equation, in percent.
exp	Indicates an exponential to the base e , dimensionless.
H	Henry's law constant, in kilopascals cubic meter per gram mole.
K_{OL}	Overall mass-transfer coefficient for volatilization based on the liquid phase, in meters per day.
k_E	Equilibrium partition coefficient for the continuous equilibrium between the concentration of an organic compound in solution and the concentration sorbed on the surfaces of the constant temperature bath, in meters.
k_G	Mass-transfer coefficient for the gas film, usually called the gas-film coefficient, in meters per day.
k_{GORG}	Gas-film coefficient for an organic compound, in meters per day.
k_{GWAT}	Gas-film coefficient for water, in meters per day.
k_L	Mass-transfer coefficient for the liquid film, usually called the liquid-film coefficient, in meters per day.
$k_{L,CALC}$	Liquid-film coefficient calculated from a regression equation, in meters per day.
$k_{L,EXP}$	Experimental value of the liquid-film coefficient, in meters per day.
$k_{L,ORG}$	Liquid-film coefficient for an organic compound, in meters per day.
$k_{L,OXY}$	Liquid-film coefficient for oxygen, in meters per day.
M	Molecular weight, in grams per gram mole.
M_{ORG}	Molecular weight of an organic compound, in grams per gram mole.
N	Concentration of an organic compound sorbed on the surfaces of the constant temperature bath, in micrograms per square meter.
n	Number of values in a summation, dimensionless.
P	Vapor pressure of the pure organic compound, in kilopascals.
R	Ideal gas constant, in kilopascals cubic meter per gram mole per kelvin.
rms	Root-mean-square, refers to the error E , dimensionless.
S	Water solubility, in milligrams per liter.
T	Temperature, in kelvins.
T_{bp}	Normal boiling temperature, in kelvins.
TSA	Molecular surface area, in square nanometers.
t	Time, in days.

U	Mean water velocity, in kilometers per day.
V	Volume of the water phase, in cubic meters.
V_{ORG}	Molal volume of the organic compound at the normal boiling temperature, in milliliters per gram mole.
V_{M}	Molar volume of the organic compound, in milliliters per gram mole.
X	Distance downstream from the point of addition of an organic compound, in kilometers.
Y	Water depth, in meters.
γ	Activity coefficient of an organic compound in water, dimensionless.
δ	Molecular-diffusion coefficient in air, in square meters per day.
δ_{ORG}	Molecular-diffusion coefficient of an organic compound in air, in square meters per day.
δ_{WAT}	Molecular-diffusion coefficient of water in air, in square meters per day.
η	Exponent on the molecular-diffusion coefficient in the relation between the liquid-film coefficient and the molecular-diffusion coefficient in water, dimensionless.
ν	Exponent on the molecular-diffusion coefficient in the relation between the gas-film coefficient and the molecular-diffusion coefficient in air, dimensionless.
ϕ	Constant in the reference substance concept for the liquid film, equal to the ratio of the liquid-film coefficient for the volatilization of an organic compound from water to the liquid-film coefficient for the volatilization of the reference substance from water; dimensionless.
ϕ_{A}	Apparent value of the reference substance constant observed in the presence of desorption of the organic compound from the surfaces of the constant temperature bath, dimensionless.
ϕ_{T}	True value of the reference substance constant in the absence of desorption of the organic compound from the surfaces of the constant temperature bath, dimensionless.
ψ	Constant in the reference substance concept for the gas film, equal to the ratio of the gas-film coefficient for the volatilization of an organic compound from water to the gas-film coefficient for the volatilization of the reference substance from water; dimensionless.

Volatilization of Benzene and Eight Alkyl-Substituted Benzene Compounds from Water

By R.E. Rathbun and D.Y. Tai

Abstract

Predicting the fate of organic compounds in streams and rivers often requires knowledge of the volatilization characteristics of the compounds. The reference-substance concept, involving laboratory-determined ratios of the liquid-film coefficients for volatilization of the organic compounds to the liquid-film coefficient for oxygen absorption, is used to predict liquid-film coefficients for streams and rivers. In the absence of experimental data, two procedures have been used for estimating these liquid-film coefficient ratios. These procedures, based on the molecular-diffusion coefficient and on the molecular weight, have been widely used but never extensively evaluated.

Liquid-film coefficients for the volatilization of benzene and eight alkyl-substituted benzene compounds (toluene through *n*-octylbenzene) from water were measured in a constant-temperature, stirred water bath. Liquid-film coefficients for oxygen absorption were measured simultaneously. A range of water mixing conditions was used with a water temperature of 298.2 K.

The ratios of the liquid-film coefficients for volatilization to the liquid-film coefficient for oxygen absorption for all of the organic compounds were independent of mixing conditions in the water. Experimental ratios ranged from 0.606 for benzene to 0.357 for *n*-octylbenzene.

The molecular-diffusion-coefficient procedure accurately predicted the ratios for ethylbenzene through *n*-pentylbenzene with a power dependence of 0.566 on the molecular-diffusion coefficient, in agreement with published values. Predicted ratios for benzene and toluene were slightly larger than the experimental ratios. These differences were attributed to possible interactions between the molecules of these compounds and the water molecules and to benzene-benzene interactions that form dimers. Because these interactions also are likely to occur in natural waters, it was concluded that the experimental ratios are more correct than the predicted ratios for application purposes in the reference-substance concept. Predicted ratios for *n*-hexylbenzene, *n*-heptylbenzene, and *n*-octylbenzene were larger than the experimental ratios. These differences were attributed to a sorption-desorption process between these compounds and the surfaces of the constant-temperature water bath. Other experimental problems associated with preparing water solutions of these slightly soluble compounds also may have contributed to the differences. Because these processes are not part of the true volatilization process, it was concluded that the predicted ratios for these three compounds are probably more correct than the experimental ratios for application purposes in the reference-substance concept. Any model of the fate of these compounds in streams and rivers would have to include terms accounting for sorption processes, however.

The molecular-weight procedure accurately predicted the ratios for ethylbenzene through *n*-pentylbenzene, but only if the power dependence on the molecular weight was decreased from the commonly used -0.500 to -0.427 . Deviations for the low- and high-molecular-weight compounds were similar to those observed for the molecular-diffusion-coefficient procedure.

INTRODUCTION

Organic compounds in the water bodies of the environment are subject to various chemical, biological, and physical processes. Possible chemical processes include hydrolysis, photolysis, complexation-dissociation, oxidation-reduction, and dissolution-precipitation. Possible biological processes include bacterial degradation and uptake and release by biota. Possible physical processes include sorption-desorption by sediments, volatilization, convective mass transport, and dispersion. The fate of an organic compound in a water body is determined by complex interactions of these processes.

However, not all of the processes are important for all compounds for all water bodies. The relative importance of the various processes depends on the characteristics of both the compound and the water body. Usually, only several of these processes will contribute significantly to fate determination for a specific compound in a specific water body.

Many of the organic compounds of environmental significance are low-molecular-weight, volatile compounds, and volatilization has been determined to be a significant process for these compounds (Smith and others, 1980; Rathbun and Tai, 1981, 1984a). In this context, volatilization is defined as the transfer of an organic compound from water across the water-air interface into the air.

Volatilization is generally described by the two-film model of mass transfer (Lewis and Whitman, 1924). The two-film model assumes uniformly mixed water and air phases separated by thin films of water and air in which mass transfer is by molecular diffusion. Equilibrium between concentrations in the water and partial pressures in the air is expressed by Henry's law.

An analysis of the two-film model (Mackay, 1977) has indicated, for compounds with Henry's law constants larger than about $0.1 \text{ kPa m}^3/\text{g mol}$, that most of the resistance to volatilization is in the liquid film. For these compounds, the overall mass-transfer coefficient for volatilization is virtually identical to the liquid-film coefficient of the two-film model and, therefore, the volatilization process is considered to be

liquid-film controlled. It has been suggested (Rathbun and Tai, 1981) that this situation prevails for many organic compounds of environmental significance.

Liquid-film coefficients for the volatilization of these compounds from streams and rivers are commonly estimated using the reference-substance concept with oxygen as the reference substance (Smith and others, 1980; Rathbun and Tai, 1981). This procedure requires the ratio of the liquid-film coefficient for volatilization of the compound from water to the liquid-film coefficient for oxygen absorption for the same water. Combining this ratio with the liquid-film coefficient for oxygen absorption for the stream or river gives the liquid-film coefficient for volatilization from the stream or river.

Values of this coefficient ratio can be measured in the laboratory or estimated using two procedures based on the molecular-diffusion coefficient and the molecular weight. These estimation procedures have been widely used but never extensively evaluated.

This report describes an evaluation of these estimation procedures and the reference-substance concept for liquid-film controlled volatilization from water. Laboratory measurements of the volatilization characteristics of benzene and a series of alkyl-substituted benzene compounds ranging from toluene to *n*-octylbenzene were used for this evaluation. It was expected that volatilization would be liquid-film controlled for these compounds.

BACKGROUND THEORY

The reference substance concept for liquid-film controlled volatilization with oxygen as the reference substance is expressed as

$$\phi = k_{L\text{ORG}}/k_{L\text{OXY}} \quad (1)$$

where

ϕ = the coefficient ratio assumed to be independent of mixing conditions in the water;

k_L = the mass-transfer coefficient for the liquid film, usually called the liquid-film coefficient, in meters per day; and

ORG and OXY = subscripts denoting the organic compound and oxygen.

The ϕ ratio is determined in the laboratory by measuring simultaneously the liquid-film coefficients for the volatilization of the organic compound and the absorption of oxygen in a stirred water bath. The constancy of ϕ is usually verified by conducting these experiments for a number of different water-mixing conditions. Conducting these experiments in the laboratory has the advantage that the toxic properties of many organic compounds can be safely controlled. Also, the

effects of other physical processes and chemical and biological processes that might affect the concentrations of the organic compound can be eliminated.

The reference-substance concept also is based on the assumption that the coefficient ratio, ϕ , is independent of the water quality. Thus, any organic compound in the stream or river that might affect one of the liquid-film coefficients is expected to affect the other coefficient in the same proportion so that the ratio remains constant. Verification of this assumption is difficult because of the large number of organic compounds for which volatilization is significant and also because of the large number of possible contaminants in streams and rivers. The few data available (Tsivoglou, 1967; Rathbun and others, 1978) support this assumption.

Oxygen is used as the reference substance for liquid-film controlled volatilization for two reasons. First, it has been determined (Mackay and Yuen, 1980) that virtually all the resistance to the absorption of oxygen is in the liquid film and, thus, this process is liquid-film controlled. This is a fundamental requirement of the reference-substance concept. Second, numerous equations exist in the literature (Rathbun, 1977) for predicting liquid-film coefficients for oxygen absorption in streams and rivers as a function of the hydraulic and geometric properties.

Application of equation 1 requires combining an estimate of the liquid-film coefficient for oxygen absorption for the stream or river of interest with the laboratory-determined ϕ ratio to calculate the liquid-film coefficient for the organic compound for that stream or river. Values of the ϕ ratio have been determined for a number of organic compounds (Smith and others, 1980; Rathbun and Tai, 1981, 1984a). However, the large number of organic compounds in use today and economic considerations preclude measurement of these ratios for all compounds for which volatilization might be a fate-determining process. Consequently, two estimation procedures based on the molecular-diffusion coefficient and on the molecular weight have been proposed for adjusting the ratio for one compound to the ratio for another compound. These procedures have been used extensively (Liss and Slater, 1974; Mackay and Leinonen, 1975; Dilling, 1977; Southworth, 1979; Thibodeaux, 1979; Rathbun and Tai, 1982) but never extensively evaluated.

The first estimation procedure is based on the assumption that the liquid-film coefficient depends on the molecular-diffusion coefficient D (in square meters per day) raised to some power η as expressed by

$$k_L = a_L D^\eta \quad (2)$$

where

a_L = a constant independent of the nature of the compounds, in meters to the $1 - 2\eta$ power per day to the $\eta - 1$ power.

The units of a_L are such that, when the molecular-diffusion coefficient is expressed in square meters per day, the liquid-

film coefficient has units of meters per day. Writing equation 2 for an organic compound and for oxygen and combining in ratios gives

$$k_{L\text{ORG}}/k_{L\text{OXY}}=[D_{\text{ORG}}/D_{\text{OXY}}]^\eta \quad (3)$$

where the constant a_L cancels because it is identical for the organic compound and for oxygen.

Combining equations 1 and 3 gives

$$\phi=[D_{\text{ORG}}/D_{\text{OXY}}]^\eta \quad (4)$$

Values of the exponent η vary, depending on the model assumed for the volatilization process. For the two-film model (Lewis and Whitman, 1924), η is 1.0. For the penetration model (Danckwerts, 1951), η is 0.50. For the film-penetration model (Dobbins, 1964), η varies from 0.50 for rapid mixing rates to 1.0 for slow mixing rates. Most experimental values range between 0.50 and 0.75, with 0.50 being the value generally recommended (Mackay, Shiu, and others, 1982).

