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Micellar Solubility and Micelle/Water Partitioning of Polychlorinated Biphenyls in Solutions of Sodium Dodecyl Sulfate

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An experimental method is described to determine enhanced solubilities and partitioning of extreme hydrophobics in micellar systems. Experimental data are presented on the enhanced solubilities, chemical activity coefficients and micelle/water partition coefficients of 14 polychlorinated biphenyls (PCBs) in solutions of sodium dodecyl sulfate (SDS) below and above the critical micellar concentration (cmc). The method described in this study proves to be highly accurate. Solubility data obtained are in accordance with data from other studies. Experimental micelle/water partition coefficients turn out to be sufficiently accurate to distinguish between isomers. Solubilities of PCBs in micellar solutions above the cmc depend linearly on SDS concentration, and the solubility enhancement is 2–4 orders of magnitude. PCB partition coefficients (log K_{mw}) are independent of SDS concentrations in this study and ranged from 4.61 to 6.62. The partitioning behavior of the pertinent extremely hydrophobics between the aqueous and micellar phases is not completely comparable with simple organic solvent/water systems, and the linear correlation between log K_{ow} and log K_{mw} no longer holds.

Introduction

Low aqueous solubilities and high 1-octanol/water partition coefficients of hydrophobic chemicals result from unfavorable and weak solute/water interactions incapable of competing with the strong hydrogen bonds forces between water molecules. Aggregates of surfactants, or micelles, act as colloids and can enhance solubilities of hydrophobic compounds dramaticly (*1*–*4*).

Caused by the immense industrial production of surfactants and the widespread use of these compounds, surfactants give rise to a concern over the direct and indirect effects they may have in the environment. Beside their own toxicity to aquatic organisms, they might increase the bioavailability of hydrophobic contaminants by enhancing their solubility, extracting them from sediments, and reducing their volatilization to the atmosphere (*1*, *5*).

Surfactants are produced not only by industries but also by bacteria and higher organisms. In the gastrointestinal tract, surfactants produced by the liver and provided to the gut via the bile have an important function during the digestion processes of dietary lipids. These bile salt micelles might well play a role in the transport over the gut wall of hydrophobic contaminants from food intake (*3*, *7*–*9*). In spite of this wide field of applications and of potential environmental risks, much of the molecular events and thermodynamics of solubilizing hydrophobic solutes in surfactant micelles has yet to be elucidated, and still little is known of the interactions between extreme hydrophobic contaminants like polychlorinated biphenyls (PCBs) and surfactant micelles.

Kile and Chiou investigated solubility enhancement of 1,2,3-trichlorobenzene and DDT in micellar solutions and concluded that for nonionic surfactants the enhancement effect is closely proportional to the nonpolar chain content of the surfactant, whereas in the ionic surfactants like sodium dodecyl sulfate (SDS) this relation is less obvious (*1*). Valsaraj and Thibodeaux found excellent correlations between micelle/water partition coefficients (log K_{mw}) and the 1-octanol/water partition coefficient (log K_{ow}) for a group of volatile organic chemicals with a log K_{ow} value lower than 3(*4*). They used head space analysis to detect differences of compound concentration in the gas phase between batches with and without SDS. The same method was conducted by Anderson to determine Henry's law constants and micelle/water partition coefficients of benzene, toluene, and *o*-xylene (*5*). Using micellar HPLC to investigate micelle/water binding constants and the free energy of transfer from water to micelles, Pramauro et al. studied a series of 30 substituted phenols (*10*). They concluded that there are some similarities between classical two-phase systems like 1-octanol/water and micellar systems but observed also many discrepancies. They argued that biological systems are more similar to amphiphilic micellar aggregates than to simple two-phase systems. Laher and Barrowman studied the effect of the composition of mixed bile salt micelles on the solubility properties of three polycyclic aromatic hydrocarbons and the PCB mixture Araclor 1242, and the relation between micelle/water partitioning and toxicity of tetrachlorinated benzenes was investigated by Astles et al. (*3*, *11*). An extended thermodynamic model of the solubilization of

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nonionic molecules into ionic surfactant micelles was described by Aamodt et al. (*12*).

In order to determine enhanced solubilities and micelle/water partition coefficients of a series of PCBs in solutions of anionic surfactants, we developed a method to conduct these investigations rapidly and accurately with few losses during cleanup procedures. The method should provide us with solubility data that are consistent with the most accurate data from the literature and with partition coefficients that are independent of both solute and micellar concentration (*13–15*). The partition coefficients should possess by preference the same range of errors, standard deviations of 0.05–0.1 log unit, as the slow stirring technique used for 1-octanol/water partition measurements (*16*). In this paper, we present and apply this method to investigate the enhanced solubility and micelle/water partitioning in SDS of 14 PCBs with log K_{ow} values in a range of 5.0–8.5. By studying the relationship between log K_{mw} and log K_{ow} data collected from the literature, the properties of the bulk solvent 1-octanol and the micellar phase of SDS are compared.

