

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/230787472>

Solubility of Polychlorinated Biphenyls in Water

Alcohol 2. Predictive

ARTICLE in ENVIRONMENTAL SCIENCE AND TECHNOLOGY · JANUARY 1995

Impact Factor: 5.33

CITATIONS

2

READS

12

2 AUTHORS:



An Li

University of Illinois at Chicago

89 PUBLICATIONS 2,179 CITATIONS

SEE PROFILE



Anders Andren

University of Wisconsin–Madison

100 PUBLICATIONS 3,838 CITATIONS

SEE PROFILE

Solubility of Polychlorinated Biphenyls in Water/Alcohol Mixtures. 2. Predictive Methods

AN LI[†] AND ANDERS W. ANDREN*

Water Chemistry Program, University of Wisconsin-Madison,
660 North Park Street, Madison, Wisconsin 53706

Five methods were evaluated for their ability and accuracy to estimate the solubilities of polychlorinated biphenyl (PCB) congeners in mixtures of water and *n*-alcohols. The evaluation was performed by comparing the estimates with the experimental solubility data from 77 different systems containing PCBs, alcohols, and water. Within their specific applicable scopes, the overall estimation errors were 39%, 24%, 22%, 32%, and 35% for the log-linear model, the excess free energy approach, the phenomenological model, the extended regular solution theory, and the UNIFAC method, respectively. While the log-linear and UNIFAC methods are useful predictive tools, the phenomenological model provides valuable mechanistic information for the solution process.

Introduction

Most contaminants in the environment exist as a part of liquid or solid mixtures. However, property estimation techniques have generally been developed and tested for simple binary solute/solvent systems. Since environmental behavior of a chemical is very likely different from the predictions based on its pure properties, it is of great practical significance to develop techniques that can predict the behavior of chemicals in multiple-component systems.

Aqueous solubility is among the most important properties needed for environmental modeling. Although solubility phenomena have been studied for centuries, our present knowledge regarding liquid structure and intermolecular forces does not allow us to build theories based on a detailed picture at molecular levels. This is especially true for components of complex aqueous systems. Consequently, most researchers have applied thermodynamic and empirical models to describe and predict solute behavior in multiple solvent systems. Progress in the fields of chemical engineering and pharmaceuticals have produced a number of thermodynamic and semiempirical models. These methods have been reported to be applicable to the prediction of solubility of environmental contaminants in

multiple-component solvent systems (1-4). However, the lack of an adequate database on the solubility of hydrophobic chemicals in a variety of solvents, mixed and pure, has prevented an effective examination on how well these predictive methods work.

The purpose of this paper is to evaluate the usefulness and accuracy of several published thermodynamic and group contribution methods in interpreting and predicting the solubility of selected polychlorinated biphenyl congeners in mixtures of water and a normal alcohol. The models evaluated include the following: the log-linear model (5-9), the excess free energy approach (10-12), the phenomenological model (13, 14), the extended regular solution theory (15-17), and the UNIFAC method (18-20). Evaluation is performed by comparing the estimates with experimental solubility data reported in our previous paper (21).

Theory

Log-Linear Model. Yalkowsky and co-workers (5-9) introduced a log-linear model

$$\ln x_2 = z_3 \ln x_{2,3} + z_1 \ln x_{2,1} = \ln x_{2,3} + \sigma z_1 \quad (1)$$

to describe the phenomenon of the exponential increase in aqueous solubility for nonpolar drugs as the polar cosolvent concentration is increased. In eq 1, $x_{2,1}$ and $x_{2,3}$ are the mole fraction solubility of solute (subscript 2) in cosolvent (subscript 1) and water (subscript 3), z 's are the solute-free volume fractions of the solvent components. When the solute solubility is low ($x_2 < 0.01$), $z_1 + z_3 = 1$. The σ is called the solubilizing power of the cosolvent and is defined as the difference between the logarithmic solute activity coefficients in pure water and in pure cosolvent. This model is based on the assumption that the solvent components are randomly mixed and that the solvent composition at the solute-solvent interface is the same as the bulk composition. The model treats mixed solvents as linear combinations of their components. Thus, it implies a solvent mixture ideality; any deviations from this ideality are considered the results of molecular interactions that are absent in the solutions of the solute in single solvents.

Excess Free Energy Approach. By using Wohl's expansion for the excess Gibbs energy (22), Williams and Amidon (11-13) derived an equation for the infinite dilution activity coefficient of solute in solvent mixture as a power series in the volume fractions of solvent components. By ignoring four-body and higher order interactions, the reduced three-suffix equation for the mole fraction solubility of the solute in mixed solvent is

$$\ln x_2 = z_1 \ln x_{2,1} + z_3 \ln x_{2,3} + A_{1-3} z_1 z_3 (2z_1 - 1) \times \\ (q_2/q_1) + 2A_{3-1} z_{12} z_3 (q_2/q_3) - C_2 z_1 z_3 \quad (2)$$

where q 's are the molar volumes, A 's are the solvent-solvent interaction constants, and C_2 is the interaction constant between solute and mixed solvent. Values of A_{1-3} and A_{3-1} are determined from binary solvent phase equilibrium data or estimated by models, such as UNIFAC (18). C_2 must be obtained from experimental solubility data in mixed solvents or through a linear regression of known C_2 's with solute octanol/water partition coefficients. Equation 2 can be shortened by ignoring three-body interactions or

* To whom all correspondence should be addressed: telephone: 608-262-2470; fax: 608-262-0454; e-mail address: awandren@seagrant.wisc.edu.