Application of equation 4 requires a value of the molecular-diffusion coefficient of oxygen in water. This coefficient has been extensively studied; a review (St.-Denis and Fell, 1971) listed 12 measurements at 298.2 K ranging from 1.62×10^{-4} to 2.25×10^{-4} m²/d. The range of values was attributed to different experimental techniques and to the difficulty of measuring the molecular-diffusion coefficient of slightly soluble gases in water. Another analysis (Duda and Vrentas, 1968) pointed out that two of the largest values were the result of the wetted-sphere procedure which is known to result in large values. Also, several of the smallest values were for measurements in the presence of other substances such as hemoglobin and inorganic salts, which could have affected the measurements in some way. For these reasons, the molecular-diffusion coefficient of oxygen in water at 298.2 K used in the present study was limited to an average of the values of Baird and Davidson (1962) and Duda and Vrentas (1968). This value is 1.77×10^{-4} m²/d. Substituting this value into equation 4 gives

$$\phi=[(5.65 \times 10^3)(D_{\text{ORG}})]^\eta \quad (5)$$

The second estimation procedure based on molecular weight assumes that the liquid-film coefficient depends on the reciprocal of the square root of the molecular weight, M (in grams per gram mole), as expressed by

$$k_L=b_L M^{-0.500} \quad (6)$$

where

b_L = a constant independent of the nature of the compound, in meters per day times (grams per gram mole) to the 0.500 power.

The units of b_L are such that, when the molecular weight

is expressed in grams per gram mole, the liquid-film coefficient has units of meters per day. Writing equation 6 for an organic compound and for oxygen and combining in ratios gives

$$k_{L\text{ORG}}/k_{L\text{OXY}}=(M_{\text{ORG}}/32.0)^{-0.500} \quad (7)$$

where the constant b_L cancels because it is identical for the organic compound and for oxygen. Combining equations 1 and 7 gives

$$\phi=(M_{\text{ORG}}/32.0)^{-0.500} \quad (8)$$

The basis of equation 6 is Graham's law of diffusion, which indicates that the diffusion coefficient is inversely proportional to the square root of the molecular weight. Therefore, it follows from equation 6 that the assumption that the liquid-film coefficient is proportional to the molecular-diffusion coefficient to the 1.0 power is inherent in equation 8. This corresponds to a value of η of 1.0 in equation 2 as indicated by the two-film model. However, as discussed previously, most of the experimental values of η range between 0.50 and 0.75. Thus, the molecular-weight procedure may be in error for this reason.

Also, Graham's law was the empirical result of measurements of the rates of effusion of gases through a small orifice (Glasstone, 1946). Therefore, application of Graham's law to the molecular diffusion of organic solutes through water might be questioned.

EXPERIMENTAL PROCEDURE

Liquid-film coefficients for the volatilization of benzene and a series of eight alkyl-substituted benzene compounds (toluene through n-octylbenzene) from water were measured in a constant-temperature, stirred water bath simultaneously with the liquid-film coefficient for oxygen absorption. The procedure for the experiments consisted of the following steps: (1) Stripping distilled water with nitrogen gas to decrease the dissolved-oxygen concentration; (2) preparing a water solution of the benzene compounds; (3) adding the water solution to the bath and mixing at a constant rate; (4) sampling as a function of time; (5) determining the concentrations of the organic compounds and oxygen in the samples; and (6) computing liquid-film coefficients for volatilization of the benzene compounds and for oxygen absorption from the experimental concentration-versus-time data.

One of the reasons for selecting this series of benzene compounds for study was the existence of extensive solubility data (Ben-Naim and Wilf, 1980). These solubility data were the basis of the experimental design.

The original plan was to conduct the experiments in groups of three compounds with a common compound between adjacent groups. Thus, group 1 was to consist of

benzene, toluene, and ethylbenzene; group 2 was to consist of ethylbenzene, n-propylbenzene, and n-butylbenzene; group 3 was to consist of n-butylbenzene, n-pentylbenzene, and n-hexylbenzene; and group 4 was to consist of n-hexylbenzene, n-heptylbenzene, and n-octylbenzene. The experiments could have been done with all nine compounds volatilizing simultaneously; however, this would have greatly complicated the sampling and sample-analysis procedures. Also, the possibility of interactions among the nine compounds would have had to be considered in the design of the experiments.

During the preparation of the water solutions as required by step 2 of the procedure, it became apparent that the reported solubility values for the high-molecular-weight compounds were much too large because the compounds were not dissolving to the extent indicated by the solubility data. Therefore, the original experimental plan was modified, and the n-heptylbenzene and n-octylbenzene experiments were conducted separately. The group 3 data were used for n-hexylbenzene. This modification was necessary to get sufficient quantities of these compounds into solution for measurement purposes.

The experiments were conducted in a stainless-steel water bath 910 mm long by 460 mm wide by 305 mm deep. A water depth of 267 mm was used for all experiments, giving a water volume of 112 L. Distilled water was used for all experiments. The water bath was equipped with a heater and a temperature controller. All experiments were at a water temperature of 298.2 K. Water mixing was obtained with an oscillating plate located on the bottom of one end of the bath and a variable-speed stirrer with a 51-mm-diameter blade located near the center of the bath. The plate oscillated at 21 cycles per minute for all experiments. The stirrer rate was varied from about 700 to about 2,300 revolutions per minute to obtain a range of water-mixing conditions. The constant-temperature water bath was placed in a fume hood with a face velocity of 38 m/min to obtain a constant flow of air over the water surface.

Water solutions for the experiments were prepared by mixing quantities of the appropriate compounds in water in a glass container on a magnetic stirrer. Chemicals from the Aldrich Company were used without further purification. A 1-L glass bottle with a ground-glass stopper was used for the group 1 compounds. A 13-L glass carboy covered with a piece of Teflon and Parafilm was used for the group 2 compounds. Two and sometimes three 13-L carboys were used for the group 3 compounds. Four or five 13-L carboys were used for the n-heptylbenzene and n-octylbenzene compounds.

Solutions for the group 1 and group 2 compounds were mixed overnight. Solutions for the group 3 and n-heptylbenzene and n-octylbenzene compounds were mixed from 24 to 48 hours. No difficulties were experienced preparing the solutions for the group 1 and group 2 compounds. However, for the other compounds, floating organic material was usually observed on the surface of the water despite the

fact that the quantities added to the carboys were considerably less than the reported solubility values (Ben-Naim and Wilf, 1980). This floating organic material was removed with an eyedropper or a water-aspirator pump before adding the solution to the constant-temperature water bath. Despite this precaution, some floating material was usually observed in the water bath for the higher molecular-weight compounds. This floating material appeared to evaporate rapidly, however, and none was visible at the time the first sample was collected.

Samples were collected in glass containers by siphoning from about middepth at about the center of the bath with a glass siphon. Samples for the group 1 and group 2 compounds were collected in 40-mL glass vials with Teflon-faced septa and plastic screw caps. Samples for the group 3, n-heptylbenzene, and n-octylbenzene compounds were collected in either 40- or 120-mL glass serum bottles with Teflon-faced septa and crimped aluminum caps. The larger bottles were used for the n-heptylbenzene and n-octylbenzene compounds where a larger sample was needed to obtain sufficient sample for analysis. Samples for dissolved oxygen were collected in 300-mL BOD (biochemical oxygen demand) bottles. Samples for dissolved oxygen were fixed immediately with the Winkler reagents (Carritt and Carpenter, 1966) and the analyses completed within several hours. Analyses for the organic compounds were done on the day of the experiment. Durations of the experiments ranged from about 4 hours for the group 1 compounds for a rapid mixing condition to about 30 hours for n-octylbenzene for a slow mixing condition.

Concentrations of the group 1 and group 2 compounds were determined using a purge-and-trap procedure with a Tekmar LC-2 liquid sample concentrator followed by analysis in a Varian 2700 gas chromatograph with a flame ionization detector. Concentrations of the group 3, n-heptylbenzene, and n-octylbenzene compounds were determined using a solvent-extraction procedure with hexane as the solvent followed by analysis in the gas chromatograph. The solvent-extraction procedure was similar to that of Henderson and others (1976). The analytical column was a 1.83-m length of 3.18-mm o.d. nickel alloy tubing packed with 5 percent SP-1200/1.75 percent Bentone-34 on Supelcoport. Temperature programming was used, with the temperature conditions varying depending on the compounds being analyzed.

The gas chromatograph was calibrated daily using hexane solutions of the appropriate compounds. Concentrations were adjusted to include the range of concentrations expected in the experimental samples. Purge-and-trap recoveries ranged from about 100 percent for benzene to about 60 percent for n-butylbenzene. Reproducibility was generally better than 5 percent. Liquid-extraction recoveries for the group 3 compounds were generally about 100 percent. Reproducibility was generally better than 3 percent. Liquid-extraction recoveries for n-heptylbenzene and n-

octylbenzene were about 90 percent. Reproducibility was in the 3- to 5-percent range.

Dissolved-oxygen concentrations were determined using the Winkler procedure (Carritt and Carpenter, 1966). Titrations were done directly in the sample bottles using a Metrohm Dosimat to add the titrant. The sodium thiosulfate titrant was standardized daily, and reagent blanks were determined daily.

Liquid-film coefficients for volatilization of the organic compounds and for oxygen absorption were calculated from the concentration versus time data and the equation

$$C_E - C = (C_E - C_0) \exp(-k_L t / Y) \quad (9)$$

where

C_E = concentration of the compound, in micrograms per liter, or oxygen, in milligrams per liter, in the water in equilibrium with the concentration of the compound or oxygen in the air above the water;

C = concentration in the water at time t , in days;

C_0 = concentration in the water at time zero; and

Y = water depth, in meters.

For the organic compounds, it was assumed that the fume hood removed the compounds as soon as they volatilized so that the concentration in the air was zero; thus, C_E also was zero. For oxygen, C_E was the saturation concentration in water corresponding to the atmospheric concentration. This saturation concentration for the appropriate water temperature and barometric pressure was calculated from the equations of Mortimer (1981). A two-parameter, nonlinear, least-squares procedure (Rathbun and Tai, 1984b) was used to calculate the k_L values from equation 9 and the experimental data.

RESULTS AND ANALYSIS OF THE VOLATILIZATION OF BENZENE COMPOUNDS FROM WATER

Experimental ϕ Values

The experimental liquid-film coefficients for the volatilization of the benzene compounds from water are plotted in figures 1 through 11 as a function of the liquid-film coefficient for oxygen absorption. The lines in these figures are from linear least-squares regressions of the experimental data, with the regressions forced through the zero-zero point at the origin. The regressions were first computed using standard linear regression procedures where nonzero intercepts were allowed. Values of the intercepts ranged from -0.184 for ethylbenzene to $+0.175$ for n-hexylbenzene. Statistical analyses of these intercepts indicated that none were significantly different from zero at the 2.5-percent level of significance. Decreasing the confidence limits by using the 5-percent level of significance indicated that the intercepts

for all compounds except n-hexylbenzene were not significantly different from zero. This indicates somewhat greater scatter in the data for this compound. It was concluded on the basis of these arguments that the intercepts were not significantly different from zero statistically and, therefore, the regression lines could be forced through zero. This procedure also is supported by the physical argument that if one coefficient is zero, then the other also must be zero, and the regression line should pass through the origin.

The slopes of the lines in figures 1 through 11 are equal to the ϕ ratio as defined by equation 1. These ratios are presented in table 1. The fact that the relations in figures 1 through 11 are linear for a considerable range of water-mixing conditions, as indicated by the liquid-film coefficient for oxygen absorption, indicates that the ϕ ratios are independent of these mixing conditions. It was concluded, therefore, that the reference-substance concept as expressed by equation 1 is applicable to the prediction of the liquid-film coefficients for the volatilization of these compounds from streams and rivers. This conclusion will be modified somewhat when the two estimation procedures are discussed below.

The ϕ ratios for ethylbenzene and n-butylbenzene were determined in two different groups (table 1). Statistical analysis of these ratios indicated that the ratios for both compounds from the two groups were not significantly different at the 5-percent level. This provides support for the experimental procedures used, because the n-butylbenzene concentrations in the group 2 experiments were determined using the purge-and-trap procedure and those in the group 3 experiments were determined using the solvent-extraction procedure.

Also shown in table 1 are the normalized root-mean-square (rms) errors of prediction of the organic liquid-film coefficients from the regression equations. These errors, E , were computed from

$$E = \left[\frac{\sum_{i=1}^n (k_{L\text{EXP}} - k_{L\text{CALC}})^2}{n} \right]^{0.5} \frac{(100)(n)}{\sum_{i=1}^n k_{L\text{EXP}}} \quad (10)$$

where

EXP = subscript denoting experimental values of the organic liquid-film coefficients measured by the procedure described previously;

CALC = subscript denoting values calculated from the regression equations; and

n = the number of values.

The errors in table 1 are approximately constant through n-butylbenzene but are larger for the higher molecular-weight compounds. These larger errors are probably indicative of the experimental problems associated with the low solubility of these compounds. Also, the largest error was for

n-hexylbenzene, which is consistent with the scatter in the data for this compound noted previously in the analysis of regression intercepts.

