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Solubility of Polychlorinated Biphenyls in Water/Alcohol Mixtures. 1. Experimental Data

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The solubilities of 4-monochlorobiphenyl, 2,4,6-trichlorobiphenyl, and 2,2',4,4',6,6'-hexachlorobiphenyl in mixtures of water and *n*-alcohols were measured using batch equilibrium techniques. The *n*-alcohols have carbon numbers ranging from one to eight. Measurements were made over a wide range of alcohol concentrations. The presence of methanol, ethanol, and 1-propanol enhances the aqueous solubility of the solutes, and the degree of enhancement increases with increasing hydrophobicity of both solute and alcohol. Deviations from a log-linear relationship were observed. Partially water-miscible alcohols (1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, and 1-octanol), when saturated in water, tend to exert smaller effects on the solubility of solutes as the alkyl chain of the alcohols becomes longer. Equations were obtained through regression of the experimental solubility with the volume fraction of alcohol. These equations can be used to predict the solubility of the PCB congeners in mixtures of water and alcohols.

Introduction

It has been recognized that many organic solvents that are widely used in industry may have a significant impact on the distribution and movement of hydrophobic organic contaminants in the environment (1-10). The presence of polar organic cosolvents such as low molecular weight alcohols, ketones, and glycols has been reported to influence the behavior of hydrophobic organic chemicals (HOCs) by enhancing the solubility in the aqueous phase (1-3), by reducing sorption by soils (5-8), and by decreasing volatilization from water (9). Less work has been done on the effect of organic solvents with limited water miscibilities. These partially water-miscible organic solvents were shown to act as cosolvents in enhancing the aqueous solubilities of HOCs when they exist in an amount exceeding 10^{-3} M (4). Rao et al. (8) have also shown that complex behavior was observed when HOCs partition to soils in the presence of partially water-miscible organic solvents at waste disposal sites.

Although the environmental impact of polychlorinated biphenyls (PCBs) has been studied for decades, experimental aqueous solubility data exist for only a limited number of congeners. Even less is known regarding their solubility behavior in multiple-component solvent systems. The lack of adequate data can be attributed to difficulties encountered in the laboratory measurements of PCBs solubilities, which are due mainly to their highly hydrophobic nature. Experimental difficulties can be greatly intensified when another organic solvent, especially a hydrophobic one, is involved. A review of the present literature shows that few measurements of the solubility of PCBs in organic/aqueous mixed systems have been reported (10).

In this study, the solubilities of three PCB congeners in mixtures of water and normal alcohols were measured

using batch equilibration methods. The use of alcohols with carbon numbers ranging from one to eight enables a systematic investigation of the influence of chain length, the hydrogen-bonding capability, and the polarity of organic solvents on their cosolvency effects toward hydrophobic organic solutes. The experimental data from 77 different ternary systems are presented. Logarithm solubility ($\log S$) of PCB solutes is regressed versus the volume fraction of the alcohol in solvent mixtures; the resulting linear and polynomial equations can be used to predict aqueous solubilities of PCB congeners in water/alcohol mixtures. Patterns and extent of deviations from log-linear relationship are discussed based on the polarity of alcohols. Solubilization of PCBs by alcohols in the water-rich region is discussed.

Experimental Section

Two experimental methodologies were employed depending on the amount of PCB solute dissolved in the sample. For samples containing 40% or more alcohols, equilibration was achieved by shaking. Separation of solid PCBs from solution was conducted by filtration, and high-performance liquid chromatography (HPLC) was used for solute quantitation. On the other hand, samples containing little or no alcohol, and therefore smaller amounts of dissolved PCBs, underwent stirring, centrifugation, liquid-liquid extraction, and gas chromatographic (GC) analysis. Details of the experiments are given below.

Chemicals. 4-Chlorobiphenyl, 2,4,6-trichlorobiphenyl, and 2,2',4,4',6,6'-hexachlorobiphenyl were selected as the test solutes. These were purchased from Ultra Scientific Inc. (Hope, RI) and reported to be $\geq 99\%$ pure. The normal alcohols used had the following purities as reported by the manufacturers: methanol, 99.96% (EM Science); ethanol, 200 proof (Quantum Chemical Corp.); 1-propanol, 100% (J. T. Baker Chemical Co.); 1-butanol, 99.9% (Fisher Scientific); 1-pentanol, certified (Fisher Scientific); 1-hexanol, purified (J. T. Baker Chemical Co.); 1-heptanol, 98% (Aldrich Chemical Co.); and 1-octanol, 99% (EM Science). 2,2,4-Trimethylpentane (isooctane), used as a solvent for gas chromatography, was from EM Science and had a purity greater than 99.98%. Water that had passed through a Milli-Q water purification system (millipore Corp., Bedford, MA) was used in all experiments.

