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Henry's Law Constants for the Polychlorinated Biphenyls

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■ Henry's law constants were predicted from the ratio of the liquid (or subcooled liquid) vapor pressure and aqueous solubility for each polychlorinated biphenyl (PCB) congener. The liquid vapor pressures and aqueous solubilities were derived for each PCB congener by using correlations of Gibbs' free energy of vaporization against gas-liquid chromatographic retention indexes and Gibbs' free energy of solubilization of a liquid against molecular surface area. The predicted values were in fair agreement with experimental values, and the error for these constants was estimated to be a factor of 5 in the temperature range 0.0-40.0 °C. For the PCB congeners, Henry's law constants were independent of molecular weight and increased approximately an order of magnitude with a 25.0 °C increase in temperature. The average value for Henry's law constants and air-water partition coefficients for the Aroclor PCB mixtures were approximately 4.0×10^{-4} atm·m³/mol at 25.0 °C.

Introduction

One of the major problems in modeling and predicting the behavior of polychlorinated biphenyls (PCBs) in the environment has been the lack of accurate Henry's law constants. Henry's law constants are used to predict exchange rates of vapors across the air/water interface and fugacity potentials for aqueous systems.

In part, Henry's law constants have not been available due to analytical difficulties in measuring this property. Measurements are often performed with nanomoles or less of the compound. In addition, PCBs were sold commercially as mixtures called Aroclors, and each mixture was composed of numerous, 50-75, PCB congeners (1). Many of these compounds are not readily available in pure form, and thus, much preparatory work is required before any measurements can be performed.

Historically, investigators have circumvented this lack of experimental data by treating each Aroclor mixture as a single entity when estimating Henry's law constants (H 's) (2-6). An average H was determined by dividing the vapor pressure of the mixture by its aqueous solubility (2). The problem with this approach is that PCB congeners behave in the environment as individual compounds and not as a mixture. Consequently, to model their behavior correctly, H 's are needed for each congener.

Recently, Bopp (7), in an attempt to eliminate this problem, grouped PCB congeners by degree of chlorination. The aqueous activity coefficient for each degree of chlorination was assumed to be independent of tempera-

ture, and the logarithm of the subcooled liquid vapor pressure was considered to be linearly related to chlorine number. These assumptions were used in predicting vapor pressures and solubilities for each degree of chlorination. The predicted values were used to calculate H for each degree of chlorination.

Four recent investigations (8-11) now permit calculation of H for each PCB congener and elimination of the assumptions employed by Bopp. These investigations were performed using the best techniques currently available for measuring aqueous solubilities (9, 12) and vapor pressures (13). The requisite data were derived by measurements of vapor pressures of 4 PCB congeners and aqueous solubilities of 18 PCB congeners. These measurements include vapor pressure and solubility data for decachlorobiphenyl, the highest chlorinated PCB congener.

The object of this investigation is to use the recently acquired data to calculate and evaluate H for each PCB congener. Temperature effects and the influence of chemical structure on the H 's are also considered.

Determination of Henry's Law Constants

Henry's law expresses the proportionality between the concentration of a gas dissolved in a solvent and its partial pressure (14). In equation form, Henry's law is

$$P = HC \quad (1)$$

where P is the partial pressure of the gas, C is the concentration of the dissolved gas, and H is Henry's law constant. Henry's law represents a limiting behavior for any gas-solvent system as its partial pressure approaches zero. Typically, Henry's law breaks down when partial pressures exceed 5-10 atm and/or when the dissolved concentrations exceed 3 mol % (14). Henry's law constant is a function of temperature only for a particular gas-solvent system. However, each gas-solvent system has a unique H value.

Henry's law constants are usually determined by measuring the equilibrium partial pressure and dissolved concentration of the gas and then calculating the ratio of these two quantities. For most environmental contaminants, the aqueous solubilities and vapor pressures of the pure substances are very low. Consequently, Henry's law is valid up to dissolved concentrations equal to the aqueous solubility and to partial pressures equal to the vapor pressure of the pure substance. The validity of Henry's law at these partial pressures and aqueous concentrations makes it possible to derive the H 's by calculating the ratio of the vapor pressure of the pure compound to its aqueous solubility.