Evaluation of the ϕ -Estimation Procedures

Molecular-Diffusion-Coefficient Procedure

The first estimation procedure for ϕ (equation 5) requires molecular-diffusion coefficients of the benzene compounds in water. Data for benzene, toluene, and ethylbenzene were available at several temperatures from two studies

(Witherspoon and Bonoli, 1969; Tominaga and others, 1984). Results of these two studies were similar. Diffusion coefficients interpolated at 298.2 K from the results of these studies were compared with values predicted using the Hayduk-Laudie equation, which is the equation recommended for predicting diffusion coefficients at infinite dilution (Reid and others, 1977). Predicted values were 10.1 percent less than the experimental values for benzene, 4.18 percent less for toluene, and 9.87 percent less for ethylbenzene. Thus, the predicted values were in reasonable agreement with the experimental values. However, because the differences between experimental and predicted values indicated no dependence on molecular weight or any other

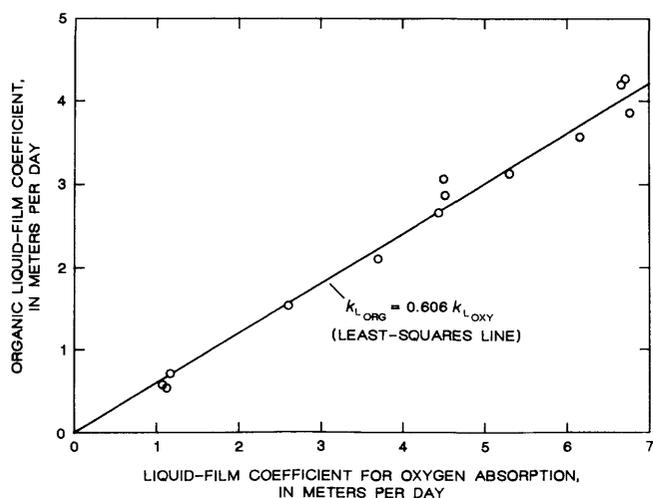


Figure 1. Liquid-film coefficients for volatilization of benzene from water as a function of liquid-film coefficient for oxygen absorption.

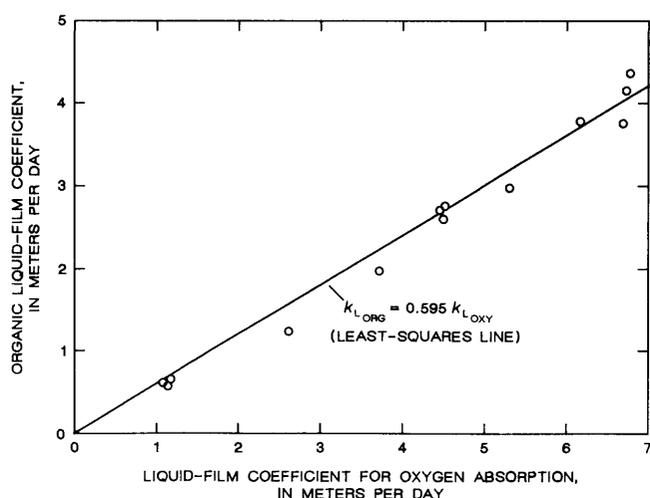


Figure 3. Liquid-film coefficients for volatilization of ethylbenzene from water as a function of liquid-film coefficient for oxygen absorption, group 1 experiments.

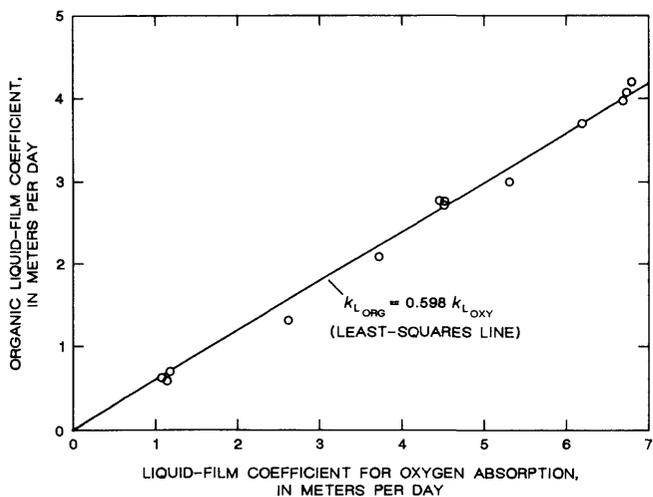


Figure 2. Liquid-film coefficients for volatilization of toluene from water as a function of liquid-film coefficient for oxygen absorption.

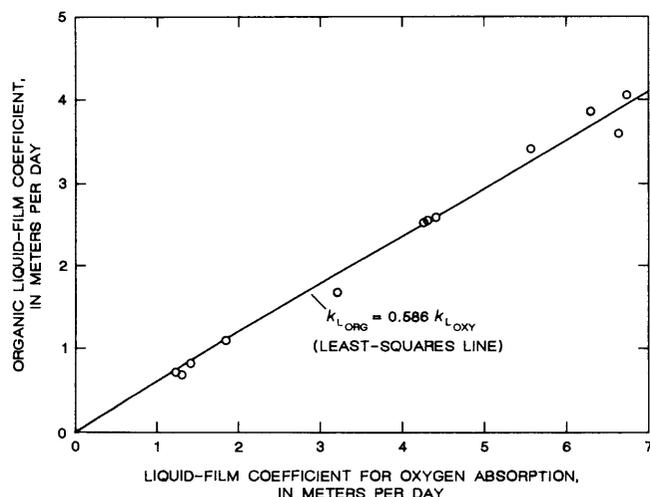


Figure 4. Liquid-film coefficients for volatilization of ethylbenzene from water as a function of liquid-film coefficient for oxygen absorption, group 2 experiments.

consistent pattern, it was difficult to determine which of the three values was most similar to the true value and, therefore, which should be used as the basis for extrapolation to the higher molecular-weight compounds. For this reason, the Hayduk-Laudie equation was used to predict the molecular-diffusion coefficients for all the benzene compounds considered in this study.

With water as the solvent at 298.2 K, the Hayduk-Laudie equation (Reid and others, 1977) becomes

$$D_{\text{ORG}} = 1.30 \times 10^{-3} V_{\text{ORG}}^{-0.589} \quad (11)$$

where

V_{ORG} = the molal volume of the organic compound at the normal boiling temperature, in milliliters per gram mole.

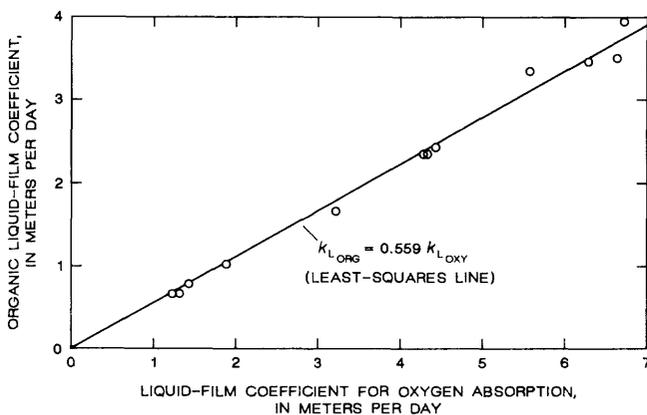


Figure 5. Liquid-film coefficients for volatilization of n-propylbenzene from water as a function of liquid-film coefficient for oxygen absorption.

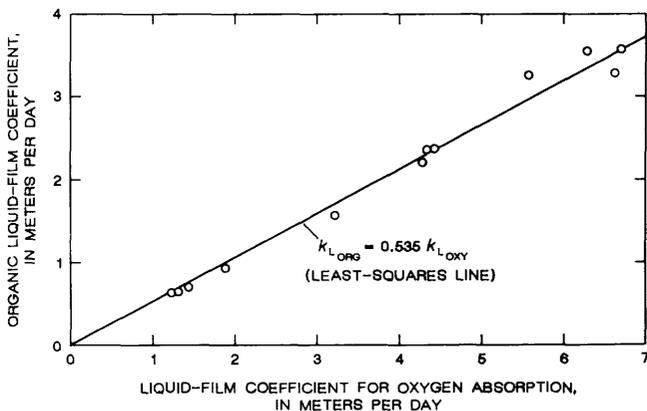


Figure 6. Liquid-film coefficients for volatilization of n-butylbenzene from water as a function of liquid-film coefficient for oxygen absorption, group 2 experiments.

Molal volumes were calculated using the LeBas method (Reid and others, 1977).

Experimental values of ϕ from table 1 are plotted in figure 12 as a function of molecular-diffusion coefficients calculated from equation 11. Logarithmic-logarithmic scales were used because equation 5 indicates that ϕ should be a linear function of the diffusion coefficient on such scales. It is apparent that deviations from this expected linear relation occur for both the high- and low-molecular-weight compounds.

The experimental ϕ values for the approximately linear range from ethylbenzene through n-pentylbenzene were fit to equation 5 by varying the exponent η until the normalized rms error of the form of equation 10 was minimized. This procedure resulted in an η value of 0.566, which is similar to values from the literature (Smith and others, 1980;

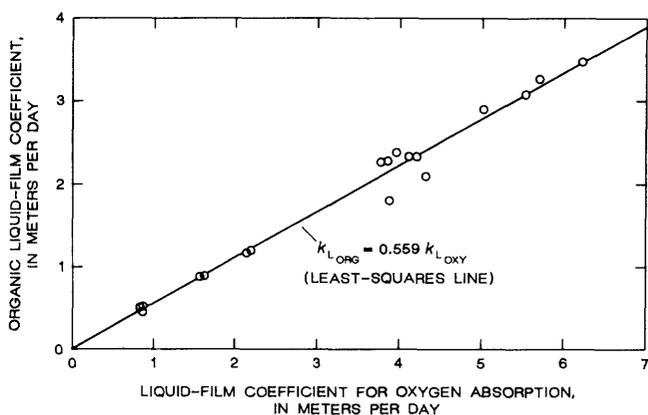


Figure 7. Liquid-film coefficients for volatilization of n-butylbenzene from water as a function of liquid-film coefficient for oxygen absorption, group 3 experiments.

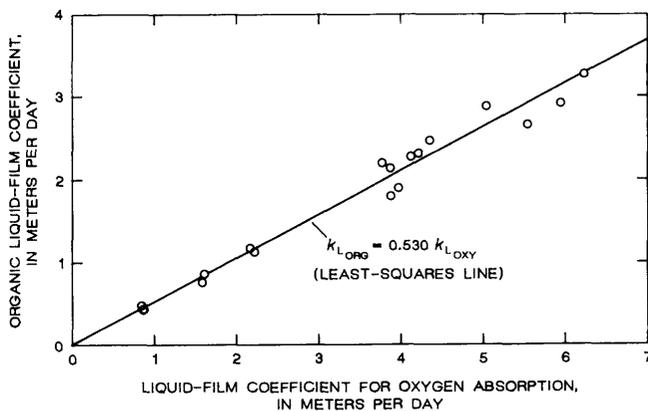


Figure 8. Liquid-film coefficients for volatilization of n-pentylbenzene from water as a function of liquid-film coefficient for oxygen absorption.

Mackay, Shiu, and others, 1982). A line based on equation 5 with an η value of 0.566 is shown in figure 12. It was concluded that the molecular-diffusion coefficient procedure with a 0.566 power dependence on the diffusion coefficient accurately predicts the ϕ values for ethylbenzene through n-pentylbenzene.

At the high-molecular-weight end of the range, the predicted values are 6.49 percent larger, 19.2 percent larger,

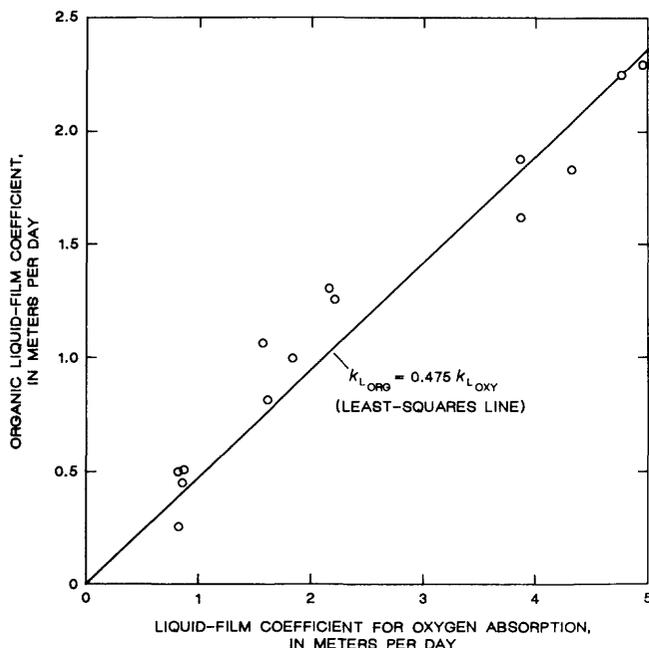


Figure 9. Liquid-film coefficients for volatilization of n-hexylbenzene from water as a function of liquid-film coefficient for oxygen absorption.