Preparation of Saturated Solutions. Excess crystalline PCB was added directly into mixtures of water and methanol, ethanol, or 1-propanol. Sixty-milliliter bottles were used for the mixtures with alcohol volume percentages of 5, 10, and 20. Equilibrium was approached by stirring the solution with Teflon-coated stirring bars. Mixtures containing 40 and 60 vol % alcohol were prepared in 4-mL vials, while those with 80 and 100% alcohol were prepared in 2-mL vials. These samples were shaken on a Model G-560 Genie II vortexer (Scientific Industries, Inc., Bohemia, NY). Additional solid PCB was added with constant shaking until PCB crystals appeared. The samples were then placed in a 25 °C water bath for 2 days.

Table 1. Experimental Aqueous Solubility Data (S) for Selected PCB Congeners and Water-Immiscible Alcohols at 25 °C

chemical	N ^a	S, mol/L	SD ^b	literature values
4-monochlorobiphenyl	31	7.00×10^{-6}	3.14×10^{-7}	$[7.07 (10), 4.77 (11), 7.83 (12)] \times 10^{-6}$
2,4,6-trichlorobiphenyl	16	8.44×10^{-7}	2.18×10^{-8}	$[9.25 (10), 9.80 (13), 8.76 (14)] \times 10^{-7}$
2,2',4,4',6,6'-hexachlorobiphenyl	17	7.87×10^{-9}	1.05×10^{-9}	$[9.19 (10), 2.49 (11), 6.28 (13)] \times 10^{-9}$
1-butanol	9	9.61×10^{-1}	1.78×10^{-2}	$[9.7 (15), 10.1 (16), 8.54 (17)] \times 10^{-1}$
1-pentanol	16	2.29×10^{-1}	3.26×10^{-3}	$[2.5 (15), 2.6 (16), 1.3 (17)] \times 10^{-1}$
1-hexanol	23	5.24×10^{-2}	1.96×10^{-3}	$[5.9 (15), 6.2 (16), 4.14 (17)] \times 10^{-2}$
1-heptanol	23	1.30×10^{-2}	4.23×10^{-4}	$[1.46 (15), 1.55 (16), 1.13 (17)] \times 10^{-2}$
1-octanol	22	3.20×10^{-3}	1.41×10^{-4}	$[3.8 (15), 4.51 (16)] \times 10^{-3}$

^a Number of determinations. ^b Standard deviation.

Water and one of the immiscible alcohols (alcohols which are not completely miscible with water) were mixed and stirred in either glass bottles with Teflon-lined caps or Erlenmeyer flasks with glass stoppers. After being stirred for 24 h, the excess alcohol was removed, leaving only a small droplet on the surface of the aqueous phase. Less concentrated aqueous solutions of butanol or pentanol were prepared by diluting the saturated solutions with Milli-Q water. Excess PCB solid was then added to the solution with continued stirring. For samples saturated with an immiscible alcohol, the amounts of PCB and alcohol were adjusted during stirring so that both were in excess. The presence of crystalline PCB and the excess alcohol were verified at equilibrium.

The time for PCBs to reach equilibrium in water depends on the crystalline of individual congener, the agitation forces, and the solvent systems. In an effort to determine equilibration time, PCB solubilities in aqueous solutions containing ethanol, 1-pentanol, or 1-octanol were measured for time periods from 24 h up to 6 months. After an agitation time of 3, 5, and 10 days for 4-chlorobiphenyl, 2,4,6-trichlorobiphenyl and 2,2',4,4',6,6'-hexachlorobiphenyl, respectively, plus a 24-h unagitated equilibration time in a 25 °C constant temperature water bath, no further significant change in solute solubility was detected when either agitation or equilibration time was extended. No equilibration time periods shorter than these were used in this study.

Analysis. After equilibration, samples containing low concentrations of PCBs were transferred into 25-mL Corex centrifuge tubes and left to stand in a 25 °C water bath overnight. The samples were then centrifuged for 1 h at 5000 rpm (37000g) in a Beckman Model J2-21M centrifuge. The oily globule of the immiscible alcohol was then removed from the centrifuge tube by pipetting. While most of the solid PCB was at the bottom, some small flakes floated on the surface of the solution. These flakes were also removed. The sample was centrifuged for another 1 or 2 h and allowed to stand unagitated for 2-h before further treatment.