We used this method to derive H 's for each PCB congener. The reasons for employing this approach were

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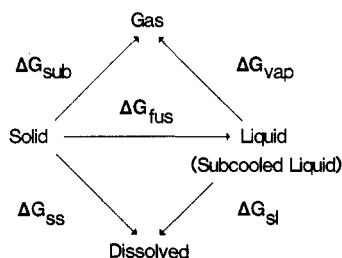


Figure 1. Thermodynamic cycle and Gibbs' free energies.

fourfold. First, excellent aqueous solubility and vapor pressure data exist for many PCB congeners. Second, the temperature dependence of both vapor pressure and aqueous solubility are well understood and are more easily modeled than the temperature dependence of Henry's law constant. Third, methods for predicting solubilities and vapor pressures when experimental data are unavailable have been developed (15–18). Fourth, vapor pressures and solubilities used in this investigation are well below the previously stated limits where Henry's law is not valid. (For biphenyl, the compound with the highest vapor pressure and solubility in this investigation, the vapor pressure and solubility values are 1.0×10^{-5} atm and 8.2×10^{-7} mol/mol at 25 °C.)

To calculate H 's for all congeners, vapor pressures and aqueous solubilities were calculated at the temperature of interest for the PCB congeners with experimental data. Correlations were then constructed from these calculated sets of data. Subsequently, vapor pressures and solubilities were predicted for each PCB congener, and H for each congener was determined from the ratio of these two properties.

The derived H 's were determined by using the liquid (or subcooled liquid) states for both vapor pressure and solubility. The ratio of the solid-state properties was not selected because both predictive methods employed here estimate the properties for the (subcooled) liquid state. Furthermore, this method eliminates the need to account for the change in fugacity between the solid and subcooled liquid states and the errors in making this correction.

Prediction of Vapor Pressures

When recently acquired vapor pressure measurements on four compounds (10) were combined with previously published determinations (19–28), vapor pressure–temperature relationships for 15 PCB congeners were assembled [Table I of supplementary material (see paragraph at end of paper regarding supplementary material)]. For the temperature of interest, vapor pressures were calculated by using these relationships. These values were then used in creating a correlative equation which allowed the prediction of vapor pressures for all congeners.

A comparative study of vapor pressure estimation procedures for PCB congeners has been performed (16), and the most accurate correlative method was used here. This correlative method constructs a relationship between the Gibbs free energy of vaporization, ΔG_{vap} , and the gas–liquid chromatographic retention index for each compound.

The thermodynamic cycle and Gibbs free energies employed by this correlative method are displayed in Figure 1. From basic chemical thermodynamics (29), the Gibbs free energies of sublimation, ΔG_{sub} , and vaporization may be determined by

$$\Delta G_{\text{sub}} = -RT \ln p_s^0 \quad (2)$$

$$\Delta G_{\text{vap}} = -RT \ln p_l^0 \quad (3)$$

where R is the ideal gas constant, T is the temperature of

interest, and p_s^0 and p_l^0 are the vapor pressures of the pure solid and liquid at temperature T .

From equilibrium thermodynamics (14), the Gibbs free energy of fusion, ΔG_{fus} , can be determined by

$$\Delta G_{\text{fus}} = \Delta S_{\text{fus}}(T_{\text{mp}} - T) \quad (4)$$

where ΔS_{fus} is the entropy of fusion of the solid and T_{mp} is the melting point of the solid. ΔS_{fus} was assumed to be a constant for all compounds and was set equal to as the average of 16 individual determinations for PCBs by Miller et al. (8), 13.1 cal/(mol·K). For liquids, ΔG_{fus} is equal to zero. The Gibbs free energy for the transformation between the subcooled liquid and vapor states for a solid is calculated as follows:

$$\Delta G_{\text{vap}} = \Delta G_{\text{sub}} - \Delta G_{\text{fus}} \quad (5)$$

The gas–liquid chromatographic retention indexes (RI) for each PCB congener were derived from the half-retention indexes of Albro et al. (30) for the Apiezon L stationary phase column using the method of Sisson and Welti (31) as described by Albro et al. (30).

The correlative equation was determined by regressing the ΔG_{vap} against the RI for the 15 PCB congeners with experimental values by using an equation of the form

$$\Delta G_{\text{vap}} = m\text{RI} + b \quad (6)$$

where m is the slope and b is the intercept. Using additional constants and/or dependent variables did not improve the fit of the data. Comparison of the predicted and experimental vapor pressures revealed an average factor of error (AFE) of 1.75 at 25.0 °C. (The factor of error is defined as the ratio of the predicted to experimental value. However, if this ratio is less than 1.0, the reciprocal of this ratio is used.) The AFE varied slightly from this value when different temperatures were used in creating the correlations. The AFE for all temperatures between 0 and 40 °C at 5 °C increments was 1.76 with a standard deviation of 0.042. The r^2 for these regression equations had a minimum of 95.0% in this range.

The vapor pressure for each PCB congener was predicted by obtaining the ΔG_{vap} from the correlative equation. The vapor pressure (for the subcooled liquid state) was calculated from the ΔG_{vap} by using eq 3.