[†] Current address: Department of Chemistry, Middle Tennessee State University, Murfreesboro, TN 37132.

expanded to include additional interaction parameters that account for higher order interactions. It can also readily be expanded to multiple-component solvent mixtures.

Phenomenological Model. The phenomenological model (13, 14) depicts the solution phenomenon as a four-step process and quantifies the cosolvent effect by examining the standard free energy change in each step. The free energy of cavity formation in mixed solvent reflects the extent of solvent-solvent interactions; it is called the general medium effect and is defined by the product of the surface area of the cavity (A) and the solvent mixture surface tension γ modified by a curvature effect factor (g). The value of γ is calculated as the sum of surface tensions of the pure solvent components weighted by their mole fractions in the solvation shell. The solvation step is described as a consequence of stepwise competitive exchange equilibria of water and cosolvent with solute; the free energy of solvation arises from solute-solvent interactions. The energy cost of inserting the solute into the solvent cavity is fully accounted in the solvation effect. The intersolute effect is due predominantly to the crystallinity of the solute if the solution is dilute with respect to solute concentration. The total solvent effect, $\delta_M \Delta G^\circ$, is then represented by the difference in unitary free energy of the dissolution processes at cosolvent mole fraction x_1 and in pure water. It is given by

$$\delta_M \Delta G^\circ = \frac{(S_1 + gA\gamma')K_1x_1x_3 + (S_2 + 2gA\gamma')K_1K_2x_1^2}{x_3^2 + K_1x_1x_3 + K_1K_2x_1^2} \quad (3)$$

for a solvation scheme consisting of two steps. The equation for one-step solvation, eq 4, was shown to be superior to eq 3 if the highest cosolvent mole fraction is below 0.3 (14):

$$\delta_M \Delta G^\circ = \frac{(S_1 + gA\gamma')K_1x_1}{x_3 + K_1x_1} \quad (4)$$

In eqs 3 and 4, $S_1 = -kT \ln K_1$ and $S_2 = -kT \ln (K_1K_2)$ represent the standard free energy change in stepwise solvation processes, where k is the Boltzmann constant. K 's are stoichiometric equilibrium constants for the corresponding steps in the solvation process. $\gamma' = (\gamma_1 - \gamma_3)/\nu$ where γ_1 and γ_3 are the surface tensions of pure cosolvent and water, respectively, and ν is the number of solvation steps. The mole fraction solute solubility, x_2 , is then calculated by adding the solvent effect calculated by eqs 3 or 4 to the solubility of the solute in pure water:

$$\ln x_2 = \ln x_{2,3} - \delta_M \Delta G^\circ / kT \quad (5)$$

This model can be used to describe the observed solubility phenomena and to separately examine the free energies of cavity formation and solvation. The model can, in principle, be expanded to solvation schemes containing more than two steps.

Extended Regular Solution Theory. Regular solution theory was introduced by Hildebrand and Scatchard (23) to describe solutions that maintain ideal entropy of mixing (excess entropy = 0) but involve heat change during mixing (excess enthalpy $\neq 0$). Solutions of organic chemicals in polar solvents are not regular since significant solvation or association occur. Martin et al. (15-17) modified the activity coefficient equation in regular solution theory by adding the solute-solvent interaction energy W , which, for a given solute, was found to correlate with the solubility

parameter of solvent, δ_v . Thus, unknown W 's can be obtained from polynomial regression of known W 's with δ_v , and solubility (x_2) in the solvent can be calculated by

$$\ln x_2 = \frac{\Delta S_{f,2}(T_{f,2} - T)}{RT} - \frac{V_2z_v^2}{RT}(\delta_v^2 + \delta_2^2 - 2W) \quad (6)$$

where T is the temperature of the solution and $T_{f,2}$ is the melting point temperature of the solute, both expressed in degrees Kelvin. R is the gas constant. The entropy of melting of the solute, $\Delta S_{f,2}$, depends primarily on molecular geometry. For rigid aromatic compounds, $\Delta S_{f,2}$ is approximately constant at $13.5 \text{ cal K}^{-1} \text{ mol}^{-1}$ (24). V_2 is the molar volume, δ_2 is the solubility parameter of the solute, and z_v is the volume fraction of the solvent. For dilute solutions, $z_v \approx 1$. For a mixed solvent, δ_v can be calculated based on δ 's of the pure components weighted by their volume fractions in the solute-free solvent mixture:

$$\delta_v = \delta_1z_1 + \delta_3z_3 \quad (7)$$

UNIFAC Method. The basic assumption of the UNIFAC (UNIQUAC functional-group activity coefficients) model (18) is that a physical property of a fluid is due to the sum of contributions made by the molecule's functional groups. UNIFAC divides the activity coefficient, γ , into a combinatorial part, γ_c , which reflects the size and shape of the molecules, and a residual portion γ_r , which depends on the functional group interactions:

$$\ln \gamma_{\text{UNIFAC}} = \ln \gamma_c + \ln \gamma_r \quad (8)$$

The parameters of each functional group, including volume and area parameters (calculated via the normalization of van der Waals volume and surface area), and parameters of interaction with other functional groups (obtained by reduction of phase equilibrium experimental data) are put into a series of UNIFAC equations, from which γ_c and γ_r are calculated. The solute solubility, x_2 , can then be obtained by using

$$\ln x_2 = \frac{\Delta S_{f,2}(T_{f,2} - T)}{RT} - \ln \gamma_{\text{UNIFAC}} \quad (9)$$

Due to the group contribution nature, UNIFAC is very flexible when used in nonideal systems. However, its accuracy depends very strongly on its group interaction parameters. Several group interaction parameter tables have been published (19, 20). However, most of these tables were developed from experimental phase equilibria data at relatively high solute concentrations compared to the solubilities exhibited by hydrophobic substances. In addition, most interaction parameters were deduced from databases containing very little data of higher molecular weight aromatic organic compounds. Therefore, the group interaction parameters often have to be adjusted according to the experimental data in order to eliminate systematic errors of prediction (2).

Methods

Experimental Solubility Data. Experimental solubilities of 4-chlorobiphenyl (MCB), 2,4,6-trichlorobiphenyl (TCB), and 2,2',4,4',6,6'-hexachlorobiphenyl (HCB) in binary water/alcohol mixtures were obtained in our previous work (21). A total of 77 different solute-solvent systems were involved, and the solubility values range from 10^{-9} to 10^{-1} mol/L.

TABLE 1

Estimated Model Parameters

parameter	solute	cosolvent				
		methanol	ethanol	propanol	butanol	pentanol
Log-Linear Model						
σ^a	MCB	11.62	12.44	12.66		
σ^a	TCB	13.28	13.56	14.11		
σ^a	HCB	16.62	16.19	16.84		
Excess Free Energy Model						
A_{1-3}		0.743	1.329	2.215		
A_{3-1}		0.469	0.911	1.071		
Phenomenological Model						
K_1	MCB	2.49	3.99	6.66	6.17	8.10
K_2	MCB	1.30	3.22	9.87		
gA^b	MCB	86.64	79.88	67.54	91.93	93.7
K_1	TCB	2.78	2.41	5.66	6.96	8.15
K_2	TCB	1.27				
gA^b	TCB	99.93	104.39	105.40	108.39	111.75
K_1	HCB	3.76	3.43	8.38	12.33	
K_2	HCB	1.21				
gA^b	HCB	125.88	123.07	125.65	127.69	

^a σ in units of \ln (mole fraction solubility). ^b gA in 10^{-20} m²/molecule.

Data from mixtures of water and a completely miscible alcohol were used to evaluate all selected models. Data from solvent systems composed of water and a partially miscible alcohol were also used in the evaluation of the phenomenological model, extended regular solution theory, and UNIFAC method. Experimental solubilities of selected PCB congeners in all but three solvent systems are lower than a mole fraction of 0.01, with a majority being less than 10^{-5} . The low solute concentration validates the dilute solution approximation $z_1 + z_3 = 1$ and the use of infinite dilution activity coefficients in solubility estimations (25). The three exceptions are the solubilities of 4-chlorobiphenyl in pure methanol, ethanol, and 1-propanol. Since these mole fraction solubilities are lower than 0.05, we used the dilute solution approximation for these systems as well to keep the consistency of data treatment. For the same reason, activity coefficients at infinite dilution were used for calculation of solubilities in all systems. In order to estimate the model parameters, solute solubilities in pure organic solvent are required by some models. Not all of these are experimentally available. It was found that solubilities of the three PCB congeners in pure alcohols estimated by the UNIFAC procedure have an average error of 40% (maximum 54%) when compared with experimental values, which is well within the experimental error range usually associated with PCB solubility measurements (26). Therefore, the UNIFAC method was used to estimate the unavailable solubility values when they were needed in model parameter calculations.