About 2 mL of the solution in the top part of the centrifuge tube was discarded by pipetting from the surface. Then, 10 mL of aqueous solution was taken by a new pipet from the center of the remaining solution for analysis. The pipet was washed by isooctane. The same isooctane was used for the first liquid-liquid extraction. Most samples were extracted four times using isooctane, while those containing more than 5% alcohols were extracted five times. The efficiency of liquid-liquid extractions was determined to be >99% by performing recovery tests for all three PCBs in 20% ethanol, pentanol-saturated, and octanol-saturated water. The extracts were diluted, if necessary, and analyzed by HP-5830 GC with a 1-m glass-packed column (5% SP2250 + 95% SP2401)

and an electron capture detector. External standards were prepared by dissolving known amounts of the solutes in isooctane, and these were subsequently used for quantification. For each analytical group, a control sample containing only water as the solvent was also prepared and analyzed with other samples. About half of the total samples were analyzed in duplicates to determine the analytical precision.

Samples containing large amounts of PCBs were filtered to separate the solute crystals. Filtration was performed immediately after the sample was taken out of the 25 °C water bath to avoid the influence of temperature variation. The filter was comprised of glass wool, packed in a DB-16 stainless steel needle. After the filter was washed with an aliquot of the sample, an exact volume was taken by gentle suction into a glass syringe. The needle was then detached, and the samples were transferred into a volumetric flask. Solute adsorbed onto the syringe wall was washed by methanol into the volumetric flask. The sample was further diluted by methanol if necessary. Quantitation of the solute was conducted on a Waters HPLC system using an Econosil C18 column (10- μ m particle size, 250 mm long \times 4.6 mm diameter) and a UV detector. The wavelength of the UV detector was set at 254 nm.

The concentrations of immiscible alcohols in selected samples were analyzed by GC with a 0.53 mm \times 15 m DB-WAX megabore capillary column (J & W Scientific, Folsom, CA) and a flame ionization detector. External standards were prepared by dissolving exact amounts of the alcohol in acetone. An alcohol having either one more or one less carbon atom than the analyzed alcohol was used as internal standard to correct for volume variations due to GC injection errors. Both the original sample and that subjected to centrifugation were analyzed for alcohol concentration levels. No significant losses of the immiscible alcohols during centrifugation were found. The average was taken as the cosolvent concentration for each group of samples, into which the same amount of an immiscible alcohol was added or saturated. The volume fractions of methanol, ethanol, and 1-propanol were calculated from the amounts of water and alcohols that were measured separately and then combined in preparing the solvent mixtures.

Results and Discussion

Experimental solubilities of the test PCB congeners in pure water and those of water-immiscible alcohols are summarized in Table 1 along with literature values for comparison. Most literature values of PCB solute water solubilities were obtained via a generator column technique. The data in Table 1 shows good agreement between the results obtained by the batch equilibration method used in this study and the generator column technique.

Table 2. Experimental Solubility of Selected PCB Congeners in Water/Alcohol Mixtures