Prediction of Aqueous Solubilities

Aqueous solubilities have been measured by using the generator column technique (9, 12) for 18 PCB congeners at 25.0 °C and for biphenyl and 4-chlorobiphenyl at other temperatures (8, 9, 11). Additional solubility data, measured by using different techniques, are available (32); however, the accuracy of the data is unknown, and the precision is poor. Uncertainties in the nongenerator column data arise because of analytical difficulties in measuring submicromolar aqueous solubilities (12). The generator column method is an established technique which circumvents most of these analytical difficulties and has uncertainties which are substantially less than other techniques (12). Consequently, we have chosen to use only the generator column data to minimize overall uncertainties in the predicted H 's. The approach employed here consisted of determining aqueous solubilities for the 18 congeners with experimental values for the temperature of interest. Since aqueous solubilities are limited for temperatures other than 25.0 °C, a relationship defining the dependence of solubility on temperature was developed. By use of the 18 solubility values, a correlative equation was found, and solubilities were determined for each congener. Experimental solubilities, melting points,

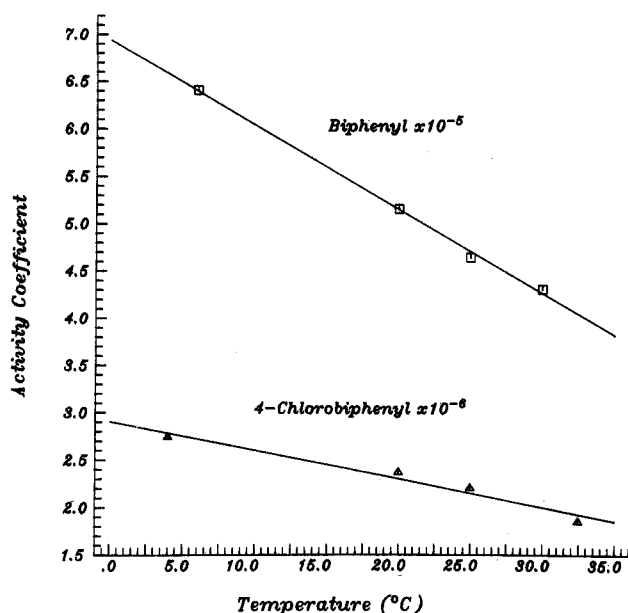


Figure 2. Temperature dependence of biphenyl and 4-chlorobiphenyl activity coefficients.

and entropies of fusion are listed in Table II of the Supplementary Material for the 18 PCB congeners.

From equilibrium thermodynamics (14), the mole fraction solubility of a compound is

$$x = f_s / (f_l \gamma) \quad (7)$$

where x is the mole fraction solubility, γ is the aqueous activity coefficient, and f_s/f_l is the fugacity correction factor for changing from the solid to subcooled liquid states. If the compound is a liquid at the temperature of interest, this correction factor is equal to 1.00. This ratio can be evaluated with little error by using the following formula (14):

$$\ln (f_l/f_s) = \Delta S_{\text{fus}}(T_{\text{mp}} - T)/(RT) \quad (8)$$

Entropies of fusion and melting points exist for nearly all of the 18 PCB congeners. The only experimental data not available are the entropies of fusion for 4-chlorobiphenyl and 2,5-dichlorobiphenyl. These values were set equal to the average value for the 16 other compounds, 13.1 cal/(K·mol). Consequently, the temperature dependence of the γ or x can be defined, and the temperature dependence of the other variable can be calculated. We have chosen to define the temperature dependence of the γ because this variable is more consistent and uniform in behavior within a family of compounds.

For biphenyl and 4-chlorobiphenyl, activity coefficients were calculated and plotted vs. temperature (Figure 2). This plot reveals that the γ is not a constant in the range 5–30 °C and that its temperature dependence is linear. Regression analysis of the γ against temperature yielded excellent fits of the data. The regression lines for biphenyl and 4-chlorobiphenyl are shown in Figure 2 (r^2 of 99.8 and 96.3%).

Since no experimental solubilities are available at temperatures different from 25.0 °C for higher chlorinated PCBs, we have examined the dependence of the γ -temperature relationship with increasing molecular weight using 11 different polynuclear aromatic hydrocarbons (33). Plots and regression analyses of the calculated γ 's vs. temperature revealed linear behavior between these variables for 10 different compounds with molecular weights ranging from 128.2 (naphthalene) to 228.3 (chrysene). The average r^2 for these regression analyses was 98.5%.

Benzene was the only compound not obeying this relationship. The percentage change in the γ was independent of molecular weight between the temperatures of 5 and 30 °C for the 10 polynuclear aromatic hydrocarbons with linear behavior.