Methods and Experimental Section

Micelle/Water Partitioning. The main reason amphiphilic molecules start to aggregate into micelles is to reduce the energetically unfavorable interaction between the hydrophobic tails and the water. The gain in free energy by bringing the tails together starts to dominate over the loss in entropy due to aggregation. As a consequence, the micelles consist of a hydrophilic outer layer formed by the polar head groups facing the aqueous environment and a separated hydrophobic core region consisting of the hydrophobic chains. This hydrophobic core is assumed to be a distinct pseudo-phase that is fluid in character, though more structured and rigid than organic solvents like 1-octanol (*12, 17*). Above a compound's specific threshold concentration, the critical micelle concentration (cmc), monomers start to aggregate in spherical micelles (*18*). The value of the cmc depends on surfactant chemistry, temperature, ionic strength, and the presence of organic additives of the solution (*2, 19*). Above the cmc, the addition of more surfactant results in the incorporation of more molecules into micelles, which can increase in size and in number; the number of monomers will stay constant. At low temperatures, detergents form insoluble crystals above the maximum solubility concentration. The monomer concentration is in equilibrium with the crystals until the critical micellar temperature (cmt) is reached, above which micelles start to form.

Enhanced solubility of hydrophobic compounds in surfactant solutions is due to partitioning of the compound between water and micellar phases. Molecules with a polar side and an apolar face are mainly solubilized near the surface of the micelle with the polar group at the surface, whereas purely hydrophobic compounds will preferentially be solubilized in the core region of the micelles (*12*).

Surfactant micelles do exist in relation with their aqueous environment only; hence, it is impossible to measure concentrations of solute in the micellar phase directly. Commonly the solubilization potential of a surfactant is expressed by the enhanced solubility of a solute or by the molar solubilization ratio, which is defined as the extra number of moles of solute that can be solubilized per mole of surfactant present in the solution (*2, 3*).

In perspective to the application of data in environmental fate models, such as the fugacity model of Mackay, it is more convenient to use the concept that enhanced solubility of hydrophobic compounds in surfactant solutions is due to the partitioning of compound into the hydrophobic core of the micelles and to express the solubilization potential of the surfactant by the compound's micelle/water partition coefficient (K_{mw}) where the subscripts m and w denote respectively micelle and water (*20*). K_{mw} is the ratio of the concentrations (mol/m^3 or g/m^3) of the compound in the micellar phase (C_m) to the concentration of the compound in the aqueous phase at the cmc ($C_{w(cmc)}$):

$$K_{mw} = C_m/C_{w(cmc)} = (\bar{V}_{w(cmc)}/\bar{V}_m)(\gamma_{w(cmc)}/\gamma_m) \quad (1)$$

where $\bar{V}_m$ is the molar volume of the micellar phase (in the case of SDS, 290 cm^3/mol), $\bar{V}_w$ is the molar volume of water (i.e., 18 cm^3/mol), and K_{mw} is the product of the ratio of the solvent molar volumes and the ratio of the solutes activity coefficients in the aqueous phase at the cmc ($\gamma_{w(cmc)}$) and in the micellar phase (γ_m). In the presence of an excess of compound, the activity coefficient of the solute is the reciprocal of the mole fraction solubility of the solute (X), corrected by the fugacity ratio (F) if the solute is a solid at ambient temperature and pressure (i.e., $\gamma = F/X$). At infinite dilutions, when the mole fraction X is very small, the activity coefficient can be assumed to be constant. Its logarithm normally varies in proportion to $(1 - X)^2$, which is essentially constant at values of X below 10^{-2} (*21*). For extremely hydrophobic chemicals, as studied here, aqueous solubilities are so low that this criterium is met, but in the micellar phase concentrations may be much higher.

In the experimental setup as used in this study, containing pure solute (p), solute dissolved in water (w), and solute dissolved in the SDS micellar phase (m), a total mass (M) balance equation of the solute before (0) and after (x) the addition of surfactant can be derived:

$$M_{total} = M_{w(0)} + M_{p(0)} = M_{w(x)} + M_{p(x)} + M_m \quad (2)$$

M_{total} is the mass of solute that is introduced into the solution, and the aqueous solubility ($S_{0.0}$) without surfactant is simply the difference between M_{total} and $M_{p(0)}$ divided by the volume of the water (i.e., $(M_{total} - M_{p(0)})/V_w$). The enhanced solubility at a particular surfactant concentration (x) then is the difference between M_{total} and $M_{p(x)}$ divided by the volume of the surfactant solution, which is considered to be equal to the volume of the water ($(M_{total} - M_{p(x)})/V_w$).