alcohol	alcohol vol fraction	4-chlorobiphenyl			2,4,6-trichlorobiphenyl			2,2',4,4',6,6'- hexachlorobiphenyl		
		N ^a	S, mol/L	95% CI ^b	N ^a	S, mol/L	95% CI ^b	N ^a	S, mol/L	95% CI ^b
none	0	31	7.00×10^{-6}	1.15×10^{-7}	16	8.44×10^{-7}	1.16×10^{-8}	17	7.87×10^{-9}	5.41×10^{-10}
methanol	0.05	3	9.67×10^{-6}	1.30×10^{-6}	3	1.26×10^{-6}	9.74×10^{-8}			
	0.10	3	1.32×10^{-5}	2.86×10^{-6}	3	1.88×10^{-6}	1.06×10^{-7}			
	0.20	3	2.72×10^{-5}	5.18×10^{-6}	3	5.19×10^{-6}	5.98×10^{-8}	3	1.17×10^{-7}	9.65×10^{-9}
	0.40	2	2.86×10^{-4}	4.18×10^{-5}	2	7.68×10^{-5}	3.47×10^{-5}	2	4.00×10^{-6}	1.94×10^{-6}
	0.60	2	3.43×10^{-3}	1.44×10^{-3}	2	1.16×10^{-3}	3.33×10^{-3}	2	1.46×10^{-4}	2.76×10^{-5}
	0.80	2	3.71×10^{-2}	5.36×10^{-3}	2	1.91×10^{-2}	2.66×10^{-3}	2	3.22×10^{-3}	8.92×10^{-4}
ethanol	1.00	2	3.53×10^{-1}	8.86×10^{-2}	2	2.22×10^{-1}	2.17×10^{-2}	2	5.77×10^{-2}	1.19×10^{-2}
	0.05	3	9.90×10^{-6}	1.03×10^{-6}	3	1.36×10^{-6}	2.19×10^{-7}			
	0.10	3	1.41×10^{-5}	5.92×10^{-6}	3	2.02×10^{-6}	1.62×10^{-7}	4	4.99×10^{-8}	9.96×10^{-9}
	0.20	3	3.53×10^{-5}	1.77×10^{-6}	3	6.40×10^{-6}	6.74×10^{-7}	3	1.76×10^{-7}	3.49×10^{-8}
	0.40	2	1.01×10^{-3}	5.60×10^{-4}						
	0.60	2	1.32×10^{-2}	4.01×10^{-3}						
propanol	0.80	2	9.45×10^{-2}	9.22×10^{-2}						
	1.00	2	5.62×10^{-1}	8.07×10^{-2}						
	0.05	3	1.11×10^{-5}	1.15×10^{-6}	3	1.47×10^{-6}	3.01×10^{-7}	3	2.53×10^{-8}	2.47×10^{-8}
	0.10	3	1.88×10^{-5}	4.04×10^{-7}	3	3.01×10^{-6}	1.62×10^{-7}	3	5.63×10^{-8}	2.57×10^{-8}
	0.20	3	1.19×10^{-4}	1.30×10^{-4}	3	3.96×10^{-5}	2.36×10^{-6}	4	4.58×10^{-6}	3.88×10^{-8}
	0.40	2	1.10×10^{-2}	6.03×10^{-3}						
butanol	0.60	2	4.86×10^{-2}	7.49×10^{-3}						
	0.80	2	1.45×10^{-1}	4.13×10^{-2}						
	1.00	2	5.50×10^{-1}	3.14×10^{-2}						
	2.31×10^{-2}	4	8.79×10^{-6}	5.26×10^{-7}	3	1.12×10^{-6}	2.32×10^{-7}	4	1.29×10^{-8}	3.02×10^{-9}
	4.61×10^{-2}	4	1.23×10^{-5}	1.20×10^{-6}	3	1.53×10^{-6}	2.13×10^{-7}	4	2.76×10^{-8}	1.06×10^{-8}
	6.89×10^{-2}	4	1.73×10^{-5}	1.69×10^{-6}	3	2.49×10^{-6}	3.69×10^{-7}	4	4.21×10^{-8}	7.30×10^{-9}
pentanol	8.94×10^{-2}	3	2.77×10^{-5}	1.52×10^{-6}	4	5.98×10^{-6}	7.51×10^{-7}	4	5.44×10^{-7}	1.48×10^{-7}
	6.16×10^{-3}	4	7.79×10^{-6}	3.53×10^{-7}	4	9.49×10^{-7}	2.97×10^{-8}			
	1.23×10^{-2}	4	8.56×10^{-6}	3.24×10^{-7}	4	1.07×10^{-6}	2.78×10^{-8}			
	1.80×10^{-2}	4	9.47×10^{-6}	4.00×10^{-7}	4	1.16×10^{-6}	6.96×10^{-8}			
	2.41×10^{-2}	11	1.02×10^{-5}	2.65×10^{-7}	6	1.39×10^{-6}	1.10×10^{-7}	9	1.74×10^{-8}	4.85×10^{-10}
	6.34×10^{-3}	7	7.62×10^{-6}	2.22×10^{-7}	6	1.04×10^{-6}	9.52×10^{-8}	12	8.81×10^{-9}	1.35×10^{-9}
hexanol	1.82×10^{-3}	9	6.81×10^{-6}	4.31×10^{-7}	6	8.89×10^{-7}	3.46×10^{-8}	11	8.57×10^{-9}	9.70×10^{-10}
heptanol	4.92×10^{-4}	11	6.83×10^{-6}	3.42×10^{-7}	6	8.37×10^{-7}	8.09×10^{-8}	13	8.86×10^{-9}	2.57×10^{-9}
octanol										

Table 2 summarizes the experimental solubilities of selected PCB congeners in various water/alcohol mixtures. To establish the accuracies of these data, the 95% confidence intervals were calculated from the standard deviations of replicate solubility measurements. Sixty-three of the 77 solubility data reported in Table 2 are accurate to within 30%. Four of the solubility values are associated with an uncertainty between 50% and 100%, while only three of the reported values have uncertainties greater than 100%.

Observed solubility values were regressed with solute-free volume fractions of the alcohol. Polynomial equations with orders from one to three were tested for best fit. Results are summarized in Table 3, along with the squared regression coefficients. These equations can be used to estimate the solubilities of selected PCB congeners in mixtures of water and alcohols with any proportion in the indicated range.