We have also examined the temperature dependencies of the γ 's for the polynuclear aromatic hydrocarbons, biphenyl, and PCBs using UNIFAC (34). UNIFAC yielded very inaccurate γ 's for all of the compounds, and the predictive power of UNIFAC diminished rapidly with increasing molecular weight in the PCB family (e.g., UNIFAC predicted the γ for biphenyl to be greater than that of decachlorobiphenyl). However, the γ -temperature relationship was predicted to be linear for all PCBs and polynuclear aromatic hydrocarbons ($r^2 > 95\%$ for all linear regressions). For the 10 polynuclear aromatic hydrocarbon compounds exhibiting linear behavior, an average decrease of 38.0% in the experimental γ occurred over a temperature range of 5–30 °C, and UNIFAC predicted a decrease of 44.2%. For biphenyl and 4-chlorobiphenyl, experimental decreases in the γ 's were 33.2% (6–30 °C) and 30.6% (4–32 °C). UNIFAC predicted decreases of 39.5% and 53.8%. For the other PCB molecular weight classes, UNIFAC predicted decreases of ca. 68% in the γ with a change in temperature of 5–30 °C.

The analyses done using UNIFAC and the experimental data indicate that the γ is not constant. In addition, the γ data for the polynuclear aromatic hydrocarbons suggest that the γ -temperature relationship is constant in a family of compounds. Consequently, we have assumed that the γ -temperature relationships for biphenyl and 4-chlorobiphenyl are typical of all PCBs. For these compounds, the relationship between temperature and the γ is linear, and γ 's decrease 31.9% and 25.8% with an increase in temperature from 0 to 25 °C. We have adopted the average decrease of 28.8% in the γ with an increase in temperature from 0 to 25 °C as the γ -temperature relationships for all PCB congeners.

The solubilities for the 18 congeners at the temperature of interest were calculated by determining the activity coefficient for each congener at 25.0 °C using the melting point, entropy of fusion, solubility data at 25.0 °C, and eq 7 and 8. By use of γ at 25 °C and the γ -temperature relationship, γ at the temperature of interest was determined. By use of eq 7 and 8, and the γ for the temperature of interest, the solubility was determined. These 18 solubilities were then used in creating a correlative equation for predicting the solubilities for all PCB congeners.

Methods for correlating and predicting aqueous solubilities have been examined extensively (15). We used the method of Hermann (35, 36) as applied by Pearlman (37) and others (32, 38). This method constructs a correlation between the Gibbs free energy of solubilization of the (subcooled) liquid and molecular surface area for the compounds of interest.

The thermodynamic cycle and Gibbs free energies employed by this correlative method are displayed in Figure 1. From basic chemical thermodynamics (29), the Gibbs free energies of solubilization of a solid, ΔG_{ss} , and of a liquid, ΔG_{sl} , can be calculated by

$$\Delta G_{ss} = -RT \ln x_s \quad (9)$$

$$\Delta G_{sl} = -RT \ln x_l \quad (10)$$

where x_s and x_l are the mole fraction solubilities of the solid and liquid. From the thermodynamic cycle, the Gibbs free energy of solubilization of the subcooled liquid can be determined as follows:

$$\Delta G_{sl} = \Delta G_{ss} - \Delta G_{fus} \quad (11)$$

where ΔG_{fus} is calculated as previously discussed.

For the 18 PCB congeners, the ΔG_{sl} was determined by using the above equations and the solubilities at the temperature of interest.

The molecular surface areas for all PCB congeners were calculated by using the numerical method of Pearlman (37), obtained in program form from the Indiana Quantum Exchange Program, Indiana University, Bloomington, IN. Input data to the program consisted of atomic coordinates, a solvent radius of 0.0, and van der Waals' radii. Atomic coordinates were created in-house by using a Fortran program (39). Atomic bond distances and angles for the biphenyl structures were taken from the work of Trotter (40). van der Waals' radii for all atoms and bond lengths for chlorine were obtained from Bondi (41) and Weast (20). On the basis of the gas-phase electron diffraction data of Bastiansen (42), the angle between the two phenyl rings for each PCB congener was set at the smallest angle where no overlap occurs between the adjacent ortho atoms. These angles were 39°, 57°, 57° or 123°, 73°, and 73° for zero, one, two, three, and four ortho chlorines, respectively.

The correlative equation was found by regression of ΔG_{sl} vs. surface area, area using an equation of the form

$$\Delta G_{\text{sl}} = A + B\text{area} + C\text{area}^3 \quad (12)$$

where A , B , and C are the regression coefficients. Other forms of the correlation equation were evaluated prior to the selection of this equation form. The addition or removal of constants and/or dependent variable terms to the regression equation did not improve the fit of the data. Comparison of the predicted and experimentally derived solubilities revealed an AFE for the correlative equation of 1.96 for any temperature between 0 and 40 °C. The minimum r^2 for the regression equations was 95.1% in this range.