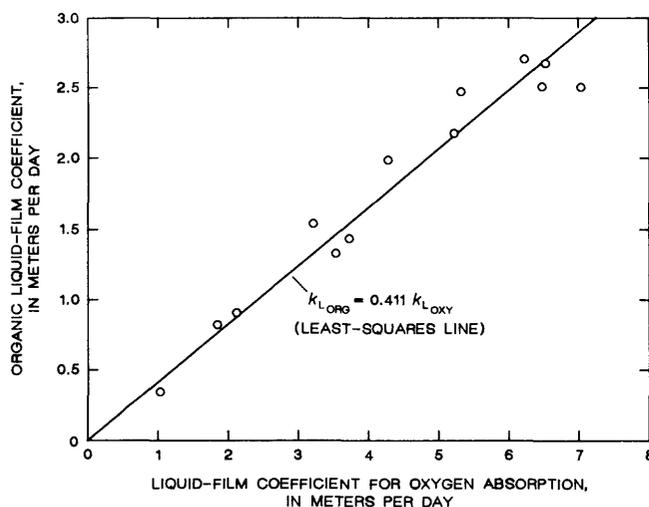


Figure 10. Liquid-film coefficients for volatilization of n-heptylbenzene from water as a function of liquid-film coefficient for oxygen absorption.

and 33.7 percent larger than the experimental values for n-hexylbenzene, n-heptylbenzene, and n-octylbenzene, respectively. Possible explanations for these deviations include the effects of sorption and desorption of these compounds on the stainless steel of the water bath and other experimental problems associated with the low water solubility. These possibilities are discussed in more detail later after an analysis of water solubility. At the low-molecular-weight end of the range, the ϕ values predicted by equation 5 with an η value of 0.566 are 11.1 percent larger and 5.35 percent larger than the experimental values for benzene and toluene, respectively. Possible explanations for these deviations include interactions of the aromatic molecules with water molecules and also with each other. These possibilities are discussed in more detail later.

Molecular-Weight Procedure

The second estimation procedure for ϕ (equation 8) requires only molecular weights; therefore, it is easily applied because molecular weights are readily available. Experimental values of ϕ from table 1 are plotted in figure 13 as a function of molecular weight. Logarithmic-logarithmic scales were used because equation 8 indicates that ϕ should be a linear function of the molecular weight on such scales. Again, it is apparent that deviations from the expected linear relation occur for both the high- and low-molecular-weight compounds.

A line corresponding to equation 8 is shown in figure 13, and it is apparent that the line is approximately parallel to, but displaced from, the ϕ values for ethylbenzene through

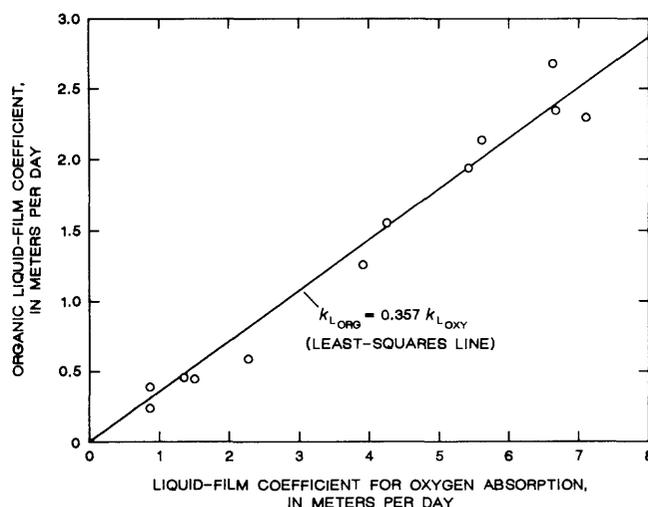


Figure 11. Liquid-film coefficients for volatilization of n-octylbenzene from water as a function of liquid-film coefficient for oxygen absorption.

Table 1. ϕ ratios determined by the linear regression of the experimental data and errors of the regressions

Compound	ϕ	Error (percent)
Benzene	0.606	6.40
Toluene	.598	4.40
Ethylbenzene (group 1)	.595	7.10
Ethylbenzene (group 2)	.586	5.84
n-Propylbenzene	.559	5.49
n-Butylbenzene (group 2)	.535	6.56
n-Butylbenzene (group 3)	.559	7.04
n-Pentylbenzene	.530	8.00
n-Hexylbenzene	.475	13.7
n-Heptylbenzene	.411	9.91
n-Octylbenzene	.357	10.9

n-pentylbenzene for which an approximately linear relation exists. If the value of the exponent in equation 8 is varied to minimize the rms error of prediction, as was done for the molecular-diffusion-coefficient equation, the result is

$$\phi = (M_{\text{ORG}}/32.0)^{-0.427} \quad (12)$$

A line corresponding to this equation also is shown in figure 13. At the high-molecular-weight end of the range, the predicted ϕ values are 5.33 percent larger, 17.3 percent larger, and 31.0 percent larger than the experimental values for n-hexylbenzene, n-heptylbenzene, and n-octylbenzene, respectively. At the low-molecular-weight end of the range, the ϕ values predicted by this equation are 12.6 percent larger and 6.40 percent larger than the experimental values for benzene and toluene, respectively. These deviations are similar to those observed for the molecular-diffusion-coefficient procedure; possible explanations for these deviations are presented below with the discussion of the deviations from the molecular-diffusion-coefficient procedure.

An alternative equation for predicting ϕ as a function of molecular weight may be derived from equations 4 and 11. As might be expected for a homologous series of compounds, the molal volume at the normal boiling temperature was strongly correlated with the molecular weight according to

$$V_{\text{ORG}} = 0.589 M_{\text{ORG}}^{1.17} \quad (13)$$

Combining equation 13 with equations 4 and 11, the numerical value for the molecular-diffusion coefficient of oxygen, and the best-fit value of η gives

$$\phi = 3.69 M_{\text{ORG}}^{-0.390} \quad (14)$$

Values of ϕ predicted from equation 14 are comparable to those predicted from equation 12. Equations 12 and 14 indicate that ϕ can be accurately predicted from molecular

weights. However, in each case, the dependence on molecular weight was considerably less than the commonly assumed -0.500 power dependence. It was concluded that the molecular-weight procedure can accurately predict the values for ethylbenzene through n-pentylbenzene, but only if the power dependence on the molecular weight is decreased considerably with respect to the -0.500 dependence commonly used. Additional research is needed to determine if this conclusion applies to other classes of compounds.

Finally, it is of interest to combine equations 11 and 13. The result is a dependence of the molecular-diffusion coefficient on the molecular weight to the -0.689 power. This is considerably different from the -0.500 power dependence predicted by Graham's law indicating, as previously discussed, that this law may not be strictly valid for the molecular diffusion of organic compounds in water.

Analysis of Deviations from the Estimation Procedures

The molecular-diffusion-coefficient and molecular-weight procedures both predicted reference-concept ratios, ϕ , that were larger than the experimental values for the high-molecular-weight and low-molecular-weight compounds. These deviations were larger than might be expected from experimental errors. The low-molecular-weight compounds are discussed below. Possible explanations for the deviations for the high molecular-weight compounds are dependent on water solubility. Therefore, an analysis of the water solubility of these compounds is necessary at this point.

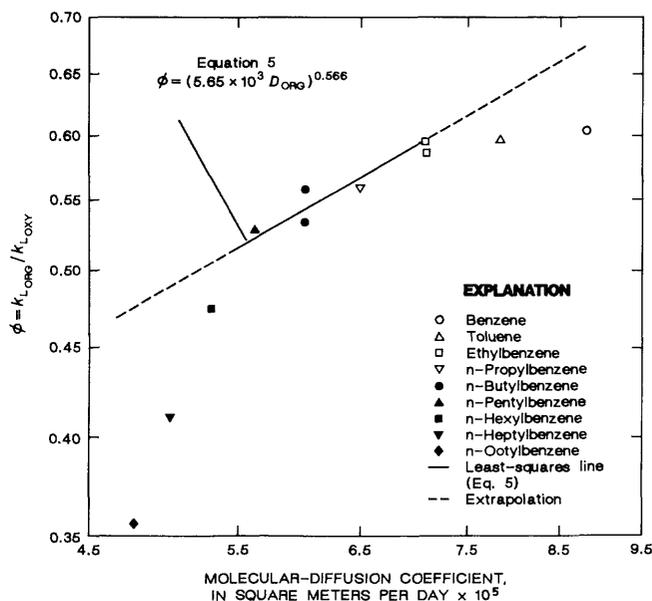


Figure 12. ϕ values as a function of molecular-diffusion coefficient. Both scales logarithmic.

Water Solubility

The experimental design was based on the solubility data of Ben-Naim and Wilf (1980), as discussed previously. Two methods of solubility measurement were used in their work. The first consisted of mixing an excess of the solute with water for about 48 hours, allowing the phases to separate for about 24 hours, and sampling the water phase for determination of the concentration. The second consisted of saturating the water through contact with the vapor of the solute. This method has the advantage that the possibility of supersaturation of the water with the solute is decreased. Both methods were applied to benzene, toluene, and ethylbenzene. Because the two methods gave almost identical results for these three solutes, only the first method was used for subsequent measurements on the higher molecular-weight homologs.

Preparation of the water solutions for the volatilization experiments of this study indicated, however, that these published solubility values for the higher molecular-weight compounds were much too large. There have been a number of recent measurements of the water solubilities of benzene through n-hexylbenzene using the coupled-column, liquid-chromatographic procedure (Tewari and others, 1982; May and others, 1983; Miller and others, 1985; Owens and others,

1986). This procedure eliminates many of the experimental problems associated with the equilibration method used previously (May and others, 1978). These studies did not, however, include measurements for n-heptylbenzene and n-octylbenzene. Water-solubility values for these compounds were estimated, therefore, from the solubility values of the other compounds and several procedures appropriate for homologous series of compounds.

Water-solubility values from these four studies, references cited in these studies, and water-solubility values from Amidon and Anik (1981) and Mackay and Shiu (1981) were evaluated for benzene through n-hexylbenzene. Values differing by more than three standard deviations of the means were excluded as outliers. Mean values and coefficients of variation were computed, and the results together with the number of values included in each computation are presented in table 2.

Twenty-two values were excluded as outliers. Of these 22 outliers, 18 were larger and 4 were smaller than the mean; the 4 that were smaller were for benzene, toluene, and ethylbenzene. These results indicate that solubility measurements for this series of compounds tend to err toward larger values and that this tendency increases with molecular weight.

Water-solubility values for n-heptylbenzene and n-octylbenzene were estimated using correlations of solubility with molecular surface area (Amidon and Anik, 1981) and molar volume (McAuliffe, 1966), a correlation of the reciprocal of the solubility with normal boiling temperature (Wasik and others, 1982), and a correlation of the activity coefficient as a function of the number of carbon atoms in the molecule (Tsonopoulos and Prausnitz, 1971). It has been reported (Mackay and Shiu, 1975) that the activity coefficient defined by the Raoult's law convention is the reciprocal of the mole fraction solubility for dilute aqueous solutions of organic compounds.

Molecular surface areas for benzene through n-butylbenzene were obtained from Amidon and Anik (1981). Areas for n-pentylbenzene through n-octylbenzene were calculated using an incremental area of 0.318 nm² for each additional CH₂ group (Valvani and others, 1976). Water-solubility values at 298.2 K are plotted on a logarithmic scale in figure 14 as a function of the molecular surface area. The least-squares line has the equation

$$S = 5.23 \times 10^7 \exp(-4.01 \text{ TSA}) \quad (15)$$

where

S = water solubility, in milligrams per liter; and

TSA = molecular surface area, in square nanometers.

The rms error computed from an equation of the form of equation 10 is ± 10.5 percent.

Molar volumes were calculated from molecular weight and density data from a standard handbook reference (Weast, 1985). Water-solubility values at 298.2 K are plotted on a

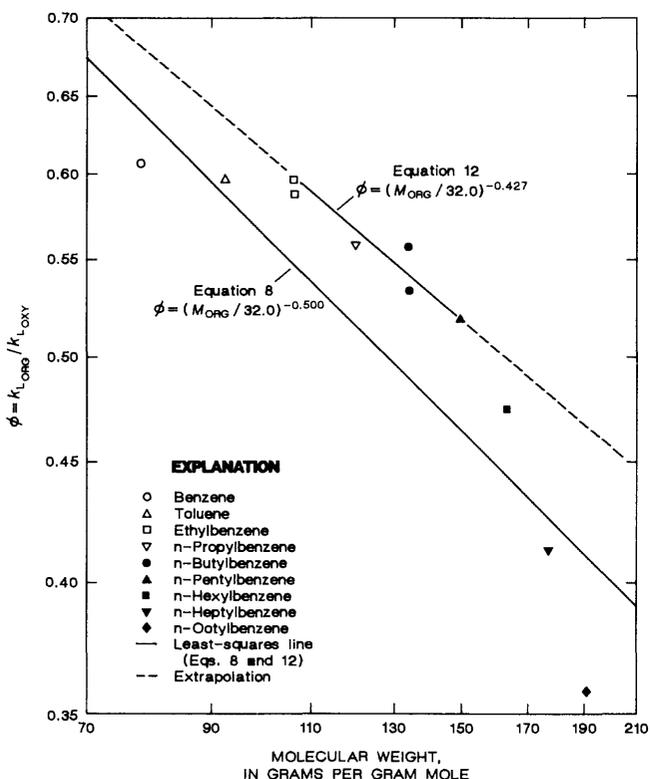


Figure 13. ϕ values as a function of molecular weight. Both scales logarithmic.