Model Parameter Calculations. The σ values used in the log-linear model (eq 1) were calculated for each PCB congener from the differences of the natural logarithm of mole fraction solubilities ($\ln x_2$) in pure cosolvent and in pure water. Table 1 lists the σ values used for solubility prediction by the log-linear model. Three parameters in eq 2 have to be determined in order to evaluate the excess free energy approach. The solvent-solvent interaction constants, A_{1-3} and A_{3-1} (Table 1), were obtained from the intercept and slope of a linear regression equation, in which the activity coefficients of both solvent components are calculated by UNIFAC at different compositions of the water/alcohol mixtures over the full range of miscibility. The solute-water-cosolvent interaction constants (C_2 's)

TABLE 2

Estimated Parameters for Extended Regular Solution Theory

	δ_2^a	V_2^b	polynomial regression equation
MCB	21.94	151.8	$W = 282.33 - 0.8586\delta_1 + 0.4470\delta_1^2$
TCB	23.21	169.8	$W = 460.62 - 8.5814\delta_1 + 0.5414\delta_1^2$
HCB	24.62	196.8	$W = 459.31 - 6.3209\delta_1 + 0.5080\delta_1^2$

^a δ_2 in MPa^{1/2}, ^b V_2 in cm³/mol.

were obtained by linear regression of the differences between experimental solubility data and those calculated by eq 2 without the C_2 term. In the case of the phenomenological model, experimental solubility data in the form of $\delta_M \Delta G^\circ$ were fitted into eq 3 by a nonlinear regression function of SigmaPlot. Equation 4 was used for systems having no more than five data points, all of which appeared in the water-rich region. An estimated solubility by UNIFAC in pure alcohol was used with each data set in fitting eq 4. Surface tension data of pure solvents were obtained from the literature (27, 28). The independent variable is the mole fraction of alcohol, x_1 . The product gA and the equilibrium constants K_1 and K_2 served as curve-fitting parameters. The resulting values of K_1 , K_2 and gA are summarized in Table 1.

In order to use the extended regular solution theory, δ_1 of pure alcohols were obtained from the literature (29). Values of δ_2 for the three PCB congeners were calculated using Fedors fragment constants for evaporation energy and molar volume (30) and are listed in Table 2. Values of W were calculated for each system using experimental solubility data (21). A second-order polynomial regression of W against δ_1 was performed over all systems. Resulting regression equations are given in Table 2. Back-calculated W 's from these equations were then used in eq 6 to obtain values for x_2 .

A UNIFAC program written in Turbo Pascal was used to calculate the activity coefficients of PCBs in each solvent mixture. The group interaction parameters are those based on the vapor-liquid equilibria (VLE) data (19), with the exception of the parameters between aromatic chlorine and water (a_{ACCl/H_2O} and $a_{H_2O/ACCl}$). The values of these two parameters were obtained by minimizing the summed differences between UNIFAC calculated activity coefficients and experimental values derived from aqueous solubility data of 41 PCB congeners (2). No solubility data in mixed solvents were involved in determining the values of UNIFAC group interaction parameters used in this study.

Error Analysis. Error analyses for model predictions were based on the procedure of Fu and Luthy (1). The average error, y , and root mean square error, rms- y , were computed in logarithmic space:

$$y = \sum (\ln x_{\text{calculated}} - \ln x_{\text{measured}}) / n \quad (10)$$

$$\text{rms-}y = [\sum (\ln x_{\text{calculated}} - \ln x_{\text{measured}})^2 / n]^{0.5} \quad (11)$$

and the bias and accuracy are then given by the antilog of y and rms- y , respectively. In this method, the perfect prediction corresponds to a bias and an accuracy of 1. A bias greater than 1 indicates that overestimates result more frequently from the model than underestimates, while a bias less than 1 means the opposite. Accuracy represents the degree of deviation of the estimates from the experi-

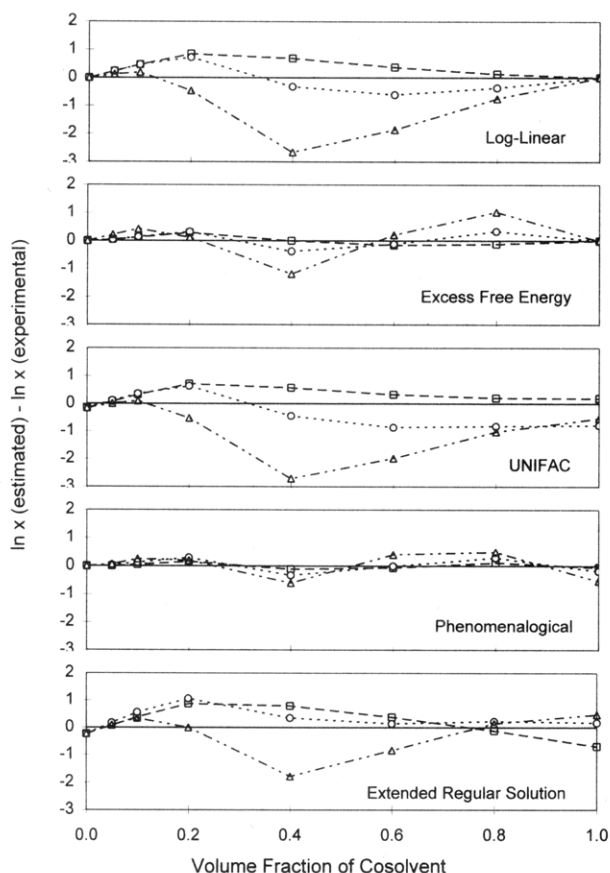


FIGURE 1. Estimation of solubilities of 4-chlorobiphenyl in water/cosolvent mixtures. Legend for cosolvents: (□) methanol; (○) ethanol; (△) 1-propanol. A solid line indicates perfect fit.