Cosolvency of Water-Miscible Alcohols. An approximate linearity has often been found when the logarithm of the aqueous solubility ($\log S$) of nonpolar organic chemicals is plotted against the polar cosolvent concentration in the solvent mixture (1-3, 10, 18-22). The PCB solubility data obtained in this research show that such a log-linear relationship generally holds for methanol (Figure 1). The squared linear regression coefficients in a plot of $\log S$ for all three PCB congeners versus the solute-free volume fraction of methanol are all close to unity (see Table 3). The errors associated with these linear equations are around 0.1 log unit. However, deviations exist in the water-rich region (see Figure 1). For this reason, third-order polynomial regression equations are

Table 3. Equations Describing PCB Solubility in Water/Alcohol Mixtures^a

alcohol	range ^b	equation coefficients				r ²
		a	b	c	d	
4-Monochlorobiphenyl						
methanol	0-1.0	-5.336	4.819			0.995
	0-1.0	-5.155	2.191	5.667	-3.167	1.000
ethanol	0-0.2	-5.174	3.528			0.995
	0-1.0	-5.211	3.476	6.165	-4.724	0.998
1-propanol	0-0.2	-5.155	4.213	-7.955	88.23	1.000
	0-1.0	-5.373	9.067	-3.486	-5.553	0.988
1-butanol	0-0.088	-5.157	4.610	0.613	273.4	0.999
1-pentanol	0-0.025	-5.152	6.662			0.996
2,4,6-Trichlorobiphenyl						
methanol	0-1.0	-6.237	5.554			0.998
	0-1.0	-6.081	3.198	5.260	-3.035	1.000
ethanol	0-0.2	-6.091	4.386			0.995
1-propanol	0-0.2	-6.074	4.540	0.620	92.27	1.000
1-butanol	0-0.088	-6.075	7.529	-117.0	1604	1.000
1-pentanol	0-0.025	-6.076	8.442			0.986
2,2',4,4',6,6'-Hexachlorobiphenyl						
methanol	0-1.0	-8.181	7.029			0.998
	0-1.0	-8.119	5.289	5.040	-3.466	1.000
ethanol	0-0.2	-8.062	6.749			0.988
1-propanol	0-0.2	-8.104	14.54	-116.3	563.5	1.000
1-butanol	0-0.088	-8.125	26.02	-684.8	7114	0.983
1-pentanol	0-0.025	-8.104	13.93			1.000

^a $\log S = a + bz + cz^2 + dz^3$, where S is PCB solubility (in mol/L) and z is the solute-free volume fraction of alcohol. ^b Range of solute-free volume fraction alcohol.

also listed in Table 3 for methanol in the volume fraction range of 0-1.

From Figure 1, there appears to be two regions, divided at a methanol volume fraction of 0.2, above which the

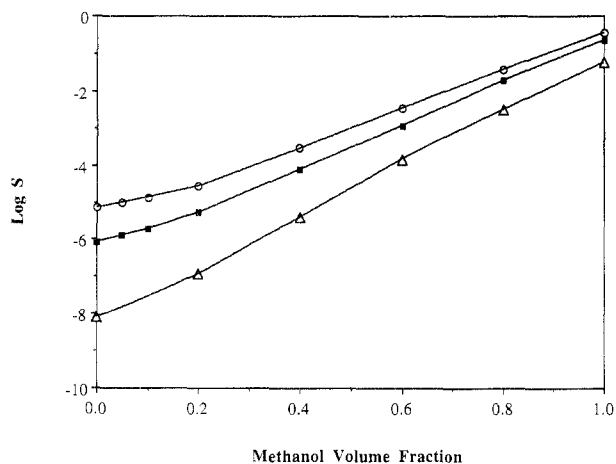


Figure 1. Effect of methanol on the solubilities of selected PCB congeners. Legends for solutes: (O) 4-monochlorobiphenyl; (■) 2,4,6-trichlorobiphenyl; (Δ) 2,2',4,4',6,6'-hexachlorobiphenyl.