In predicting the solubilities for each PCB congener, ΔG_{sl} was determined by using the correlative equation. From eq 10, mole fraction solubility, x_1 , for the subcooled liquid (or liquid) state was predicted.

Evaluation of Calculated Henry's Law Constants

Henry's law constants were calculated from the ratio of the predicted subcooled liquid vapor pressures and aqueous solubilities for the temperature of interest for each PCB congener. To assess the accuracy of these predictions, we compared these values to those determined experimentally using the batch technique (43, 44), the purging technique (45, 46), and the ratios of the vapor pressure to aqueous solubility at 25 °C from Tables I and II in the supplementary material. However, before reporting the results of this analysis, a discussion of the possible weaknesses and errors in experimentally determined H 's is presented.

Methods for measuring the H 's are analytically difficult for compounds with low vapor pressures and aqueous solubilities. Difficulties arise because air and water samples containing a few nanograms or less of the compound must be quantified. In addition, for the purging technique, the purge gas leaving the system must be in equilibrium with the liquid solute concentration. Matter-Muller et al. (47) have reviewed the theory for this technique and shown that water depths which are larger than those in use may be necessary for attaining equilibrium. Establishing equilibrium is dependent upon the experimental apparatus and its operating conditions, e.g., gas flow rates and water depths. If equilibrium is not attained, the measured H 's will be too low.

For the data of Mackay et al. (45), the gas leaving the system was at equilibrium (47). However, for the data of

Atlas et al. (46), we were unable to determine whether the exiting purge gas was at equilibrium because of insufficient data. Atlas et al. (46) reported a reproducibility of 10–20% for their determinations.

For the batch technique employed by Murphy et al. (43), an excess amount of an Aroclor mixture or of a single PCB congener was equilibrated with air and water in a closed container. Good agreement was reported between the measured and published values for single congeners. However, differences in measured values were noted when an Aroclor mixture rather than the pure congener was used as the source of the compound. The differences were attributed to analytical error. However, the presence of excess Aroclor mixture in the equilibration vessel may be partly responsible for this difference. These investigators estimated the error in the measured H 's to be a factor of 2–3.

The total uncertainty in the predicted H 's is a combination of the errors in the experimental vapor pressures and aqueous solubilities, the predictive correlations, and the assumed γ -temperature relationship. The error in the experimental vapor pressures is at best 6% but may be much larger, a factor of 2–3. The error in the experimental solubilities is estimated to be 3% by May et al. (12). The error in the predictive correlations was estimated by comparing the ratio of the vapor pressure to aqueous solubilities for the experimental data used in creating the correlations to the predicted ratio. For temperatures of 0, 5, 10, ..., and 40 °C, an overall AFE of 3.33 was obtained. We are unable to derive an error estimate for the γ -temperature relationship, but we believe that an error of a factor of 2–3 would be the upper limit. Combining these errors yields a worst-case total uncertainty, AFE, of ca. 5.0 for the predicted H 's. This AFE, we believe, is very conservative; the error in the predicted H 's is probably lower.

For comparison purposes, we have assumed that the error reported by Murphy et al. (43) is "typical" for all of the experimental determinations, ca. 2.5. For the predicted H 's, the propagation of error analysis suggests the error for these values is ca. 5.0.

H 's were predicted for comparison with experimental values obtained at temperatures of 23.0 (46), 19.0 (43), and 25.0 °C (45, 44; ratio of vapor pressure to aqueous solubility from experimental data). The measured H 's tend to be slightly higher than the predicted values (Figure 3). Also plotted in this figure are the error limits for the predicted H 's (dashed lines). Most of the experimental values, 40 of 51, fall within the error limits for the predicted H 's. When both errors are considered, only a few experimental values, 4 of 51, have error boundaries which do not intersect with the error limits for the predicted H 's.

If all values are included, the AFE between the experimental and predicted H 's is 4.26 for 51 individual measurements ($n = 51$). For the data sets of Murphy et al. (43), Atlas et al. (46), Mackay et al. (45), and Neely (44) and the experimental ratios, AFEs of 4.44 ($n = 30$), 4.88 ($n = 10$), 3.02 ($n = 1$), 1.16 ($n = 1$), and 3.41 ($n = 9$) were obtained, respectively.

