

Henry's Law Constant for Environmentally Significant Compounds

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ABSTRACT

Many nonvolatile organic compounds, e.g., polyaromatic hydrocarbons (PAHs), are readily stripped during aerobic biodegradation. This is because of the high infinite dilution activity coefficient resulting from forces generated by the water-organic interactions at the molecular level. Several models have been proposed for air-stripping based on the Henry's law constant. By definition, the Henry's law constant is the infinite dilution activity coefficient multiplied by the pure component vapor pressure. In this article, a gas saturation technique was used to measure the very low vapor pressures exhibited by these nonvolatile compounds. Literature values of other PAHs have been tabulated and are presented. For determining infinite dilution activity coefficients, a differential ebulliometry apparatus has been constructed. In this technique, the boiling point difference between pure water and a water-organic solution is measured very precisely. Thermodynamics is then used to calculate the infinite dilution activity coefficient. The method's accuracy has been tested using the phenol-water system.

Index Entries: Henry's law constant; vapor pressures; polycyclic aromatic compounds; differential ebulliometry; activity coefficients.

INTRODUCTION

In the biological treatment of waste water and soils, microorganisms are used to degrade toxic organics. However, other fates for the organic compounds are possible. The organics can be transported from the liquid

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phase by volatilization and/or stripping, or absorbed onto the biomass (1-3). For many organic compounds, stripping from the liquid phase can be significant. Oxygen is supplied to the system by contacting the waste water with large volumes of air resulting in a large interfacial area. Because of repulsive forces on the molecular level, many nonpolar organic molecules form highly nonideal solutions with water. These solutions exhibit positive deviation from ideal behavior resulting in large values for the activity coefficient (4,5). When the effects of aeration and high nonideality are combined, the potential exists for a large quantity of organics to be stripped from the solution before biodegradation can take place.

Several semi-theoretical models have been proposed to account for the fate of organics in biological systems (6-11). In these models, a major parameter that must be determined experimentally is the Henry's law constant. Unfortunately, for many organic-water systems of environmental significance, this information is not available in the literature. Additionally, it is not possible to accurately determine Henry's law constant experimentally for these systems.

Henry's Law Constant

Classical methods of determining Henry's law constants involve sampling the vapor and liquid phases of a system at equilibrium. Vapor-phase sampling is always difficult because of problems with condensation. However, when dealing with aqueous solutions of nonpolar or slightly polar compounds, this problem is further compounded. The organics owe their high volatility to the presence of the water in the liquid phase. Once a vapor sample has been removed from the system, the organic will condense.

An alternative to measuring the Henry's law constant directly is to calculate it from other fundamental thermodynamic properties. By definition, the Henry's law constant is:

$$H_c = \lim_{x \rightarrow 0} (f_i^L/x_i) = P_i^v \gamma_i^\infty \quad (1)$$

where F_i^L is the fugacity of the component i in the liquid phase, x_i is the mole fraction, P_i^v is the vapor pressure of pure i , and γ_i^∞ is the infinite dilution activity coefficient (12). The problem of determining the Henry's law constant thus reduces to determining the pure component vapor pressure and infinite dilution activity coefficient of the aqueous system.

Vapor Pressures

Vapor pressures for many PAHs are available in the literature. However, different measurement techniques have been used and the data presented in different units. Where no data are available, vapor pressures can be easily measured. The preferred techniques for measuring very low

vapor pressures are Knudsen diffusion and gas saturation. Knudsen diffusion techniques can provide accurate vapor pressure measurements. However, proper equipment design and construction are difficult and expensive (13). Also, Knudsen diffusion is sensitive to impurities. Gas saturation methods are primarily used to measure vapor pressures below 1 mm Hg. The method is based on passing an inert carrier gas through a column packed with the experimental analyte. Experimental conditions are adjusted so that complete saturation of the carrier gas occurs. The analyte is then collected using cryogenic trap, adsorbent, or organic solvent (14). By knowing the amount of analyte collected, the carrier gas flow rate, and system pressure, the vapor pressure of the analyte can be calculated. An important advantage gas saturation has over other methods is its insensitivity to impurities. Gas saturation methods have been used to measure the vapor pressures of certain PCBs (15) and PAHs (4, 14, 16–18).