Table 2. Mean values of water solubility at 298.2 K for benzene through n-hexylbenzene, number of values used to compute the mean values, and coefficients of variation

Compound	Mean value of water solubility (milligrams per liter)	Number of values	Coefficient of variation (percent)
Benzene	1,761	14	1.65
Toluene	538	14	3.75
Ethylbenzene	169	11	6.37
n-Propylbenzene	52.9	6	3.26
n-Butylbenzene	13.3	6	9.57
n-Pentylbenzene	3.63	2	8.57
n-Hexylbenzene	.980	3	5.02

logarithmic scale in figure 15 as a function of the molar volume. The least-squares line has the equation

$$S = 1.65 \times 10^6 \exp(-0.0754 V_M) \quad (16)$$

where

V_M = the molar volume, in milliliters per gram mole. The rms error is ± 23.7 percent. There is a tendency for the points in figure 15 to be somewhat concave toward the abscissa, resulting in the large error.

Normal boiling temperatures were obtained from a standard handbook reference (Weast, 1985). Reciprocal values of the water solubility at 298.2 K are plotted on a

logarithmic scale in figure 16 as a function of the normal boiling temperature. The least-squares line has the equation

$$1/S = 4.06 \times 10^{-13} \exp(0.0570 T_{bp}) \quad (17)$$

where

T_{bp} = normal boiling temperature, in kelvins. Substantial deviations from the least-squares line of equation 17 occurred for benzene and toluene; therefore, these points were excluded from the regression. This is not important for the present purpose because extrapolation of the least-squares line of equation 17 is at the other end of the boiling temperature range. Considering all seven points, however, there is a tendency for the points to be slightly convex toward the abscissa. The rms error of the unextrapolated linear part of the line in figure 16 is ± 9.07 percent.

Finally, activity coefficients for n-heptylbenzene and n-octylbenzene were computed from the equation of Tsonopoulos and Prausnitz (1971). This equation was based on data for benzene through n-butylbenzene; therefore, application to the higher molecular-weight compounds involves extrapolation. The activity coefficients were converted to water-solubility values using the equation

$$S = M(55.6)(10^3)/\gamma \quad (18)$$

where

55.6 = molar volume of water, in milliliters per gram mole; and

γ = activity coefficient.

Equation 18 was derived using the conclusion of Mackay and Shiu (1975) that the activity coefficient is equal to the reciprocal of the mole fraction solubility for dilute aqueous solutions. Estimated water-solubility values were 0.332 mg/L for n-heptylbenzene and 0.0935 mg/L for n-octylbenzene.

Water-solubility values for n-heptylbenzene and n-octylbenzene, estimated from equations 15, 16, and 17 and from the activity coefficients, are presented in table 3. The mean values and the coefficients of variation also are

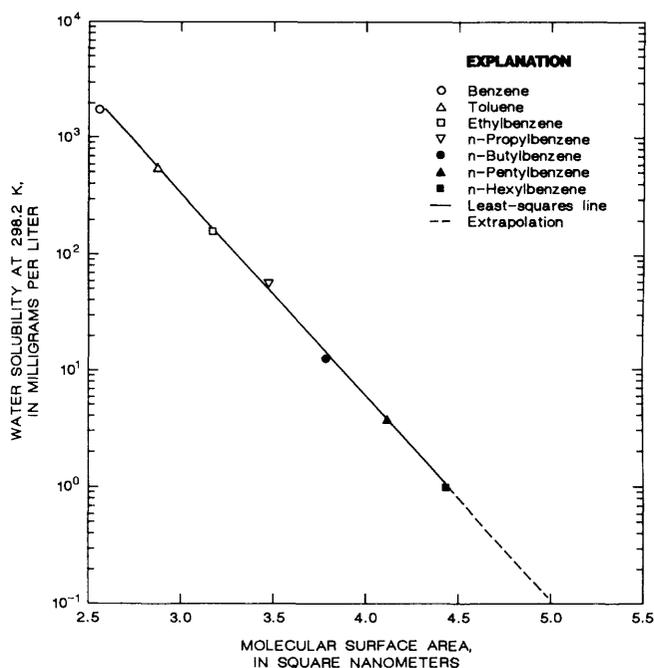


Figure 14. Water solubility as a function of molecular surface area for benzene through n-hexylbenzene.

presented in table 3. The coefficient of variation for n-heptylbenzene is somewhat larger than the coefficients of variation for the experimental water-solubility values for the lower molecular-weight compounds in table 2, and the coefficient of variation for n-octylbenzene is considerably larger.

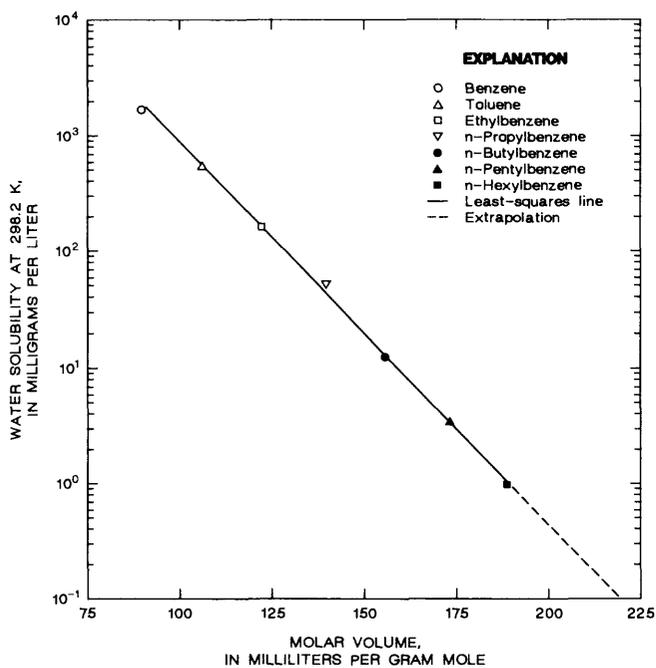


Figure 15. Water solubility as a function of molar volume for benzene through n-hexylbenzene.

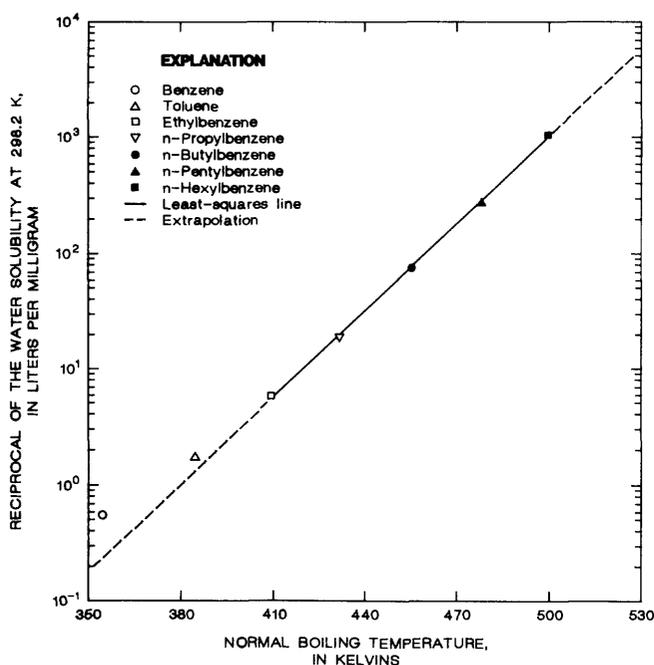


Figure 16. Reciprocal values of water solubility as a function of normal boiling temperature for benzene through n-hexylbenzene.

This is apparently indicative of the errors involved in extrapolating correlations outside the range of data on which the correlations are based. Despite these variations, the estimated mean values in table 3 are considered to be far more accurate than the experimental values from the literature (Ben-Naim and Wilf, 1980) of 16.7 mg/L for n-heptylbenzene and 13.7 mg/L for n-octylbenzene. These latter values are much too large, probably because the experimental method did not accurately distinguish between compound molecules that were truly in solution and those that were dispersed and retained in the liquid by the process of accommodation (Peake and Hodgson, 1966, 1967).

Deviations of the High-Molecular-Weight Compounds

One possible explanation for the smaller than expected ϕ values for n-hexylbenzene, n-heptylbenzene, and n-octylbenzene is rapid sorption to the surfaces of the experimental apparatus followed by slow desorption into the water during the volatilization experiment. It is well known that the tendency of organic compounds to sorb on surfaces increases as the solubility decreases. See for example, Chiou and others (1979) who reported that the logarithm of the soil-water distribution coefficient for a series of organic compounds decreased linearly with the logarithm of the solubility.

In the present study, published water-solubility values (Ben-Naim and Wilf, 1980) were large enough that sorption was not expected to be a problem. Also, only stainless steel, glass, and Teflon were in contact with the solutions, and these materials are all relatively inert with respect to sorption processes. As the study progressed, however, it became apparent that these solubility values were much too large and, therefore, sorption may have been a problem.

The solutions were in contact with glass and Teflon generally only in the sample containers. Recovery studies for the liquid-extraction procedure discussed previously indicated that recovery was about 100 percent for the group 3 compounds and about 90 percent for n-heptylbenzene and n-octylbenzene. These recoveries indicate that sorptive losses on glass and Teflon were small.

One experiment was conducted to determine if these compounds would sorb to stainless steel. A water solution of the three compounds was prepared in a glass bottle, and two control samples were collected. The solution then was pumped with a stainless-steel metering pump through a length of 9.5 mm o.d. stainless-steel tubing. This length of tubing had a volume of 130 mL and an inside surface area of 0.082 m². About 70 mL of solution was wasted before collecting two samples. The pump then was stopped and the end of the tubing was capped. This sampling process was repeated after 2.7, 5.9, and 24 hours. Analysis of the samples indicated an immediate loss of all compounds relative to the control samples but virtually no variation with time thereafter. About 38 percent of the n-hexylbenzene and 61 percent of the n-

Table 3. Estimated values of water solubility at 298.2 K for n-heptylbenzene and n-octylbenzene, mean values, and coefficients of variation

Compound	Water solubility (milligrams per liter) estimated from				Mean (milligrams per liter)	Coefficient of variation (percent)
	Surface area	Molar volume	Boiling temperature	Activity coefficient		
n-Heptyl- benzene	0.283	0.301	0.357	0.332	0.318	10.3
n-Octyl- benzene	.0790	.0902	.121	.0935	.0959	18.6

heptylbenzene were lost from solution. The n-octylbenzene concentrations were near the limit of detection, and only one sample contained a measurable concentration. This concentration was about 40 percent of the control-sample concentration.

These somewhat qualitative results indicate that these compounds sorb on stainless steel, that the extent of sorption increases with increasing molecular weight and decreasing solubility, and that sorption equilibrium is apparently established rapidly. Because of this rapid equilibrium, it is presumed the process was surface sorption. Therefore, it follows that desorption from the surfaces also likely will occur readily when the water-solution concentration is decreased to less than the equilibrium concentration. Rapid sorption equilibrium of the type apparently occurring here is analogous to the simplest and most widely used linear sorption isotherm for describing the sorption of organic compounds by soils (Travis and Etnier, 1981).

It is hypothesized, therefore, that rapid sorption equilibrium occurred on the surfaces of the stainless-steel bath when the water solution was added to the bath at the beginning of an experiment. As the concentration in solution was decreased by volatilization, the sorbed compound desorbed into the water to maintain equilibrium conditions, resulting in a slower rate of change of concentration than normal for volatilization and, consequently, an apparent liquid-film coefficient smaller than the true value.

Mathematically, these processes may be described by

$$\frac{dC}{dt} = -k_L \frac{A_v}{V} C - \frac{A_s}{V} \frac{dN}{dt} \quad (19)$$

where

A_v = surface area, in square meters, for volatilization;

V = water volume, in cubic meters;

A_s = surface area, in square meters, for sorption; and

N = surface concentration of sorbed compound, in micrograms per square meter.

The qualitative sorption experiment indicated that sorption on the stainless steel was rapid and, coupled with the fact that volatilization is a relatively slow process, the assump-

tion of a continuous equilibrium between the sorbed concentration and the concentration in solution seems reasonable. This equilibrium may be described by

$$N = k_E C \quad (20)$$

where

k_E = equilibrium partition coefficient, in meters.

For a reasonably flat water surface, the water depth, Y , is related to the volume and surface area by

$$Y = V/A_v \quad (21)$$

Combining equations 20 and 21 with equation 19 and rearranging gives

$$\frac{dC}{dt} = \left[\frac{-k_L/Y}{1 + A_s k_E/V} \right] C \quad (22)$$

The term in brackets is the volatilization coefficient that would be determined in an experiment when desorption effects are present. In the absence of desorption effects, that is, when k_E equals zero, the volatilization coefficient would be k_L/Y , and this is consistent with equation 9 presented previously. Because A_s , k_E , and V are all positive quantities, it follows that the apparent volatilization coefficient in the presence of desorption effects will be less than the true coefficient as hypothesized previously.

The apparent volatilization coefficient determined by equation 22 can be converted to an apparent ϕ factor, ϕ_A , by dividing by k_{LOXY}/Y (equation 1). Doing this and solving for k_E gives

$$k_E = \frac{V}{A_s} (\phi_T/\phi_A - 1) \quad (23)$$

where

ϕ_T = true ϕ factor in the absence of desorption effects as defined by equation 1.

The factor V/A_s was constant for all experiments.