Comparison of the experimental and predicted H 's reveals fair agreement between these values. The experimental values tend to be higher than those predicted, and we are unable to explain this trend. Sources of bias in either the predicted or observed H 's are not apparent. Reasons such as nonequilibrium conditions when the measurements were performed, the use of the Aroclor mixtures rather than pure compounds as the source of each congener, and analytical error may bias the experimental values. Also, the predictive models may not be totally

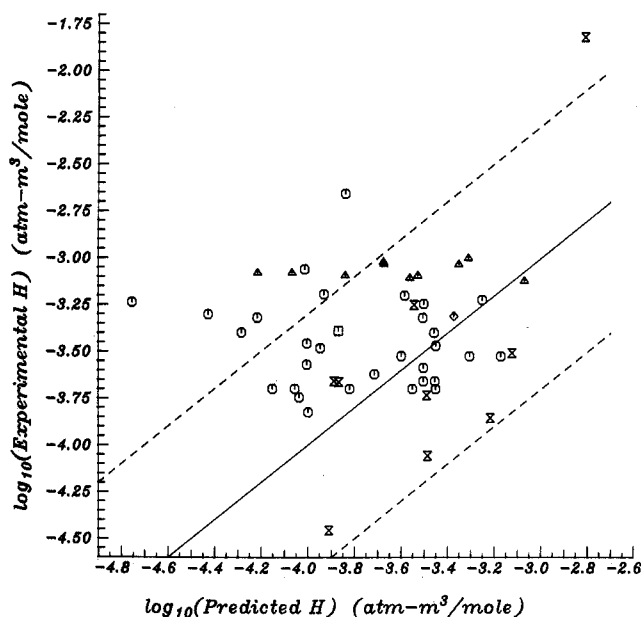


Figure 3. Experimental Henry's law constants of Murphy et al. (43) (O), Atlas et al. (46) (Δ), Mackay, et al. (45) (\square), Neely (44) (\diamond), and the ratios of experimental vapor pressures to aqueous solubilities (hourglass) vs. predicted Henry's law constants. The solid line is where the predicted and experimental H 's are equal. The dashed lines are the upper and lower error limits on the predicted H 's.

correct. Unfortunately, we cannot conclusively demonstrate which of the above sources of error is/are responsible for the observed trend. The poor agreement between the observed and predicted H 's suggests that additional data of highest quality are needed. Additional data would permit a more rigorous evaluation of the predictive methods and eliminate the sources of experimental error presented above.

In view of the analytical difficulties in measuring the H 's and the errors in the predictive method, we believe the accuracy of the predicted values to be reasonable. The error analysis based on available data suggests that the AFE for the predicted H 's in the range 0–40 °C is ca. 5.0. However, the AFE may be much lower.

Examination of Henry's Law Constants

Predicted Henry's law constants for all PCB congeners are plotted in Figure 4 for 25.0 °C and are listed in Table III according to IUPAC number (48) (supplementary material). For temperatures other than 25.0 °C, these values are reported elsewhere (49). The distribution of the H 's displayed in this figure is representative for the temperature range 0.0–40.0 °C. A systematic variation in the H 's with molecular weight of the PCB congeners was not observed (Figure 4). The data of Murphy et al. (43) and Atlas et al. (46) support this observation. However, Bopp (7) using a small data base recently reported that a significant variation of the H 's with molecular weight may exist. Examination of a large data base (Figure 4) indicates that the H 's do not vary systematically with molecular weight when all PCB congeners are considered. However, if the PCB congeners are grouped according to the number of ortho chlorines (Figure 4), a significant variation with molecular weight does occur. In all five groups, zero, one, two, three, and four ortho chlorines, the H 's decrease with increasing molecular weight. Also, the H 's increase in value with increasing number of ortho chlorines for the same molecular weight class. These trends are not apparent in the data of Murphy et al. (43) and Atlas et al. (46), possibly due to the limited number of experimental values for each

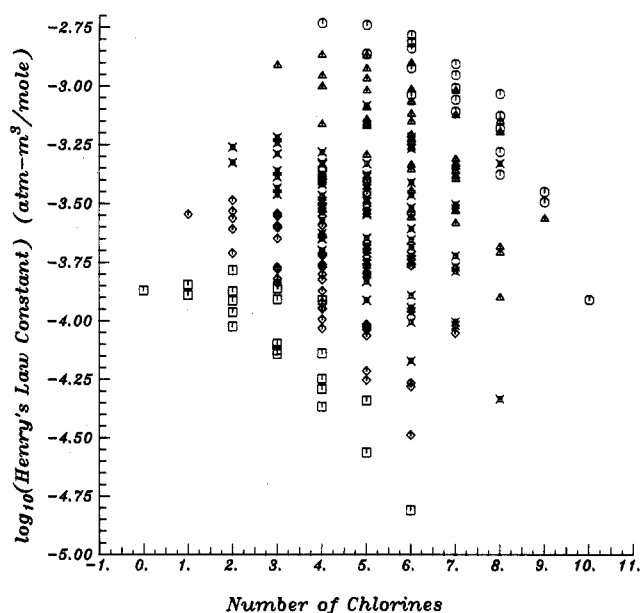


Figure 4. Dependence of predicted Henry's law constants on chlorine content at 25.0 °C. The number of ortho chlorines; zero, one, two, three, or four, are symbolized by (\square), (\diamond), (\times), (Δ), and (O), respectively.

degree of ortho substitution.