Table 4. Comparison of Log-Linear Regressions with Methanol Volume Fractions Below and Above 0.2^a

solute	range ^b	<i>a</i>	<i>b</i>	<i>r</i> ²
4-chlorobiphenyl	0-0.2	-5.161	2.949	0.999
	0.2-1.0	-5.593	5.169	1.000
2,4,6-trichlorobiphenyl	0-0.2	-6.092	3.955	0.998
	0.2-1.0	-6.349	5.830	1.000
2,2',4,4',6,6'-hexachlorobiphenyl	0-0.2	-8.104	5.863	1.000
	0.2-1.0	-8.267	7.145	0.998

^a Log *S* = *a* + *bz*, where *S* is PCB solubility (in mol/L) and *z* is the solute-free volume fraction of alcohol. ^b Range of solute-free volume fraction alcohol.

slopes are significantly higher than those below. Table 4 lists the linear regression parameters in both regions. Banerjee and Yalkowsky (23) demonstrated that the solubilization of toluene exhibited a linear rather than a logarithmic function of methanol or propylene glycol content when this content is below 10-20% by volume, beyond which the log-linear pattern is obeyed. They attributed this change to the onset of the interactions between extended hydration shells of the cosolvent molecules. Changes in PCB solubilities observed in this study are better represented by log-linear relationships than by linear ones when the methanol concentration is below 20%. The increase of log *S* in the ethanol system also shows satisfactory linearities in the water-rich region. As for 1-propanol, however, the log-linear range is quite limited. A polynomial equation is therefore used to describe the enhancement in PCBs solubility at a volume fraction below 0.2 for this alcohol.

Figure 2 illustrates the solubility of 4-chlorobiphenyl in mixtures of methanol, ethanol, and 1-propanol. Over the entire range of solvent composition, the log-linear manner is observed for neither ethanol nor propanol. Instead, the profiles of 4-chlorobiphenyl solubility exhibit significant curvatures. A positive (upwards) deviation from the linearity replaces the initial negative deviation as the alcohol concentration in the mixture increases. The deviations from the linearity are contained within 0.5 log unit, with ethanol being the cosolvent. In the case of cosolvent propanol, the solubility of 4-chlorobiphenyl at a 0.4 volume fraction, 1-propanol is about 1.2 log unit higher than the value predicted based on the log-linear regression equation. Therefore, polynomial equations must be used to fit the data over the full range of alcohol concentrations shown in Table 3.

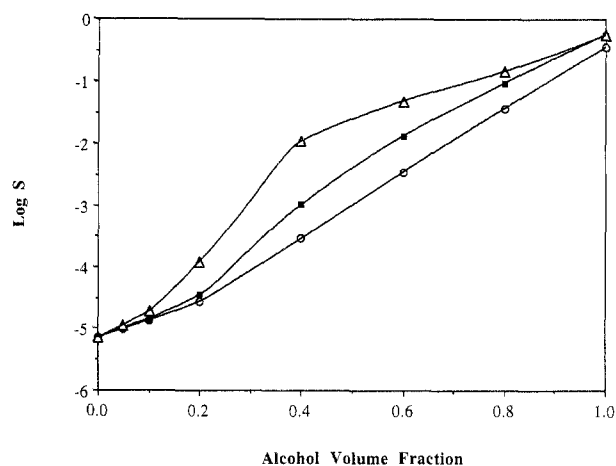
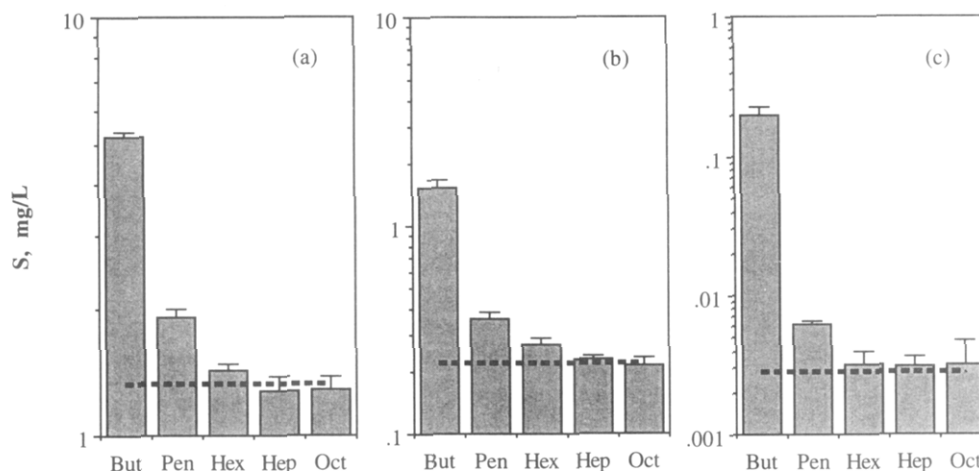


Figure 2. The effects of water-miscible alcohols on the solubility of 4-chlorobiphenyl. Legends for alcohols: (O) methanol; (■) ethanol; (Δ) 1-propanol.