Insufficient data were collected in this study to determine experimentally the magnitude of the water-to-stainless-steel partition coefficient, k_E . However, the hypothesis can be evaluated indirectly by determining if the partition coefficient correlates with the water solubility, such as is true for several other types of partition coefficients (Briggs, 1981).

Values of the factor $k_E A_s/V$ were calculated from equation 23 for n-hexylbenzene, n-heptylbenzene, and n-octylbenzene and are plotted on a logarithmic scale in figure 17 as a function of water solubility (tables 2 and 3) on a logarithmic scale. The experimentally determined values of ϕ from table 1 were used for ϕ_A , and the ϕ_T values were calculated from equation 5 using the best-fit value of 0.566 for η determined from the experimental data for ethylbenzene through n-pentylbenzene. The least-squares line in figure 17 indicates a reasonable correlation of the limited data. This indicates that the results are not inconsistent with the hypothesis that the smaller than expected ϕ values for n-hexylbenzene, n-heptylbenzene, and n-octylbenzene were the result of rapid sorption followed by desorption of these compounds from the surfaces of the stainless-steel bath during the volatilization experiments. Data were limited, however, to the three points shown in figure 17.

The hypothesis also is supported by the fact that extrapolation of the least-squares line in figure 17 to the solubility of n-pentylbenzene (3.63 mg/L, table 2) results in a predicted ϕ value of 0.545, similar to the experimental value. This value is 2.83 percent larger than the experimental value of 0.530 (table 1), and this small difference is probably within the range of experimental error. This indicates that the solubility of n-pentylbenzene was large enough such that sorption was minimal with no measurable effect on the value.

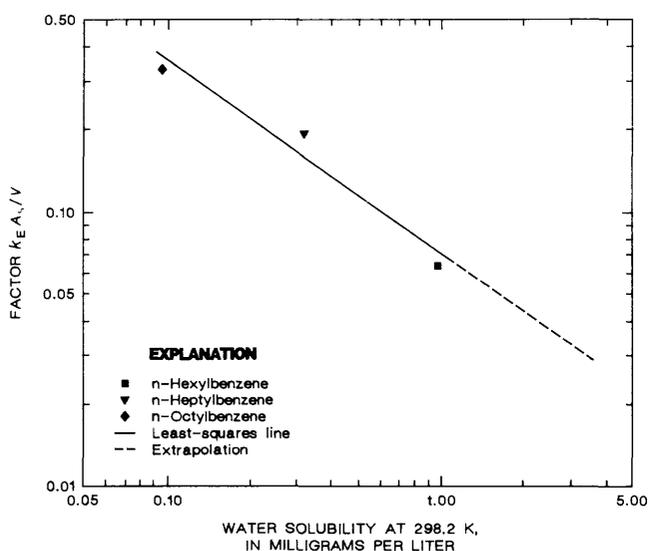


Figure 17. Values of the factor $k_E A_s/V$ as a function of solubility for n-hexylbenzene, n-heptylbenzene, and n-octylbenzene. Both scales logarithmic.

A second possible explanation for the smaller than expected ϕ values for n-hexylbenzene, n-heptylbenzene, and n-octylbenzene is the presence of undissolved quantities of these compounds in the water. As discussed previously, difficulties were experienced preparing water solutions of these compounds, and organic material was frequently observed floating on the water surface during the early stages of the experiments. Because these compounds were apparently present in excess of their water solubilities, the possibility of the process of accommodation (Peake and Hodgson, 1966, 1967) seems likely. The exact mechanism of this process has not been determined, but it is apparently some type of dispersive or micellar process resulting in the inclusion of organic compounds in water greatly in excess of the true water solubilities. It has been suggested (May and others, 1978) that this process may be one of the main reasons that water-solubility values of slightly soluble hydrocarbons measured using a mixing-equilibration technique are commonly too large.

This process could affect the volatilization experiments in the following way. If the accommodated material is uniformly distributed throughout the bath in direct proportion to the dissolved material, the accommodated material then would be sampled in the same proportion as the dissolved material and would appear as dissolved material in the analysis. However, because the accommodated material is likely to be present in the bath water in particles larger than molecular size, the effective volatilization rate would be slowed, the change in concentration with time would be decreased and, correspondingly, the liquid-film coefficient would be smaller than the true value.

This process of accommodation is expected to occur in inverse proportion to the solubility. Therefore, the greatest effect should have been observed for n-octylbenzene, with the effect decreasing with decreasing molecular weight. This was as observed in the volatilization studies, giving support to accommodation as a possible explanation for the smaller than expected values for the three high-molecular-weight compounds.

It is concluded that the most likely explanation for the smaller than expected ϕ values for n-hexylbenzene, n-heptylbenzene, and n-octylbenzene is the sorption-desorption process on the walls of the stainless-steel bath used for the experiments. The one experiment demonstrated sorption of these high-molecular-weight compounds on stainless steel, and the $k_E A_s/V$ factor correlated reasonably well with water solubility (fig. 17). Accommodation could have contributed to the smaller than expected ϕ values; however, there is no experimental support for this conclusion.

Deviations of the Low-Molecular-Weight Compounds

There are at least two possible explanations for the smaller than expected ϕ value for benzene shown in figures 12 and 13. These are interactions of the benzene molecules

with the water molecules and association of the benzene molecules with each other through hydrogen bonding to form dimers. Both of these processes would effectively increase the average molecular weight and, therefore, slow the volatilization rate.

There is evidence in the literature supporting both of these processes. It is generally recognized (Pimental and McClellan, 1960) that benzene is not inert with respect to hydrogen bonding by a proton-donating substance such as water. There have been both experimental (Tucker and others, 1981) and theoretical studies (Ben-Naim and others, 1973; Rossky and Friedman, 1980; Karlstrom and others, 1983) indicating dimerization of benzene in dilute aqueous solutions. Similarly, there have been both experimental (Backx and Goldman, 1981; Dutta-Choudhury and others, 1982) and theoretical studies (Ben-Naim and others, 1973; Karlstrom and others, 1983; Ravishanker and others, 1984) indicating benzene-water interactions. It was concluded, therefore, that the deviation for benzene was probably a result of these processes.

The ϕ value for toluene also was smaller than expected as shown in figures 12 and 13. Information from the literature regarding possible hydrogen-bonding interactions of toluene are less definitive than for benzene. Thermal-conductivity measurements and the temperature coefficient of the thermal conductivity indicated that toluene is not hydrogen bonded (Pimental and McClellan, 1960). However, infrared spectra measurements (Van Ness and others, 1977) and excess thermodynamic properties (Hwa and Ziegler, 1966) of ethanol-toluene solutions indicated definite interactions, probably a hydrogen bond between the toluene and the ethanol. Also, solute-solvent interactions were indicated for toluene-water solutions (Dutta-Choudhury and others, 1982).

The fact that the hydrogen-bonding properties of toluene are less well defined than for benzene is consistent with the suggestion (Pimental and McClellan, 1960) that the extent of hydrogen bonding in a homologous series decreases as the molecular weight increases. This occurs primarily because the increased molecular size results in steric hindrance, which decreases the ability to form hydrogen bonds and to engage in other types of molecular interactions. The ϕ values of this study also are consistent with this suggestion. The ϕ value for benzene was 11.1 percent less than the value predicted with equation 5 with an η value of 0.566, the toluene value was 5.35 percent less, and the ethylbenzene value was included in the data used in the evaluation of the η value of 0.566; thus, it was assumed to have no deviation. The results, therefore, indicate decreased deviation from the expected values as the molecular weight increases.

Henry's Law Constants

The relative importance of the liquid-film and gas-film resistances to volatilization of an organic compound is deter-

mined by the Henry's law constant of the compound. Knowledge of this constant is necessary, therefore, to evaluate the assumption that volatilization of benzene and the series of alkyl-substituted benzenes considered in this study is liquid-film controlled.

The Henry's law constant is defined by (Mackay and others, 1979)

$$H = 18 \times 10^{-6} \gamma P \quad (24)$$

where

H = Henry's law constant, in kilopascals cubic meter per gram mole; and

P = vapor pressure of the pure organic compound, in kilopascals.

It was discussed previously that the activity coefficient, γ , is related to the solubility by equation 18. Combining equations 18 and 24 gives

$$H = PM/S \quad (25)$$

Application of equation 25 requires vapor-pressure data. The most common source of vapor-pressure data for hydrocarbons is the compilation of Wilhoit and Zwolinski (1971). However, because errors in published vapor-pressure data are known to occur (Hoffman, 1984), these data were first compared with other data from the literature before use. Comparison of the data for benzene and ethylbenzene with the data of Stuckey and Saylor (1940) and Stull (1947) indicated small differences. Comparison of the data for toluene, n-propylbenzene, n-butylbenzene, and n-heptylbenzene with the data of Stull (1947) indicated small differences for toluene and n-propylbenzene, slightly larger differences in about the 1- to 5-percent range for n-butylbenzene, and large differences in the 11- to 26-percent range for n-heptylbenzene. Therefore, the conclusion was that the data of Wilhoit and Zwolinski (1971) were accurate and, consequently, these data were used in this report.

One problem exists, however, in the use of these data. The data are presented in tabular form as temperatures corresponding to fixed values of the vapor pressure. But the smallest vapor pressure presented for n-octylbenzene is 1.33 kPa with the corresponding temperature of 400.2 K. Therefore, estimating a vapor pressure for n-octylbenzene at 298.2 K from these data requires considerable extrapolation. As the molecular weight decreases, the degree of extrapolation decreases, but extrapolation to 298.2 K is required for all compounds except benzene and toluene.

Values of the constants of the Antoine equation fitted to the experimental data and used to calculate the tabular data also were presented (Wilhoit and Zwolinski, 1971). This equation has been widely used, but it has been suggested (Reid and others, 1977) that the equation should not be used outside the temperature and vapor-pressure range of the data on which it is based. Despite this admonition, it was used

to perform the needed extrapolations in the present study. The extrapolated data were evaluated for consistency, however, using several procedures for correlating vapor pressures of homologous series. These included molecular surface area (Amidon and Anik, 1981), boiling temperature (Mackay, Bobra, and others, 1982), and molar volume. The latter correlation was based largely on the fact that water solubilities of a homologous series correlate well with molar volume (McAuliffe, 1966).

The vapor pressures at 298.2 K are plotted on a logarithmic scale in figure 18 as a function of the molecular surface area. These areas were obtained as described previously. The line in figure 18 is a least-squares fit having the equation

$$P = 1.46 \times 10^5 \exp(-3.67 \text{ TSA}) \quad (26)$$

The rms error computed from an equation of the form of equation 10 is ± 8.43 percent. The fit of the least-squares line for the entire range of molecular surface areas shown in figure 18 indicates that the extrapolated vapor pressures for the higher molecular-weight compounds are reasonable values.

The vapor pressures at 298.2 K are plotted on a logarithmic scale in figure 19 as a function of the normal boiling temperature. The line is a least-squares fit having the equation

$$P = 9.69 \times 10^8 \exp(-0.0503 T_{bp}) \quad (27)$$

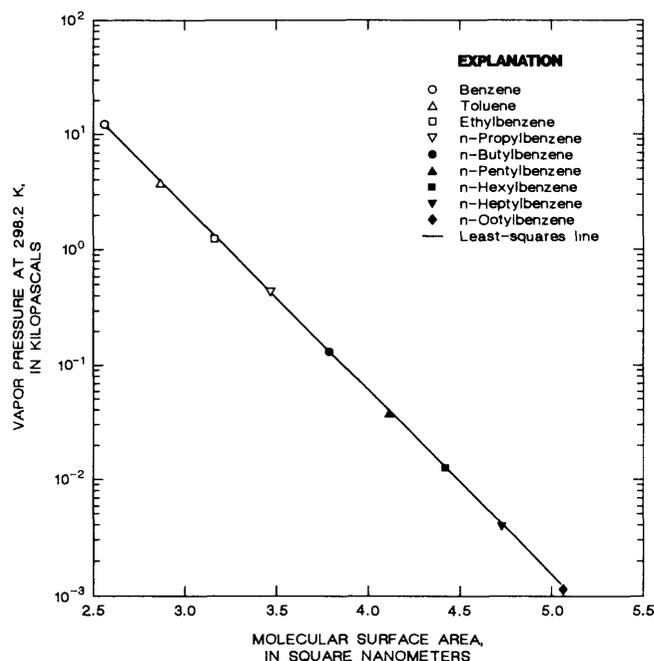


Figure 18. Vapor pressures at 298.2 K as a function of molecular surface area.

The rms error is ± 98.3 percent. This large error is indicative of the obvious deviations of the points shown in figure 19. The experimental points are definitely concave toward the abscissa, resulting in negative deviations for the least-squares line in the middle part of the boiling-temperature range and positive deviations for the line at the ends of the temperature range.

The vapor pressures at 298.2 K are plotted on a logarithmic scale in figure 20 as a function of the molar volume. The line is a least-squares fit having the equation

$$P = 6.70 \times 10^3 \exp(-0.0697 V_M) \quad (28)$$

The rms error is ± 13.1 percent. There is a slight tendency for the experimental points in figure 20 to be concave toward the abscissa. However, the fit of the least-squares line for the entire range of molar volumes again indicates that the extrapolated vapor pressures for the higher molecular-weight compounds are reasonable values. Finally, it is interesting that the plot of water solubility versus molar volume (fig. 15) also showed a similar slight concavity toward the abscissa.