This behavior is apparently related to the vapor pressures of the PCB congeners rather than their aqueous solubility. The lowest values of the H 's occur for congeners with no ortho chlorines (Figure 4). These congeners elute from a gas-liquid chromatographic column much later than PCBs with ortho chlorines (30). In general, elution sequence follows the pattern of ortho, meta, and para substitution by chlorines; shorter elution times correspond to higher vapor pressures. This elution order matches the observed pattern for the H 's and supports the hypothesis that differences in the H 's within a molecular weight class are related to vapor pressure.

The predictive model for aqueous solubility in this investigation employs total molecular surface area as the independent variable. This independent variable is quite insensitive to specific structural details of the PCB molecule. Differences in surface areas are small within a molecular weight class but are very large between molecular weight classes. Consequently, the structural detail of the molecule is masked numerically by the molecular weight information included in the total surface area value. When solubilities are predicted, almost identical values are obtained within each molecular weight class for the subcooled liquid solubility because each prediction is based largely on molecular weight information. This general invariance of solubility within a molecular weight class also strongly supports the observation that variation in the H 's is related to the vapor pressure of the PCB congeners.

The temperature dependencies of the H 's are well defined according to chlorine number. The H as a percentage of the value at 25 °C was calculated for the temperature range 0–40 °C for each PCB. These percentages were then averaged for each molecular weight class and for all congeners. These values are reported in Table IV (supplementary material) and are plotted in Figure 5 for biphenyl, the pentachlorobiphenyls, and decachlorobiphenyl. Values for the other molecular weight classes lie between the decachlorobiphenyl and biphenyl curves and follow an ascending order according to molecular weight. The overall average changes in the H 's were very similar to the values for the pentachlorobiphenyls. The largest overall changes

Table I. Air-Water Partition Coefficients for Aroclor PCB Mixtures (atm•m³/mol)

temp, °C	Aroclor						equimolar mixture
	1221	1242	1248	1254	1260	1268	
0.0	0.286 E-4 ^a	0.347 E-4	0.413 E-4	0.226 E-4	0.244 E-4	0.261 E-4	0.344 E-4
5.0	0.452 E-4	0.575 E-4	0.696 E-4	0.394 E-4	0.435 E-4	0.480 E-4	0.592 E-4
10.0	0.697 E-4	0.928 E-4	0.114 E-3	0.670 E-4	0.754 E-4	0.859 E-4	0.995 E-4
15.0	0.106 E-3	0.147 E-3	0.183 E-3	0.111 E-3	0.127 E-3	0.149 E-3	0.163 E-3
20.0	0.157 E-3	0.227 E-3	0.288 E-3	0.180 E-3	0.210 E-3	0.252 E-3	0.262 E-3
25.0	0.228 E-3	0.343 E-3	0.440 E-3	0.283 E-3	0.336 E-3	0.415 E-3	0.409 E-3
30.0	0.326 E-3	0.509 E-3	0.662 E-3	0.437 E-3	0.527 E-3	0.666 E-3	0.627 E-3
35.5	0.483 E-3	0.760 E-3	0.991 E-3	0.665 E-3	0.809 E-3	0.104 E-2	0.949 E-3
40.0	0.668 E-3	0.108 E-2	0.143 E-2	0.981 E-3	0.121 E-2	0.159 E-2	0.139 E-2

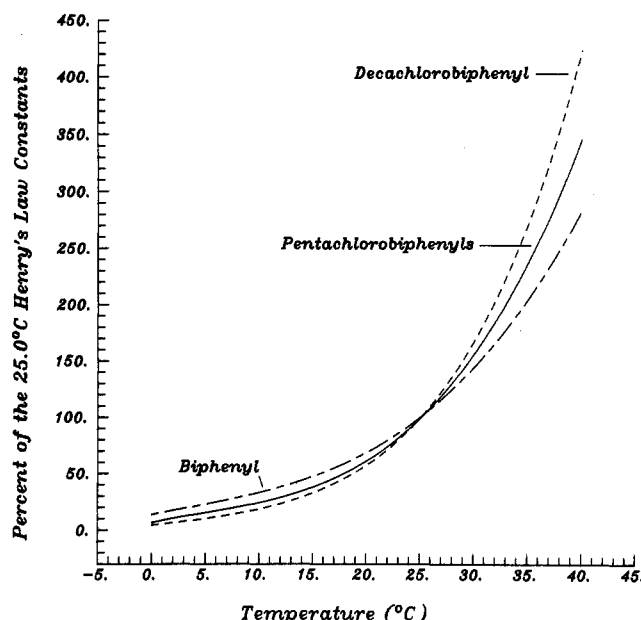
^aE, exponent.