Activity Coefficients

Infinite dilution activity coefficients can be predicted by UNIFAC or experimentally measured. Prediction by UNIFAC is advantageous since no experimental data on the properties of the solution are needed. The method is based on the group contribution approach and can provide very accurate approximations (5). However, for certain highly nonideal systems, the UNIFAC method has been reported to be very inaccurate (19). For these systems, the infinite dilution activity coefficient must be determined experimentally.

Infinite dilution activity coefficients can be experimentally determined by classical vapor-liquid equilibrium methods, gas chromatography retention behavior, and differential ebulliometry. The differential ebulliometry method consists of measuring the difference in boiling points of a pure solvent and the solvent with dissolved organic at a controlled pressure. The infinite dilution activity coefficient is then derived from the data by a rigorous thermodynamic analysis (20). The accuracy of this method is far superior to classical vapor-liquid equilibrium methods, since problems in sampling the gas phase are avoided. For systems where the relative volatility is between 0.1–10, the ebulliometric method has been found to be superior to the gas chromatography method (20).

This work consists of applying gas saturation and differential ebulliometry to determine the vapor pressures and infinite dilution activity coefficients of environmentally significant compounds in aqueous systems. The vapor pressures of four polycyclic aromatic hydrocarbons (PAHs) have been measured using a gas saturation apparatus coupled with high-pressure liquid chromatography and fluorescence detection. For determining infinite dilution activity coefficients, a differential ebulliometry apparatus has been constructed and tested with the phenol-water system. The system will be used to determine the infinite dilution activity

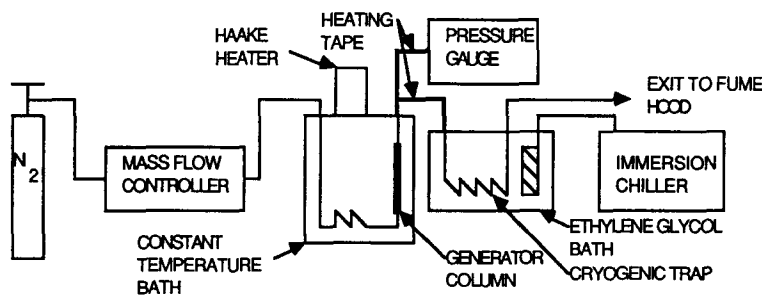


Fig. 1. Gas saturation apparatus for vapor pressure measurements.

coefficients of compounds that exhibit aqueous solubility. Once these two thermodynamic properties have been determined, the Henry's law constant will be calculated.

MATERIALS AND METHODS

Chemicals

The PAHs were purchased from Aldrich Chemical Co., Milwaukee, WI. Naphthalene was 99.9%+ pure, anthracene was 99.9% pure, chrysene and benzo[a]pyrene were 98% pure. HPLC grade acetonitrile was purchased from Baxter Scientific, Waukegan, IL.

Experimental Apparatus

Figure 1 is a schematic diagram of the gas saturation system. The system consists of five major components: a nitrogen source, mass flow controller, equilibrium cell, cryogenic trap, and pressure gage. These components were connected with 1/4" OD S.S. tubing and swagelok fittings. The tubing was cleaned with acetone and then baked in an air-circulating oven to remove any impurities.

The nitrogen used in this work was industrial-grade 99.99% pure. Gas flow rates were controlled with a Brooks Instruments mass flow controller model 5850. The accuracy of this instrument is $\pm 1\%$ of full scale.

The equilibrium cell consisted of a 1/2" \times 10" stainless-steel tube. The experimental compound was coated onto the surface of 0.3-mm glass beads. The coatings were accomplished by dissolving approx 1.0 g of the compound in toluene, adding the glass beads, and then removing the toluene by evaporation in an air-circulating oven. The beads were then secured in the equilibrium cell by placing glass wool at the ends. The temperature of the cell was controlled by placing it in an oil bath that was held at the experimental temperature with a Haake E 3 circulating heater. This device has an accuracy of $\pm 0.02^\circ\text{C}$. The pressure at the exit of the column was measured with a Heise Series 9 digital pressure gage, which has an accuracy of better than ± 5 mmHg.