It was concluded on the basis of figures 18 and 20 that extrapolating the vapor-pressure data of Wilhoit and Zwolinski (1971) using the Antoine equation resulted in reasonable vapor pressures for the higher molecular-weight compounds. These vapor pressures were used with the water-solubility values presented previously (tables 2 and 3) and equation 25 to calculate Henry's law constants.

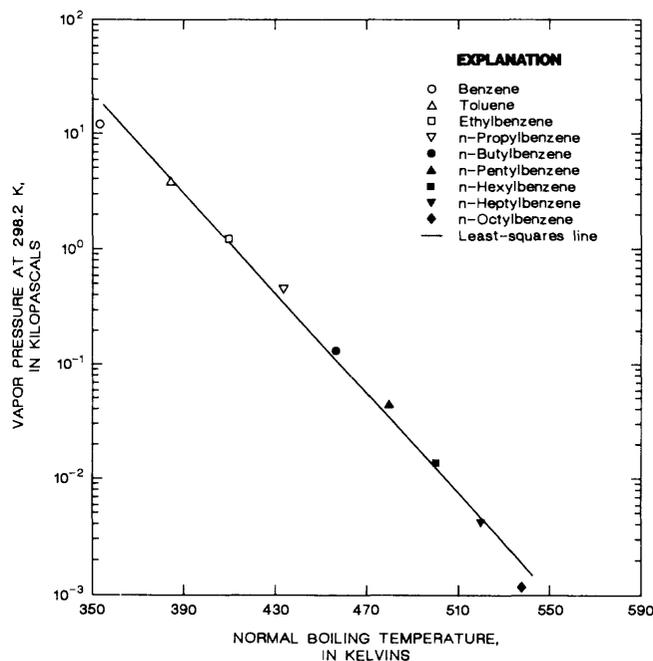


Figure 19. Vapor pressures at 298.2 K as a function of normal boiling temperature.

The calculated Henry's law constants are plotted on a logarithmic scale in figure 21 as a function of the molar volume. The line in figure 21 is for the equation

$$H = 3.50 \times 10^{-3} V_M \exp(0.00570 V_M) \quad (29)$$

This line is nonlinear because of the presence of the V_M factor in the pre-exponential term.

Equation 29 was derived by combining equations 16 and 28 with equation 25. The molecular weight in equation 25 was expressed as a function of the molar volume by noting that the densities (Weast, 1985) of the nine compounds vary little with molecular weight. The average density was 0.8630 g/mL with a coefficient of variation of ± 0.72 percent. It followed, therefore, that

$$M = 0.8630 V_M \quad (30)$$

Equation 29 provides a reasonable fit to the calculated Henry's law constants. The rms error of the form of equation 10 is ± 13.6 percent. It might be argued that there are systematic deviations from equation 29, as shown in figure 21. However, possible uncertainties in the vapor-pressure data and the water-solubility values of n-heptylbenzene and n-octylbenzene preclude determination of the exact dependence on molar volume of the Henry's law constant for this series of compounds.

An extensive compilation of Henry's law constants has been presented (Mackay and Shiu, 1981), but there apparently have been no systematic studies of the Henry's law con-

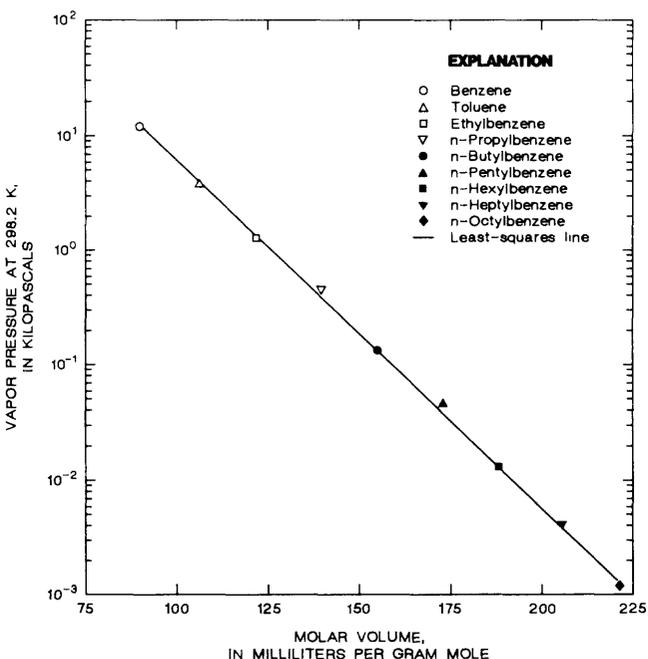


Figure 20. Vapor pressures at 298.2 K as a function of molar volume.

stants of a homologous series. Mackay, Shiu, and others (1982) pointed out that both the vapor pressure and the water solubility of a homologous series will decrease as the molecular weight increases. Therefore, the effect on the Henry's law constant will depend on the relative rates of decrease of these two properties, as indicated by equation 25, and generalizations are not possible. Also, it was pointed out (Mackay and Shiu, 1981) that the Henry's law constant of a homologous series will vary relatively little compared with the variations of the vapor pressure and water solubility. This was true in the present study where the Henry's law constant varied less than one log cycle whereas both the vapor pressure and the water solubility varied slightly more than four log cycles.

Percentage Resistance in the Liquid Film

The basic equation of the two-film model is (Mackay and Cohen, 1976)

$$1/K_{OL} = 1/k_L + RT/H k_G \quad (31)$$

where

K_{OL} = overall mass-transfer coefficient based on the liquid phase, in meters per day;

R = ideal gas constant, in kilopascals cubic meter per gram mole per kelvin;

T = absolute temperature, in kelvins; and

k_G = gas-film coefficient, in meters per day.

The reciprocal of a mass-transfer coefficient is the resistance to mass transfer (Liss and Slater, 1974). Therefore, it follows that the left side of equation 31 is the total resistance to mass

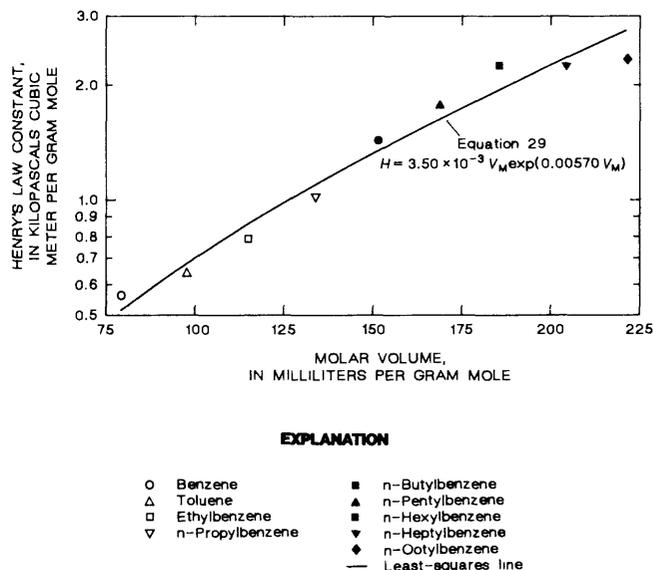


Figure 21. Henry's law constants as a function of molar volume.

transfer, the first term on the right side is the resistance of the liquid film, and the second term is the resistance of the gas film. Consequently, the percentage resistance in the liquid film is given by

$$\text{Percentage resistance in liquid film} = \frac{1/k_L}{1/k_L + RT/H k_G} (100) \quad (32)$$

Analysis of equation 32 indicates that if the Henry's law constant is large enough, then the $RT/H k_G$ term will be small with respect to the $1/k_L$ term, and therefore, most of the resistance will be in the liquid film. Also, under these circumstances, equation 31 indicates that the liquid-film coefficient will be virtually the same as the overall mass-transfer coefficient; it is this coefficient that is measured in a volatilization study. This is the assumption that was made in the present study.

Verification of this assumption requires liquid-film and gas-film coefficients, the Henry's law constant, and the temperature. All this information with the exception of the gas-film coefficients was presented previously. Gas-film coefficients are usually determined by measuring the volatilization fluxes of the pure compounds (Rathbun and Tai, 1984c), the rationalization being that there can be no concentration gradient in a pure liquid and, therefore, no liquid-film resistance. Water is commonly used as the reference substance for the gas-film coefficient because all the resistance to the evaporation of water is in the gas film. Also, water is obviously a significant part of the environment and, therefore, of concern.

The reference-substance equation for the gas-film coefficient analogous to equation 1 for the liquid-film coefficient is

$$\psi = k_{G_{ORG}}/k_{G_{WAT}} \quad (33)$$

where

ψ = constant assumed to be independent of mixing conditions in the air; and

WAT = subscript denoting water.

Mixing conditions in the air are commonly indicated by the windspeed, and ψ has been determined to be independent of windspeed for the ethylene dibromide-water pair (Rathbun and Tai, 1986).

Data from the literature (Chiou and others, 1980) for volatilization fluxes were used to determine ψ values for benzene and toluene. Results at 298.2 K were 0.616 for benzene and 0.574 for toluene. Data for the other benzene compounds were not available. The values of ψ for these other compounds can be calculated, however, using two estimation procedures (Rathbun and Tai, 1983) analogous to those discussed previously for the liquid-film coefficients.

The first estimation procedure assumes that the gas-film coefficient depends on the molecular-diffusion coefficient, δ (in square meters per day), raised to some power

ν as expressed by

$$k_G = a_G \delta^\nu \quad (34)$$

where a_G is a constant, in meters to the $1-2\nu$ power times days to the $\nu-1$ power; and the molecular-diffusion coefficient is now for the compounds in air rather than water. Writing equation 34 for an organic compound and for water as the reference substance and combining in ratios gives

$$k_{G_{ORG}}/k_{G_{WAT}} = (\delta_{ORG}/\delta_{WAT})^\nu \quad (35)$$

Combining equations 33 and 35 gives

$$\psi = (\delta_{ORG}/\delta_{WAT})^\nu \quad (36)$$

Molecular-diffusion coefficients in air for the nine benzene compounds and water were calculated using the Wilke-Lee equation as described by Reid and others (1977). These diffusion coefficients were used with equation 36 to determine the value of the exponent ν required to give the experimental ψ values of 0.616 for benzene and 0.574 for toluene. The exponents were 0.558 for benzene and 0.552 for toluene, in reasonable agreement with previous experimental values of 0.5 (Yadav and Sharma, 1979) and 0.684 (Tamir and Merchuk, 1978). Therefore, an average value of 0.555 was used for ν . This value is similar to the best-fit value of 0.566 determined previously for the liquid-film coefficients. However, no significance is attached to this similarity because the processes are different, one involving molecular diffusion through water and the other molecular diffusion through air.

The second estimation procedure is identical to that used for the liquid-film coefficients, and it assumes that the gas-film coefficient is inversely proportional to the molecular weight. With water as the reference substance, the equation has the form

$$\psi = (M_{ORG}/18.02)^{-0.500} \quad (37)$$

It was determined that equation 37 underpredicted the experimental ψ values for benzene and toluene. Agreement was achieved if the exponent was reduced to -0.331 for benzene and to -0.341 for toluene, considerably less than the theoretical -0.500 value. A similar decrease in the absolute value of the exponent was necessary for the liquid-film coefficients, although the exponent did not have to be reduced as much for agreement. These results indicate that the molecular-weight procedure for estimating ϕ and ψ values is only an approximate procedure. For this reason, only the molecular-diffusion-coefficient procedure was used for estimating the values in this study.

Values of ψ calculated from the estimated molecular-diffusion coefficients and equation 36 with a value of 0.555 for ν are given in table 4. These values of ψ were used in

Table 4. ψ ratios, gas-film coefficients, maximum and minimum experimental liquid-film coefficients, and percentage resistances in the liquid film

Compound	ψ	Gas-film coefficient (meters per day)	Maximum and minimum liquid-film coefficients (meters per day)	Percentage resistance in liquid film (percent)
Benzene	0.615	429	4.27 .522	95.8 99.5
Toluene	.576	402	4.20 .595	96.2 99.4
Ethylbenzene	.545	380	4.36 .565	96.5 99.5
Ethylbenzene (group 2)	.545	380	4.06 .683	96.8 99.4
n-Propylbenzene	.520	363	3.96 .676	97.4 99.5
n-Butylbenzene (group 2)	.499	348	3.58 .645	98.2 99.7
n-Butylbenzene (group 3)	.499	348	3.48 .463	98.3 99.8
n-Pentylbenzene	.478	334	3.29 .464	98.6 99.8
n-Hexylbenzene	.464	324	2.30 .268	99.2 99.9
n-Heptylbenzene	.451	315	2.72 .359	99.0 99.9
n-Octylbenzene	.438	306	2.68 .245	99.1 99.9

conjunction with equation 33 and a gas-film coefficient for the evaporation of water from the experimental apparatus to compute gas-film coefficients for the benzene compounds for the constant-temperature water bath. The apparatus and experimental conditions including the air-flow rate, water-mixing conditions, water depth, and temperature were identical to those used in the volatilization studies for the benzene compounds. The mean of six determinations, two each at slow, medium, and rapid water-mixing rates, was 698 m/d with a coefficient of variation of ± 2.41 percent (Rathbun and Tai, 1987). A statistical analysis indicated no significant dependence of the coefficients on mixing conditions in the water. Values of the gas-film coefficients calculated from this water coefficient and the ψ values are presented in table 4. These gas-film coefficients for each compound were constant for all experiments. This is an example of an application of the reference-substance concept where the gas-film coefficients of benzene and toluene for the apparatus of Chiou and others (1980) were adjusted to the apparatus used in this study, with water as the common reference substance.