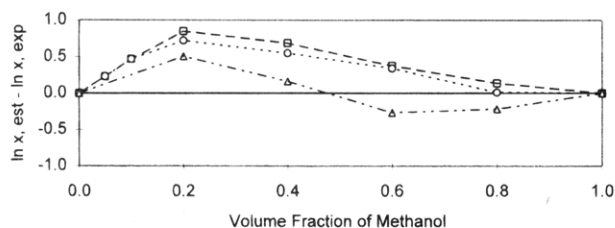


FIGURE 2. Estimation of solubilities in water/methanol mixtures by the log-linear model. Legend for solutes: (□) 4-chlorobiphenyl; (○) 2,4,6-trichlorobiphenyl; (△) 2,2',4,4',6,6'-hexachlorobiphenyl. A solid line indicates perfect fit.

mentally determined values, and a higher value indicates a greater deviation.

Results and Discussion

Figure 1 illustrates the estimation error of the log-linear model, the excess free energy approach, the phenomenological model, the extended regular solution theory, and the UNIFAC, respectively, for 4-chlorobiphenyl in mixed solvents containing water and methanol, ethanol, or 1-propanol. A comparison of estimation errors by the log-linear model among 4-chlorobiphenyl, 2,4,6-trichlorobiphenyl, and 2,2',4,4',6,6'-hexachlorobiphenyl is illustrated in Figure 2 for water/methanol systems. Figure 3 shows the estimation error of the phenomenological model, the extended regular solution theory, and the UNIFAC model for the solubilities of 4-chlorobiphenyl in water saturated with one of the partially miscible alcohols. The estimation bias and accuracy of each model are summarized in Table 3.

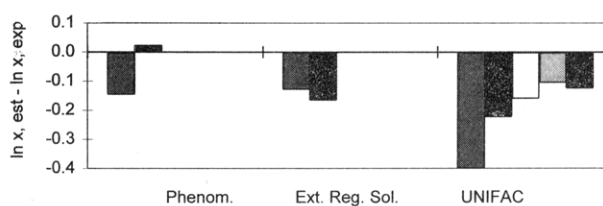


FIGURE 3. Estimation of solubilities of 4-chlorobiphenyl in water saturated by an *n*-alcohol (bars from left to right represent 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, and 1-octanol). A solid line indicates perfect fit.

Log-Linear Model. The log-linear model often provides a reasonable approximation for solubility behavior of hydrophobic organic solute in mixtures of water and organic solvents which are highly "water-like". Such a relationship is valuable in setting up an ideal situation and is exactly obeyed only as the solvent components become identical. The model fails where interactions between solvent components are strong and differ from interactions among molecules of individual pure components and where the solute strongly prefers one solvent component to another. In 1-propanol/water mixtures, for instance, significant estimation errors at a propanol volume fraction range of 0.2–0.8 (see Figure 1) may be related to the tendency of self-association of the propanol molecules as well as the excess propanol at the solute/solvent interface compared with the bulk solvent composition. In such cases, the solute solubilities are enhanced over and above those predicted by the model due to the favorable microenvironment provided by the surrounding cosolvent. On the other hand, in most cases where methanol is the cosolvent, negative deviations from log-linear estimates were experimentally observed in the water-rich region. The extent of this deviation is inversely related to the hydrophobicity of solutes having maxima at 134%, 106%, and 66% for the mono-, tri-, and hexachlorobiphenyl, respectively, all at $z_1 = 0.2$ (see Figure 2). A similar bias in this water-rich region was demonstrated for other hydrophobic solutes (3, 4, 31, 32). The microscopic picture explaining these observations is still not clear at present, although a qualitative explanation has been suggested by Banerjee and Yalkowsky (32). The simplicity of this model makes it a convenient tool for estimating solubilities of hydrophobic chemicals in various aqueous mixtures. Values of σ can be derived from a knowledge of the hydrophobic and hydrophilic molecular surface areas of the solute and the corresponding microscopic interfacial free energies between these surfaces and the solvent mixture (6). For most environmental priority pollutants, such data are not available. However, linear relationships have been reported between the σ values and the logarithm octanol/water partition coefficient (K_{ow}) of the solute for several water/cosolvent systems (3, 9, 33).