The cryogenic trap consisted of a 10' \times 1/4" OD copper coil. The coil was immersed in an ethylene glycol-water mixture held below -30°C with a Polyscience immersion chiller. The tubing connecting the equilibrium cell to the copper coil was wrapped in heating tape. An Omega CN370 temperature controller was used to maintain the tubing temperature at 20°C higher than the equilibrium cell temperature. This was done to prevent condensation of the experimental compound onto the inner tubing walls.

Experimental Procedure

After securing the equilibrium cell in place, the system was run for several days at a temperature 10°C higher than experimental temperatures. This was done to strip off any remaining impurities. Experiments were then run for anywhere from several hours to several days. The length of an experimental run depended on the temperature setting of the equilibrium cell. Typical runs were from several hours to 1 d. Flow rates used in this work were between 20–30 standard cubic cm/min.

At the end of an experiment, the experimental compound that had collected in the cryogenic trap was removed with acetonitrile for analysis. This was accomplished by injecting approx 20 mL of acetonitrile into the entrance of the column, allowing the column to sit for several hours, and then removing the acetonitrile by passing nitrogen through the coil. The volume of the solution was then adjusted to 25 mL. The concentration of the organic in the solution was then determined by HPLC analysis. The procedure was repeated until no organic could be detected in the wash solution. Typically five washes of 20 mL each were required to remove all the organic.

HPLC analysis was accomplished with a Varian model 5560 high-pressure liquid chromatograph equipped with a Separations Group VYDAC 201TP25 column. The detector for this system was a Perkin Elmer LS-4 Fluorescence Spectrometer.

RESULTS AND DISCUSSION

The apparatus was first tested with naphthalene. Vapor pressures for this compound have been reported by several researchers. Measurements were taken at 40, 45, 50, and 55°C . The results are plotted in Fig. 2 along with data from two other recent studies (4, 14).

Several experiments were run to ensure that complete saturation of the nitrogen carrier gas occurred and that no entrainment took place. These experiments involved varying the gas flow rate while keeping all other experimental conditions constant. Vapor densities were constant for flow rates < 40 sccm, indicating that saturation of the carrier gas was occurring. No entrainment could be detected except at very high flow rates.

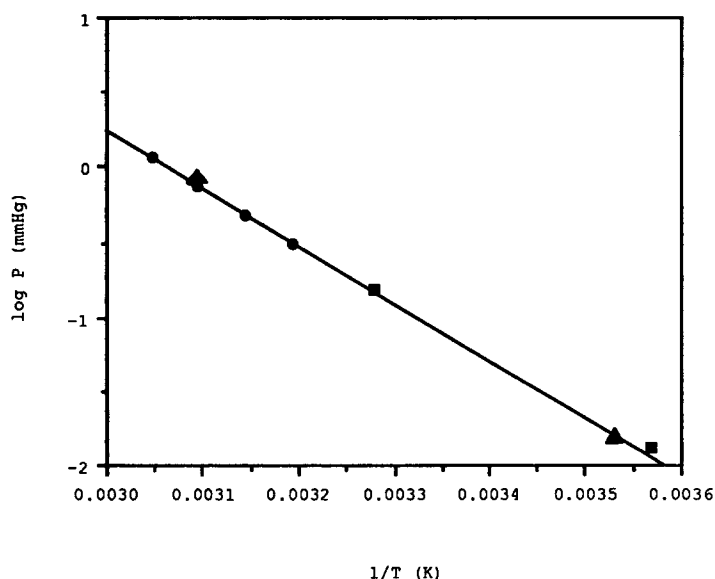


Fig. 2. Comparison of naphthalene vapor pressure data to literature. ● This Work. ▲ Sonnefeld and Zoller, 1983 (14). ■ Macknick and Prausnitz, 1979 (4).

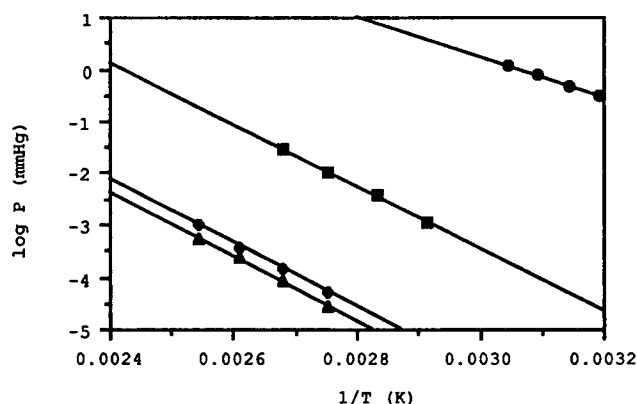


Fig. 3. PAH vapor pressures vs temperature. ■ Anthracene; ● chrysene; ▲ benzo[a]pyrene; ● naphthalene.