Percentage resistances in the liquid film were calculated from equation 32, the Henry's law constants presented previously, the gas-film coefficients presented in table 4, and the maximum and minimum experimental liquid-film coefficients for each of the compounds. Equation 32 indicates that the percentage resistance depends on the relative

magnitudes of the liquid-film and gas-film coefficients. Therefore, the maximum and minimum liquid-film coefficients were used to define the range of percentage resistances. These liquid-film coefficients are given in table 4.

Percentage resistances in the liquid film are presented in table 4 and range from 95.8 percent for the rapid water-mixing condition for benzene to 99.9 percent for the slow water-mixing condition for n-hexylbenzene, n-heptylbenzene, and n-octylbenzene. It was concluded that almost all of the resistance to the volatilization of these compounds from water is in the liquid film and, therefore, the assumption of liquid-film controlled volatilization is valid. It follows that the measured volatilization coefficients are virtually identical to the liquid-film coefficients.

DISCUSSION

The results presented in figures 1 through 11 show that a constant relation exists between the liquid-film coefficients for all the organic compounds and the oxygen absorption coefficient for a considerable range of water-mixing conditions. It was concluded that the constancy of these relations expressed by the ϕ values in table 1 could be used in conjunction with the reference-substance concept to estimate liquid-film coefficients for the volatilization of these com-

pounds from streams and rivers. Conversely, analysis of the two procedures for estimating ϕ values indicated deviations for the high- and low-molecular-weight compounds. This apparent contradiction requires discussion.

At the high-molecular-weight end of the range considered, the ϕ values predicted using the molecular-diffusion-coefficient procedure were 6.49 percent larger, 19.2 percent larger, and 33.7 percent larger than the experimental values for n-hexylbenzene, n-heptylbenzene, and n-octylbenzene, respectively. Deviations for the molecular-weight procedure were similar.

For qualitative modeling of the fate of these organic compounds in streams and rivers, such differences are probably not significant. It might be argued that the trend toward larger errors in ϕ with increasing molecular weight could result in excessive errors. However, as ϕ decreases, volatilization rapidly becomes less significant as a fate-determining step.

For quantitative modeling efforts, these differences may be significant. The differences were attributed to possible rapid sorption of these compounds to the surfaces of the constant-temperature water bath, followed by desorption into the water during the volatilization measurements. Difficulties in dissolving these compounds in water also may have resulted in accommodated material that contributed to the slower than expected rate of change of concentration with time. These experimental difficulties indicate that the predicted ϕ values are probably a more correct indication of the actual volatilization characteristics of the high-molecular-weight compounds than are the experimental values. The experimental difficulties also indicate that sorption may be a significant fate-determining process for the high-molecular-weight compounds in streams and rivers. This would require including a sorption submodel in the overall fate model.

It was concluded, therefore, that the best values of ϕ for application in streams and rivers are 0.508 for n-hexylbenzene, 0.494 for n-heptylbenzene, and 0.481 for n-octylbenzene. These values were estimated from equation 5 with an η value of 0.566 and molecular-diffusion coefficients estimated from the Hayduk-Laudie equation (Reid and others, 1977).

At the low-molecular-weight end of the range considered, the ϕ values predicted using the molecular-diffusion-coefficient procedure were 9.07 percent larger and 3.94 percent larger than the experimental values for benzene and toluene, respectively. Deviations for the molecular-weight procedure were similar.

Differences of this magnitude probably would not have a significant effect, even in a quantitative modeling effort. These differences were attributed to possible interactions of the benzene and toluene molecules with the water molecules and also to hydrogen-bonding interactions of the benzene molecules with each other to form dimers. Because these processes also would likely occur in streams

and rivers, it was concluded that the best values of ϕ for benzene and toluene for application in streams and rivers are the experimental values of 0.606 and 0.598 given in table 1.

Accepting the experimental values as the best values is equivalent to concluding that the differences for benzene and toluene are true differences and not just experimental errors or the results of experimental problems. Thus, deviations from both the molecular-diffusion-coefficient and molecular-weight procedures for estimating ϕ values occurred for the low-molecular-weight compounds. This indicates the need for additional study of these estimation procedures, perhaps for a homologous series of chlorinated hydrocarbons.

APPLICATION

Application of the results of this study is demonstrated with an example. Assume that a wastewater containing chloroform, carbon tetrachloride, 1,2-dichloroethane, and p-xylene is discharged into a stream. Concentrations in the wastewater are such that, after mixing with the stream, each compound has a concentration of 100 $\mu\text{g/L}$. It is desired to compute the distances downstream at which the concentration of each compound will be decreased 99 percent by volatilization to 1.0 $\mu\text{g/L}$. The stream has a mean water velocity of 8.6 km/d, a water depth of 0.68 m, the oxygen liquid-film coefficient is 1.6 m/d, and the water temperature is 298.2 K.

The first step is to check the Henry's law constants of these compounds to determine the relative importance of the liquid-film and gas-film resistances to volatilization. Recommended Henry's law constants at 298.2 K from Mackay and Shiu (1981) are given in table 5. All values are larger than the value of 0.100 kPa $\text{m}^3/\text{g mol}$ for which the liquid film controls the volatilization rate (Mackay and Shiu, 1981). Thus, the gas-film resistance to volatilization is assumed to be negligible for these compounds. However, the more similar the Henry's law constant is to this limiting value, the more likely deviations from the assumption are to occur.

The second step is to estimate the molal volumes at the normal boiling temperature using the LeBas method (Reid and others, 1977) and to calculate the molecular-diffusion coefficients using equation 11. Results of these calculations also are given in table 5.

The third step is to compute the ϕ values using equation 5 with the value of 0.566 for η determined in this study. Results also are given in table 5.

The fourth step is to compute the liquid-film coefficients for the organic compounds using the ϕ values from step 3 and equation 1 with the specified value of 1.6 m/d for the oxygen liquid-film coefficient. These computed liquid-film coefficients also are given in table 5.

The final step is to compute the distances downstream for the concentration to be decreased 99 percent by volatiliza-

Table 5. Parameters for the calculation of the distance downstream required for 99-percent decrease in concentration of four compounds by volatilization

Compound	Henry's law constant (kPa m ³ /g mol)	Molal volume (mL/g mol)	Molecular-diffusion coefficient x 10 ⁵ (m ² /d)	ϕ	Liquid-film coefficient (m/d)	Distance (km)
Chloroform	0.38	92.3	9.05	0.684	1.09	24.7
Carbon tetrachloride	2.0	113.2	8.02	.639	1.02	26.4
1,2-Dichloroethane	.11	93.6	8.97	.681	1.09	24.7
p-Xylene	.71	140.4	7.07	.595	.952	28.3

tion to 1.0 $\mu\text{g/L}$. This is done using the equation

$$C/C_1 = \exp(-k_L X/YU) \quad (38)$$

where

C =concentration, in micrograms per liter, at downstream distance X , in kilometers, from the point of addition of the wastewater to the stream;

C_1 =concentration, in micrograms per liter, in the stream at the point of addition;

k_L =liquid-film coefficient, in meters per day;

Y =water depth, in meters; and

U =mean water velocity, in kilometers per day.

The computed distances are given in table 5.

As expected, results in table 5 indicate that the concentrations of the more volatile compounds are decreased to the required concentration in a distance shorter than those for the less volatile compounds. The tendency to volatilize from the stream is in proportion to the magnitude of ϕ , thus the larger ϕ is, the greater the tendency to volatilize, and the shorter the distance. The results in table 5 also indicate that there is not much difference in the volatilization characteristics of the four compounds. These results are consistent with limited data in the literature (Smith and others, 1980; Rathbun and Tai, 1981, 1984a) which indicate that ϕ values of compounds for which volatilization is likely to be a fate-determining process generally are between 0.5 and 0.7.

The distances given in table 5 are hypothetical in that they consider only the process of volatilization. In a natural stream, the concentrations also would be decreased with distance downstream as a result of the process of dispersion and mixing. In addition, the chemical, biological, and other physical processes, such as sorption discussed previously, could affect the concentrations of the compounds with distance downstream. The dispersion and mixing processes are likely to affect the concentrations of the four compounds in the same way. The chemical, biological, and other physical processes are likely to affect the concentrations in different ways because of differences in the properties of the four compounds. Discussion of the possible effects of these processes is beyond the scope of this report.

Experimental values of ϕ for three of the compounds are available in the literature for comparison with the values in table 5 predicted on the basis of the results of this study. Experimental values are 0.655 for chloroform (Rathbun and Tai, 1981), 0.63 for carbon tetrachloride (Smith and others, 1980), and 0.621 for 1,2-dichloroethane (Rathbun and Tai, 1984a). These values are 4.4, 1.4, and 9.7 percent larger than the respective predicted values in table 5, indicating that equation 5 developed in this study gives reasonably accurate predictions of ϕ . An experimental value of ϕ for p-xylene was not available for comparison.

SUMMARY AND CONCLUSIONS

Liquid-film coefficients for the volatilization of benzene and eight alkyl-substituted benzene compounds (toluene through n-octylbenzene) from water were measured in a constant-temperature, stirred water bath simultaneously with the liquid-film coefficient for oxygen absorption. Measurements were made for a range of water-mixing conditions at a water temperature of 298.2 K. Specific conclusions resulting from this study are as follows:

1. The ratios of the organic liquid-film coefficients for volatilization to the liquid-film coefficient for oxygen absorption were independent of water-mixing conditions. Experimental ratios ranged from 0.606 for benzene to 0.357 for n-octylbenzene.

2. The molecular-diffusion-coefficient procedure for estimating ratios of the organic liquid-film coefficient to the liquid-film coefficient for oxygen absorption predicted a dependence on the molecular-diffusion coefficient to the 0.566 power for ethylbenzene through n-pentylbenzene, in agreement with published values. Experimental values for benzene and toluene were less than predicted by this procedure. These differences were attributed to possible interactions of the molecules of these compounds with water molecules and also to benzene-benzene interactions that form dimers. Experimental values for n-hexylbenzene, n-heptylbenzene, and n-octylbenzene also were less than predicted by this procedure. These differences were attributed to rapid sorption to the surfaces of the stainless-steel,

constant-temperature water bath, followed by desorption into the water during the course of the experiments. Difficulties in obtaining true water solutions of these compounds also may have contributed to the smaller than expected ratios for these compounds.

3. The molecular-weight procedure for estimating ratios of the organic liquid-film coefficient to the liquid-film coefficient for oxygen absorption predicted a dependence on the molecular weight to the -0.427 power for ethylbenzene through *n*-pentylbenzene. An alternative approach using an empirical relation between the molal volume at the normal boiling temperature and the molecular weight resulted in a dependence to the -0.390 power. Both of these approaches accurately predicted the ratios; however, the power dependencies on molecular weight are considerably less than the -0.500 commonly used in the literature. This difference indicates that applying Graham's law of diffusion, which is the basis of the molecular-weight procedure, to molecular diffusion in liquids may not be strictly valid.

4. The experimental values for benzene through *n*-pentylbenzene of the ratios of the liquid-film coefficients to the liquid-film coefficient for oxygen absorption are appropriate for use in the reference-substance concept for predicting liquid-film coefficients for the volatilization of these compounds from streams and rivers. Differences were determined between experimental and predicted values for benzene and toluene; the experimental values are appropriate because the possible processes contributing to the differences also are likely to be operative in streams and rivers. Differences also were determined between experimental and predicted values for *n*-hexylbenzene, *n*-heptylbenzene, and *n*-octylbenzene; the predicted values are appropriate for these compounds because they are considered to be more representative of the true volatilization process. However, sorption also may be a significant process for these compounds in streams and rivers and it needs to be considered in addition to volatilization.

5. An analysis of water-solubility data from the literature and experimental difficulties in preparing water solutions of these compounds for the volatilization studies indicated that published values of water solubility for *n*-heptylbenzene and *n*-octylbenzene are much too large. Extrapolations of correlations of water-solubility values of benzene through *n*-hexylbenzene as a function of molecular surface area and molar volume, a correlation of reciprocal values of water solubility as a function of normal boiling temperature, and a correlation of activity coefficient as a function of the number of carbon atoms in the molecule resulted in water-solubility values considered to be much more accurate than published values.

6. The Henry's law constant increased approximately exponentially with the molar volume for the homologous series of benzene compounds. The dependence was not truly exponential because of the presence of the molar volume in the pre-exponential factor. The Henry's law constants for

the compounds varied less than one log cycle; whereas the water solubility and vapor pressure varied slightly more than four log cycles.

7. The percentage resistance in the liquid film varied from 95.8 percent for benzene for a rapid water-mixing rate to 99.9 percent for *n*-hexylbenzene, *n*-heptylbenzene, and *n*-octylbenzene for a slow water-mixing rate. It was concluded that the volatilization of these compounds from water is liquid-film controlled.

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