The power of cosolvency is stronger for higher water-miscible alcohols. The solubilities of 4-monochlorobiphenyl, for example, were enhanced 0.59, 0.70 and 1.23 log units relative to its solubility in pure water by methanol, ethanol, and 1-propanol, respectively, at the same cosolvent volume fraction of 20%. This trend is in agreement with other results from investigations involving a variety of polar organic cosolvents (20, 21, 24). It is also evident that the enhancement of solubility is related to the degree of chlorination of PCBs or, more generally, to the hydrophobicity of the organic solutes as discussed in several published works (3, 10, 18, 19). The extent of solubility enhancement by the same alcohol increases as the solute hydrophobicity increases. For instance, in a 20% methanol solution, the solubilities of 4-chlorobiphenyl, 2,4,6-trichlorobiphenyl, and 2,2',4,4',6,6'-hexachlorobiphenyl were determined to be 3.89, 6.14, and 14.88 times their solubilities in pure water, respectively.

Effect of Partially Water-Miscible Alcohols. The effects of 1-butanol and 1-pentanol were investigated up to their saturation level in the solution. Pentanol, which dissolves in water in limited amounts, increases the solubilities of PCBs in log-linear pattern with respect to their concentration in the aqueous solution. Plots of log *S* versus the pentanol volume fraction show the linearity. With butanol as the cosolvent, a log-linear relationship is observed up to about 75% of the butanol saturation. The upward deviation from linearity takes place as the butanol concentration approaches its saturation level. Consequently, third-order polynomials are used to describe PCB solubilities in aqueous solutions of butanol (see Table 3). Such an analysis also indicates that the first part of the log-linear region tends to be narrower as alcohol nonpolarity increases. For example, a change in log *S* of 4-chlorobiphenyl is linear up to volume fraction of 0.2 for methanol, 0.1 for 1-propanol, 0.07 for 1-butanol, and 0.025 for 1-pentanol.

Solubilities of selected PCBs were also measured in aqueous solutions saturated by one of the higher alcohols, i.e., 1-hexanol, 1-heptanol, and 1-octanol. Limited enhancements of PCB solubilities caused by hexanol were detected while there were no significant changes observed due to heptanol and octanol. Figure 3 illustrates the solute solubilities in aqueous solutions saturated by one of the water-immiscible alcohols. The rapid drop of PCB solubility as the cosolvent alcohols change from butanol to octanol may indicate that cosolvency of water-immis-



Water Immiscible Alcohols

Figure 3. Effects of water-immiscible alcohols on the solubility of selected PCB congeners: (a) 4-monochlorobiphenyl; (b) 2,4,6-trichlorobiphenyl; (c) 2,2',4,4',6,6'-hexachlorobiphenyl. The dashed lines indicate pure water solubilities.

cible solvents is dominantly limited by the amount of cosolvent dissolved in water. It is evident, however, that some immiscible organic solvents such as octanol and chlorobenzene have a negligible influence on solute solubilities even when their contents were increased by an addition of a polar organic cosolvent, e.g., methanol (25, 26). The observed decrease in the cosolvency effect of immiscible alcohols as their polarity decreases is opposite to the cosolvency exhibited by water-miscible alcohols, for which stronger cosolvency associates with the less polar alcohol, e.g., 1-propanol. This observation on the differences in the cosolvency effects between the water-miscible and water-immiscible alcohols is in agreement with the work of Pinal et al. (26).

On a molar basis, however, water-immiscible alcohols seem to provide a greater ability to solubilize highly hydrophobic organic chemicals. This is most likely due to the relatively strong hydrophobic character of these alcohols compared to water-miscible ones. Solubilities of 2,4,6-trichlorobiphenyl are plotted in Figure 4 against molar concentration of alcohols in the water-rich region, where the linearity between $\log S$ and alcohol concentrations holds. A continuous increase in the slope was found in going from methanol to hexanol systems. Similar increases in slopes are observed for 4-chlorobiphenyl and 2,2',4,4',6,6'-hexachlorobiphenyl in going from methanol up to pentanol. These slopes reflect the solubilization potential by 1 mol of alcohol if the alcohol could dissolve in the aqueous system in this amount. With the available experimental data, it is difficult to deduce this potential for higher molecular weight in alcohols than hexanol because the effect of heptanol and octanol are negligibly small at their highest possible concentrations in water.