Excess Free Energy Approach. The excess free energy approach successfully accounts for some deviations from the log-linear pattern. The bias is small and the predictive accuracy is satisfactory (see Figure 2). The UNIFAC derived A_{1-3} and A_{3-1} for ethanol/water systems are in good agreement with the values obtained from the vapor–liquid equilibrium data (11). The uncertainty in the solute–solvent interaction parameter, C_2 , however was found to increase with decreasing polarity of the cosolvents. For 4-chlorobiphenyl in water/1-propanol mixtures, the linear regression from which C_2 was determined exhibited a regression coefficient of only 0.2. In addition, A_{1-3} and A_{3-1}

TABLE 3

Bias and Accuracy of Solubility Estimation by the Selected Models^a

system	log-linear energy	excess free energy	phenomenological	extended reg soln	UNIFAC
4-chlorobiphenyl in methanol/water	1.41/1.57 (8)	1.02/1.14 (8)	1.01/1.09 (8)	1.18/1.69 (8)	1.32/1.46 (8)
4-chlorobiphenyl in ethanol/water	1.02/1.52 (8)	1.04/1.25 (8)	1.03/1.22 (8)	1.33/1.58 (8)	0.78/1.81 (8)
4-chlorobiphenyl in propanol/water	0.51/3.29 (8)	1.09/1.90 (8)	1.04/1.46 (8)	0.79/2.09 (8)	0.43/3.55 (8)
4-chlorobiphenyl in C4–C8 alcohols/water			1.01/1.07 (9)	0.85/1.20 (9)	0.83/1.22 (12)
2,4,6-trichlorobiphenyl in methanol/water	1.34/1.48 (8)	1.02/1.11 (8)	1.01/1.07 (8)	1.10/1.23 (8)	1.54/1.64 (8)
2,4,6-trichlorobiphenyl in ethanol/water	1.32/1.42 (4)	0.99/1.04 (4)	1.01/1.05 (4)	1.35/1.49 (4)	1.51/1.96 (4)
2,4,6-trichlorobiphenyl in propanol/water	0.78/1.82 (4)	1.10/1.34 (4)	1.11/1.45 (4)	0.81/1.67 (4)	0.88/2.19 (4)
2,4,6-trichlorobiphenyl in C4–C8 alcohol/water			1.02/1.19 (9)	0.88/1.27 (9)	0.92/1.21 (12)
2,2',4,4',6,6'-hexachlorobiphenyl in methanol/water	1.03/1.29 (6)	1.06/1.15 (6)	1.01/1.09 (6)	1.12/1.34 (6)	0.86/1.48 (6)
2,2',4,4',6,6'-hexachlorobiphenyl in ethanol/water	0.90/1.19 (3)	0.95/1.25 (3)	0.97/1.16 (3)	1.46/1.62 (3)	1.10/1.29 (3)
2,2',4,4',6,6'-hexachlorobiphenyl in propanol/water	0.38/4.96 (4)	1.16/1.75 (4)	1.16/2.04 (4)	0.49/3.71 (4)	0.45/3.91 (4)
2,2',4,4',6,6'-hexachlorobiphenyl in C4–C8 alcohol/water			1.13/1.90 (5)	0.65/2.72 (5)	0.63/2.44 (9)
overall	0.92/2.17 (47)	1.05/1.42 (47)	1.04/1.37 (67)	0.97/1.78 (67)	0.85/2.00 (77)

^a Bias/accuracy (number of data points).

for aqueous mixtures of higher alcohols, such as 1-propanol, become more dependent on the solvent composition range used in their estimation. Therefore, although this model in principle is applicable to any solute-mixed solvent system (10), its reduced three-suffix form (eq 2) is not expected to work for solvent mixtures with high nonideality.

Phenomenological Model. The phenomenological model is the best among the five models in terms of fitting the experimental solubility profiles (Figure 3). This model is based on well-established physicochemical concepts, aimed at understanding the solution process on a fundamental level. In this sense, the three curve-fitting parameters (K_1 , K_2 , and gA) are all within a physically reasonable magnitude (13). The solvation equilibrium constants K 's are expected to be from 1 to 10 if the solute is an uncharged organic compound and the cosolvent is somewhat "water-like" (13). Most K values obtained in this study were in the right range (see Table 1). In addition, K 's were found to be positively related to the nonpolarity of both cosolvent alcohols and solute PCBs. Such a trend is physically meaningful, although confirmation on a wider solute range would be desirable. The cavity curvature effect factor (g) is expected to be in the range of 1/3–2/3 (13). With the gA values listed in Table 1 and the reported van der Waals molecular surface areas for solute PCBs (34), g 's range from 0.32 to 0.46 for the systems studied here. The great potential of this model is its ability to separately investigate the effects of cavity formation and solvation with the obtained model parameters, thus to provide valuable mechanistic information for the solution process. Such an analysis shows that methanol, ethanol, and 1-propanol exert their enhancing effects on the solubility of PCBs by decreasing the free energies of both cavity formation and solvation. The decrease in the cavity formation was also found to be more important than that in solvation effects. At present, this model is considered descriptive rather than predictive. A number of experimental data points from binary solvent mixtures are essential when generating reasonable model parameter values. In addition, the range of cosolvent concentration used in regression also exerts an influence on the computed parameter values. In this study, the one-step model (eq 4) was used for a cosolvent mole fraction range below 0.004–0.07 along with an estimated datum at $x_1 = 1$ to force the fitting line. Thus, resulting K_1 and gA values are less reliable than those obtained using eq 3. Use of this model to predict solute solubilities in mixed solvent systems will only become practical if model parameters

can be determined independently or through an extensive data collection effort.