To ensure that no organic was escaping the cryogenic trap, a small gas wash bottle was placed at the end of the copper coil. The bottle was filled with approx 20 mL of acetonitrile. The experimental apparatus was then run at a high temperature for a week. At the end of the run, the acetonitrile solution was analyzed by HPLC. No detectable amount of organic was present.

After testing, the apparatus was used to measure the vapor pressures of three polycyclic aromatic compounds (anthracene, chrysene, benzo[a]pyrene) at various temperatures. Figure 3 presents the results in graphical form. For anthracene, the data represent the average of two measure-

Table 1
Vapor Pressure Data for PAHs Measured by Gas Saturation

Naphthalene		Anthracene		Benzo[a]Pyrene		Chrysene	
T (K)	mmHg	T(K)	mmHg	T(K)	mmHg	T(K)	mmHg
313.15	0.3132	343.15	0.0011155	363.15	0.000027478	363.15	0.00005224
318.15	0.4882	352.15	0.0038734	373.15	0.000082604	373.15	0.00014928
323.15	0.7507	363.15	0.0104303	383.15	0.000228559	383.15	0.0104472
328.15	1.139	373.15	0.028391	393.15	0.000532108	393.15	0.0285391

ments at each temperature. The values in each case were within 4% of each other.

Temperature and pressure variations introduced little error into the experimental data. The temperature of the oil bath containing the equilibrium cell was monitored with a Keithley digital multimeter and platinum probe capable of measuring temperatures to $\pm .01^\circ\text{C}$. The data were recorded with an IBM PC. During experimental runs, the oil bath temperature was held at the experimental value to $\pm 0.02^\circ\text{C}$. The pressure at the exit of the equilibrium cell was also monitored during experimental runs. The error caused by pressure fluctuations was calculated to be $< 1\%$.

Table 1 gives the results for the vapor pressure measurements. A least-squares method was used to fit the data to the Clapeyron equation, which is given by:

$$\log_{10} P^v = -A/T + B \quad (2)$$

where the temperature is in K and the vapor pressure is in mm Hg. The constants A and B are reported in Table 2, along with other data found in the literature on PAH vapor pressures (4,14,16-18). The literature data have been converted into consistent units. For specific information on the experimental apparatus and any error involved in the measurements, the reader should refer to the original article. For the data reported in this study, modeling the vapor pressure with more than two constants is not necessary. Over small temperature ranges, the experimental error in the measurements is greater than any nonlinearity in the vapor pressure data.

For determining infinite dilution activity coefficients, a differential ebulliometry apparatus has been constructed. Figure 4 is a schematic diagram of the apparatus. The apparatus has been tested with the phenol-water system. Basically, the system consists of four ebulliometers connected to a common manifold, where the pressure is accurately controlled. An ebulliometry is a single-stage boiler equipped with a vapor lift pump to spray liquid onto a thermowell, where equilibrium is established (21). The device is used to determine the boiling point of a solution accurately. For determining infinite dilution activity coefficients, the boiling point difference of the pure solvent and solvent with dissolved solute is measured. A rigorous thermodynamic analysis is then used to calculate the infinite dilution activity coefficient.