Figure 5. Temperature dependence of predicted Henry's law constants.

in the H 's from 25.0 °C were 8.2 and 346.3% for the temperatures of 0.0 and 40.0 °C, both for decachlorobiphenyl.

Air-water partition coefficients for Aroclor mixtures were calculated from the predicted H 's for temperatures ranging from 0.0 to 40.0 °C (Table I). These partition coefficients are weighted average values based on the percentage of each congener in the PCB mixture. The compositions of the Aroclor mixtures were obtained from Albro et al. (30, 50, 51) for Aroclors 1221, 1242, 1248, 1254, and 1260 and from Mullin et al. (52) for Aroclor 1268. All of these compositions were normalized before calculating the partition coefficients.

The air-water partition coefficients for the PCB mixtures (Table I) are not significantly different for a particular temperature. The general invariance of the partition coefficients was expected since Henry's law constants were independent of molecular weight. (The last two digits of the Aroclor mixture name indicate the percent chlorine in the mixture). However, these partition coefficients change with temperature. Approximately an order of magnitude increase in the partition coefficients occurs when the temperatures change by 25.0 °C. This change was also expected on the basis of the temperature dependencies displayed by the H 's.

Summary

Henry's law constants for all of the PCB congeners have been predicted from vapor pressure and solubility data.

The predicted values are in fair agreement with the experimental Henry's law constants, and additional data are needed to resolve the disparity in these values. The average error for the predicted constants was estimated to be a factor of 5. The approach employed here allows H 's to be predicted at temperatures ranging from 0.0 to 40.0 °C.

The H 's and air-water partition coefficients determined are believed to represent the most accurate values attainable with the data available. Furthermore, this is the most internally consistent data set available for the PCB congeners.

Henry's law constants have been presented graphically for all of the congeners at 25.0 °C and in summarized form as air-water partition coefficients for the Aroclor PCB mixtures. These values demonstrate that the H 's are independent of the molecular weight and that their temperature dependence is approximately an order of magnitude increase with an increase in temperature of 25 °C.

The predicted H 's and the experimental values of Murphy et al. (43) now substantially clarify the values of the H 's for all PCB congeners. The average value for the H at 25.0 °C is ca. 4.0×10^{-4} atm•m³/mol. Previous investigations have suggested H 's (air-water partition coefficients) ranging from 10^{-2} to 10^{-7} (atm•m³/mole) for the PCB congeners (6). The lack of accurate H 's and air-water partition coefficients has caused difficulty and confusion in determining the environmental behavior of PCBs (6). These difficulties should now be reduced, allowing examination of the behavior of the individual PCB congeners.

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Supplementary Material Available

Four tables giving vapor pressure-temperature relationships, aqueous solubilities, and predicted Henry's law constants at 25 °C for PCB congeners and average percentage change in Henry's law constants from their values at 25 °C (9 pages) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper or microfiche (105 × 148 mm, 24X reduction, negatives) may be obtained from Microforms Office, American Chemical Society, 1155 16th St., N.W., Washington, DC 20036. Full bibliographic citation (journal, title of article, author, page number) and prepayment, check or money order for \$15.00 for photocopy (\$17.00 foreign) or \$6.00 for microfiche (\$7.00 foreign), are required.

Registry No. Biphenyl, 92-52-4; 2-chlorobiphenyl, 2051-60-7; 3-chlorobiphenyl, 2051-61-8; 4-chlorobiphenyl, 2051-62-9; 2,2'-dichlorobiphenyl, 13029-08-8; 2,5-dichlorobiphenyl, 34883-39-1; 4,4'-dichlorobiphenyl, 2050-68-2; 2,3',4'-trichlorobiphenyl,

38444-86-9; 2,4,6-trichlorobiphenyl, 35693-92-6; 2,2',5,5'-tetrachlorobiphenyl, 35693-99-3; 2,2',4,5,5'-pentachlorobiphenyl, 37680-73-2; 2,2',3,3',5,5',6,6'-octachlorobiphenyl, 2136-99-4; 2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl, 2051-24-3; 3,3'-dichlorobiphenyl, 2050-67-1; 2,2',4,4',6,6'-hexachlorobiphenyl, 33979-03-2.

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