Extended Regular Solution Theory. In this study, the extended regular solution theory was applied to systems containing all alcohols except hexanol, heptanol, and octanol. The W values used for \ln solubility calculations were obtained from regressions over all the data, including those of the highly nonideal and irregular systems with 1-butanol and 1-pentanol. With this in mind, the solubility estimates by this model were quite satisfactory in that the bias was comparable to those of the excess free energy and the pheonomenological models (see Table 3). For systems containing partially miscible alcohols, estimation errors of this method were lower than those of UNIFAC (see Figure 3). Since W is solute-specific, experimental solubilities in various solvents are needed to establish the relationship between W and δ_1 for any new solute of interest. In addition, δ_1 of mixed solvents is calculated based on the linear combination of the solvent components. Such an approach may be not justified for mixed solvents that involve significant excess volume upon mixing.

UNIFAC Method. Compared with the thermodynamic models described previously, UNIFAC has the highest overall bias and is often less accurate (see Table 3 and Figure 1). However, its advantages over other methods are obvious. First, it is more versatile since it works for various solution systems, including those with high nonideality. The method produced estimates of PCB solubilities in aqueous solutions of C4–C8 alcohols, with an average absolute error of only 16% ($N = 33$). In addition, UNIFAC requires no new experimental data on solute solubility in binary solvents, or pure cosolvents, to estimate model parameters. The group interaction parameters used in this study were obtained from separate studies (2, 19); no experimental data used for model evaluation were involved. The input information required is only the composition of the solvent mixture and the temperature. This feature is a major strength of UNIFAC and is extremely valuable in estimating solubility of hydrophobic environmental contaminants in multiple-component systems, which are very difficult to characterize experimentally. We also notice that group interaction parameters between aromatic chlorine and water need further confirmation and generalization (2). With the model parameters used in this study, UNIFAC underestimates solubilities of PCBs in mixed solvents in most cases (overall bias = 0.85) (see Figures 1 and 3). Nevertheless, the powerful predictive ability of UNIFAC

has an origin in its group contribution nature and makes it very promising for environmental modeling purposes.

Summary. Within their specific applicable scopes, the overall estimation biases were 0.92, 1.05, 1.04, 0.97, and 0.84 for the log-linear model, the excess free energy approach, the phenomenological model, the extended regular solution theory, and the UNIFAC method, respectively. The accuracies are 2.17, 1.42, 1.37, 1.78, and 2.03, which correspond to average absolute errors of 39%, 24%, 22%, 32% and 35%, respectively, for the five methods in the order mentioned above. These results suggest that the models produce valid estimations for the solubility of PCBs in mixtures of water and alcohols. However, mechanisms of solution phenomena in such ternary systems are far from explicitly explained by these models. No estimation technique is currently available that accounts completely for cosolvent effects due to all the complex molecular interactions. High estimation errors of the four methods selected here usually occur at maximum deviations from the ideality and for relatively nonpolar alcohols. On the other hand, the highly dilute region deserves further experimental investigation. More data are needed to accurately depict the solute solubility profiles in this region so that a mechanistic understanding can be achieved.

Acknowledgments

This work was funded by the University of Wisconsin Sea Grant College Program, National Oceanic and Atmospheric Administration, U.S. Department of Commerce, and the State of Wisconsin (Federal Grant NA90AA-D-SG469, Project R/MW/-43). We acknowledge Drs. Kenneth A. Connors and Samuel H. Yalkowsky for their valuable advice and suggestions. We thank Dr. William J. Doucette for providing UNIFAC computer software.

Author-Supplied Registry Numbers: 4-Chlorobiphenyl, 2051-62-9; 2,4,6-trichlorobiphenyl, 35693-92-6; 2,2',4,4',6,6'-hexachlorobiphenyl, 33979-03-2; methanol, 67-56-1; ethanol, 64-17-5; 1-propanol, 71-23-8; 1-butanol, 71-36-3; 1-pentanol, 71-41-0; 1-hexanol, 111-27-3; 1-heptanol, 111-70-6; 1-octanol, 111-87-5; water, 7732-18-5.