Table 2
Vapor Pressures of PAHs as a Function of Temperature

Compound	Temperature Range (K)	A (K)	B Unitless	Apparatus	Reference
Acenaphthalene	338.2-366.3	4354	12.051	Inclined Piston Manometry	15
	283.2-323.2	4535.4	12.544	gas-saturation	12
Acenaphthylene	283.2-323.2	3821.6	10.643	gas-saturation	12
Anthracene	343.2-373.2	5963.90	14.445	gas-saturation	this work
	358.4-393.1	4928.50	11.563	gas-saturation	14
	313.2-363.2	5358.80	12.754	gas-saturation	13
	282.2-323.2	4781.90	10.852	gas-saturation	12
Benzo[a]pyrene	363.2-393.2	6149.2	12.386	gas-saturation	this work
	358 -431	6181	12.482	Knudsen diffusion	16
Benzo[e]pyrene	359 -423	6220	12.617	Knudsen diffusion	16
Benzo[a]anthracene	330 -390	5925	12.926	Knudsen diffusion	16
	283.2-323.2	4245.9	7.5574	gas-saturation	12
Benzo[ghi]pyrene	389 -468	6674	12.4	Knudsen diffusion	16
Chrysene	363.2-393.2	6125.7	12.583	gas-saturation	this work
Coronene	427 -510	7100	11.991	Knudsen diffusion	16
	283.2-323.2	4616.1	12.26	gas-saturation	12
Fluorene	348.2-387.2	4290.4	11.369	Inclined-piston manometry	15
	283.2-323.2	4415.6	9.7762	gas-saturation	12
Naphthalene	313.2-328.2	3842.1	11.765	gas-saturation	this work
	283.2-323.2	3960	12.174	gas-saturation	12
	280.3-305.0	3719.2	11.384	gas-saturation	14
Phenanthrene	324.8-363.5	4554.7	11.578	gas-saturation	14
	283.2-323.2	4962.8	12.727	gas-saturation	12
Pyrene	283.2-323.2	4962.8	12.727	gas-saturation	12

Measuring the infinite dilution activity coefficient of certain PAHs may not be possible by differential ebulliometry. The aqueous solubility of these compounds is so low that it may not be possible to measure a boiling point difference. In addition, adsorption onto the glass surfaces of the ebulliometers may present a problem.

Future experiments include determining the vapor pressures of other PAH compounds, such as dibenz[a,h]anthracene, 1-methylphenanthrene, benzo[b]fluoranthene, and benzo[k]fluoranthene. The differential ebulliometry apparatus will be used in determining infinite dilution activity coefficients of certain PAHs, organic solvents, and phenolic compounds. For those compounds where both the vapor pressure and the infinite dilution activity can be determined, the Henry's law constant will be calculated.

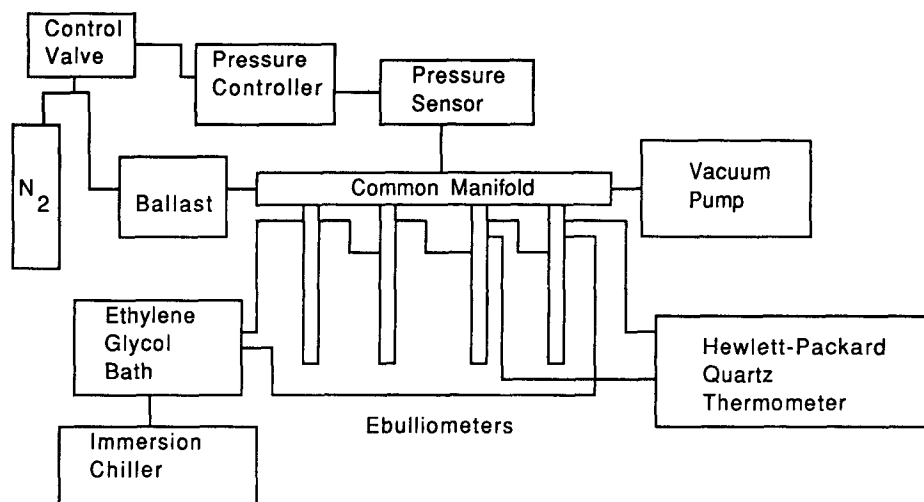


Fig. 4. Differential ebulliometry experimental apparatus.

CONCLUSIONS

Accurate values of Henry's law constants are needed when modeling biological systems. Unfortunately, for many nonpolar organic aqueous solutions, these data are not available in the literature and are not possible to measure by direct methods. Two experimental methods, gas saturation and differential ebulliometry, can be used to measure the vapor pressures and infinite dilution activity coefficients of many of these compounds. The Henry's law constant can be easily calculated once these fundamental thermodynamic properties are known. In this study, a gas saturation apparatus has been used to measure the vapor pressures of four polycyclic aromatic hydrocarbons. A differential ebulliometry apparatus has been constructed and tested. The apparatus will be used to measure the infinite dilution activity coefficients of certain organic-aqueous systems. These data can be used by any biologist, engineer, or environmental scientist who has modeling needs.

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