It should be mentioned that severe experimental difficulties were associated with alcohols of long alkyl chains, due in large measure to the tendency of self-association of these alcohols in water in the presence of solid solutes like PCBs. Such a problem is more severe for a more highly chlorinated congener like 2,2',4,4',6,6'-hexachlorobiphenyl. For instance, the solubility value of this hexachlorobiphenyl in octanol-saturated water appears to be a little higher than its pure water solubility. However, such an interpretation cannot be justified by a statistical analysis, which results in a high standard deviation of the replicates. This variability is most likely caused by the

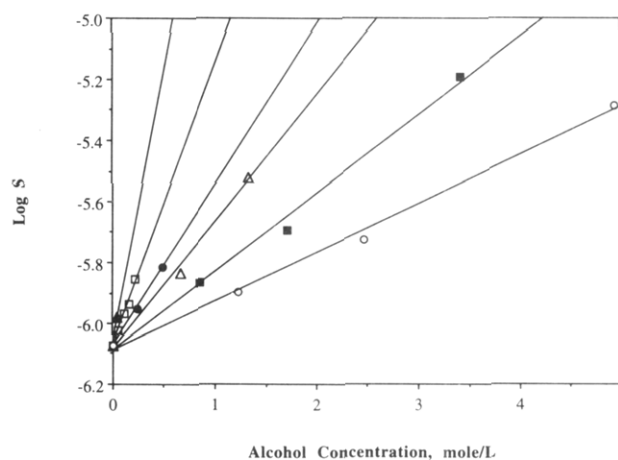


Figure 4. Effects of alcohols on the solubility of 2,4,6-trichlorobiphenyl at low alcohol concentration. Legends for alcohols: (O) methanol; (■) ethanol; (Δ) 1-propanol; (●) 1-butanol; (□) 1-pentanol; (▲) 1-hexanol.

formation of microemulsions of octanol in water. Had this occurred, the mechanism of solubilization would change from dissolution of the solute to partitioning into micelles; the apparent solubility would then be increased by a larger amount (27, 28). Such an assumption is made all the more believable by the unreasonably high solubility results of hexachlorobiphenyl in aqueous solutions saturated with 1-nonanol or 1-decanol. The cloudy appearance of these solutions would not disappear through extended periods of standing without any agitation or after centrifugation for 3 h.

Summary

The solubilities of 4-chlorobiphenyl, 2,4,6-trichlorobiphenyl, and 2,2',4,4',6,6'-hexachlorobiphenyl were experimentally determined in mixtures containing water and a normal alcohol with varied concentrations. Most of the measurements were found to be reproducible within 30% at the 95% confidence interval. Completely water-miscible alcohols (methanol, ethanol, and 1-propanol) were found to significantly increase solubilities of selected PCB congeners, their cosolvency being inversely related to their polarity. 1-butanol, 1-pentanol, and 1-hexanol were also found to increase the solubilities of PCBs, while the effects of dissolved 1-heptanol and 1-octanol were negligible. The

dependence of alcohol cosolvency on its concentration in solvent mixtures differs for the various alcohols. A plot of log *S* versus cosolvent concentrations appears to be semilogarithmic in a water-rich region. As the alcohol content increases, this log-linear relationship is generally not followed. Positive deviations from the linearity tend to start at a lower concentration and to be greater for less polar alcohols. On a molar basis, the solubilizing potential of methanol through pentanol appears to increase with cosolvent hydrophobicity. The cosolvency effect of alcohols is also found to be dependent on the degree of chlorination of PCB solutes, the solute with higher hydrophobicity tending to be solubilized to a greater extent.

Theory and experimental results show that there are inverse relationships between the solubilities of HOCs and octanol/water partition coefficients, bioconcentration factors, and oil sorption coefficients. For example, Rao et al. (8) showed that the presence of cosolvents at waste disposal sites resulted in HOC adsorption, which was much less than that predicted from a pure aqueous solvent system. The authors also showed that the power of cosolvency, as determined in solubility studies, can be used to account for the solvent-sorbate interactions in sorption by soils for the same organic pollutants (8). In our study, we demonstrated that solubility changes caused by alcohols provided information on the cosolvency as related to the polarity and concentration of the organic cosolvents, as well as to the hydrophobicity of the solute. Such information is expected to be useful for future investigation on the sorption of HOC in water/cosolvent mixed systems. These data will be also useful in predicting the partitioning of HOCs between water/organic solvents mixtures and air or biophases. An extensive set of solubility data for hydrophobic drug compounds in mixed solvent systems exist (18-22, 29-31). Similarly, data on fluid-phase equilibria for mixed systems have also appeared in the chemical engineering literature. A number of theories have been developed to explain the observed results (19, 29-32). However, little work has to date been done to examine whether highly hydrophobic environmental pollutants, such as those investigated in this study, can be accommodated by these models (33, 34). Further interpretation of the experimental solubility data of this study, using a number of theories and models, will be presented in a forthcoming paper.

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