Literature Cited

- (1) Fu, J. K.; Luthy, R. G. *J. Environ. Eng.* **1986**, *112*, 328-345.
- (2) Li, A.; Doucette, W. J.; Andren, A. W. *Chemosphere* **1994**, *29* (4), 657-669.
- (3) Morris, K. R.; Abramowitz, R.; Pinal, R.; Davis, P.; Yalkowsky, S. H. *Chemosphere* **1988**, *17*, 285-298.

- (4) Dickhut, R. M.; Armstrong, D. E.; Andren, A. W. *Environ. Toxicol. Chem.* **1991**, *10*, 881-889.
- (5) Yalkowsky, S. H.; Roseman, T. J. In *Techniques of Solubilization of Drugs*; Yalkowsky, S. H., Ed.; Marcel Dekker: New York, New York, 1981; Chapter 3.
- (6) Yalkowsky, S. H.; Valvani, S. C.; Amidon, G. L. *J. Pharm. Sci.* **1976**, *65*, 1488-1494.
- (7) Rubino, J. T.; Blanchard, J.; Yalkowsky, S. H. *J. Parenter. Sci. Technol.* **1984**, *38*, 215-221.
- (8) Rubino, J. T.; Blanchard, J.; Yalkowsky, S. H. *J. Parenter. Sci. Technol.* **1987**, *41*, 172-176.
- (9) Li, A.; Yalkowsky, S. H. *J. Pharm. Sci.* **1994**, *83*, 1735-1740.
- (10) Williams, N. A.; Amidon, G. L. *J. Pharm. Sci.* **1984**, *73*, 9-13.
- (11) Williams, N. A.; Amidon, G. L. *J. Pharm. Sci.* **1984**, *73*, 14-18.
- (12) Williams, N. A.; Amidon, G. L. *J. Pharm. Sci.* **1984**, *73*, 18-23.
- (13) Khossravi, D.; Connors, K. A. *J. Pharm. Sci.* **1992**, *81*, 371-379.
- (14) Khossravi, D. Ph.D. Dissertation, University of Wisconsin-Madison, 1992.
- (15) Martin, A.; Newburger, J.; Adjei, A. *J. Pharm. Sci.* **1979**, *68*, IV-V.
- (16) Martin, A.; Newburger, J.; Adjei, A. *J. Pharm. Sci.* **1980**, *69*, 487-491.
- (17) Adjei, A.; Newburger, J.; Martin, A. *J. Pharm. Sci.* **1980**, *69*, 659-661.
- (18) Fredenslund, A.; Jones, R. L.; Prausnitz, J. M. *AIChE J.* **1975**, *21*, 1086-1099.
- (19) Gmehling, J.; Rasmussen, P.; Fredenslund, A. *Ind. Eng. Chem. Process Des. Dev.* **1982**, *21*, 118-127.
- (20) Hansen, H. K.; Rasmussen, P.; Fredenslund, A. *Ind. Eng. Chem. Res.* **1991**, *30*, 2352-2355.
- (21) Li, A.; Andren, A. W. *Environ. Sci. Technol.* **1994**, *28*, 47-52.
- (22) Yalkowsky, S. H.; Valvani, S. C. *J. Pharm. Sci.* **1980**, *74*, 416-421.
- (23) Wohl, K. *Trans. AIChE* **1946**, *42*, 215.
- (24) Yalkowsky, S. H.; Valvani, S. C. *J. Pharm. Sci.* **1980**, *69*, 912-922.
- (25) Lyman, W. J.; Reehl, W. F.; Rosenblatt, D. H. *Handbook of Chemical Property Estimation Methods*; McGraw-Hill: New York, New York, 1982; Chapter 3, pp 21-23.
- (26) Shiu, W. Y.; Mackay, D. *J. Phys. Chem. Ref. Data* **1986**, *15*, 911-929.
- (27) Connors, K. A. *Chemical Kinetics. The Study of Reaction Rates in Solution*; VCH: Weinheim, Germany, 1990; p 390.
- (28) Yaws, C. L.; Yang, H. C.; Pan, X. *Chem. Eng. (N.Y.)* **1991**, *98*, 140-150.
- (29) Barton, A. F. M. *Handbook of Solubility Parameters and Other Cohesion Parameters*; CRC Press: Boca Raton, FL, 1983.
- (30) Fedors, R. F. *Polymer Eng. Sci.* **1974**, *14*, 147-154.
- (31) Rubino, J. T.; Yalkowsky, S. H. *Pharm. Res.* **1987**, *4*, 231-236.
- (32) Banerjee, S.; Yalkowsky, S. H. *Anal. Chem.* **1988**, *60*, 2153-2155.
- (33) Li, A.; Doucette, W. J.; Andren, A. W. *Chemosphere* **1991**, *24*, 1347-1360.
- (34) Doucette, W. J.; Andren, A. W. *Chemosphere* **1988**, *17*, 345-359.

Received for review March 7, 1995. Revised manuscript received July 5, 1995. Accepted July 20, 1995.*

ES950155K

* Abstract published in *Advance ACS Abstracts*, September 1, 1995.