Just before the cmc, the aqueous phase is saturated with surfactant monomers, and the solubility of the solute at the cmc (S_{cmc}) is the difference between M_{total} and $M_{p(cmc)}$ divided by V_w. Above the cmc, the amount of surfactants in terms of monomers remains constant. Addition of surfactant above the cmc leads to the incorporation of surfactant molecules into micelles. The enhanced solubilization of compound from the solid phase into the solution is entirely due to the increase of the micellar volume in the solution:

$$M_{p(cmc)} - M_{p(x)} = C_m V_m \quad (3)$$

The contribution of volume of the micellar phase (V_m in m^3) to the volume in the surfactant solution can be obtained from the partial specific volume of the surfactant, in the case of SDS, 0.863 cm^3/g or 249.2 cm^3/mol above the cmc (*19, 22*). Combining eqs 1 and 3, a proper partition

TABLE 1

IUPAC Number and Physical–Chemical Properties of Selected Polychlorinated Biphenyl Congeners

structure	IUPAC no.	MW (g/mol)	F-ratio[a,b]	S_w[a] (nmol/L)	log K_{ow}[a]
3,5-	14	223.1	0.872	2904[c]	5.37[d]
2,4,6-	30	257.5	0.427	777[b]	5.5[b]
4,4'-	15	223.1	0.059	269[b]	5.3[b]
2,4,5-	29	257.5	0.3	544[b]	5.6[b]
2,2',4,5-	49	292.0	0.413	54.8[b]	6.1[b]
2,2',3,3'-	40	292.0	0.113	103[b]	5.6[b]
2,3,4,5-	61	292.0	0.218	68.5[b]	5.9[b]
2,2',4,4',6,6'-	155	360.9	0.132	5.5[b]	7[b]
2,3,4,5,6-	116	326.4	0.105	14.5[b]	6.3[b]
2,2',3,3',6,6'-	136	360.9	0.138	2.22[b]	6.7[b]
2,2',3,3'4,4'-	128	360.9	0.0582	1.66[b]	7[b]
2,2',3,4,4',5,5'-	180	395.3	0.144	0.57[c]	7.21[d]
2,2',3,3',4,5,5',6-	198	429.7	0.045	0.41[d]	7.43[d]
2,2',3,3',4,4',5,5',6,6'-	209	498.7	0.00167	0.001[b]	8.26[b]

[a] Number of decimals as given in the references. [b] From ref 15. [c] From ref 14. [d] From ref 24.

coefficient can be defined according to eq 4:

$$K_{mw} = C_m/C_{w(cmc)} = (M_{p(cmc)} - M_{p(x)})/C_{w(cmc)}V_m \quad (4)$$

As the concentrations here are maximum concentrations, $C_{w(cmc)}$ can be considered as the solute's aqueous solubility at the cmc (S_{cmc}). Thus, the partitioning of a chemical between the micellar phase and the aqueous phase can easily be obtained from measurements of the mass loss of pure solute before and after the addition of surfactant.

Experimental. Sodium dodecyl sulfate (SDS) was supplied by Sigma Chemical Co., and chromosorb G(AW) 60-80 mesh from Chrompack. The experiments were conducted with 14 PCBs of which 4,4'-, 2,4,6-, 2,2',4,5'-, 2,2',3,3',4,4'-, 2,2',4,4',6,6'-, 2,2',3,4,4',5,5'- 2,2',3,3',4,5,5',6-, and decachlorobiphenyl were purchased from Promochem; 2,2',3,3'-, 2,3,4,5-, 2,3,4,5,6-, and 2,2',3,3',6,6'-chlorobiphenyl were from Ultra Scientific, and 3,5- and 2,4,5-chlorobiphenyl were from Dr. S. Ehrensdorfer. Physical–chemical properties and IUPAC numbers of the selected PCBs are listed in Table 1 in the sequence of column elution. Recovery and internal analytical standards (1,2,3,5-tetrachlorobenzene and pentachlorobenzene) were from Ultra Scientific. The solvents acetone (Merck) and 2,2,4-trimethylpentane (Rathburn) were respectively pro analysis and HPLC grade and were distilled and controlled for purity by means of FID and ECD chromatography. They proved to be more than 99.9% pure. SDS, chlorobenzenes, and PCBs were used as received from their suppliers. The water used was distilled twice.

Sufficient amounts of the PCBs were dissolved in pentane and added to the chromosorb. Under continuous stirring and mild vacuum, the solvent was evaporated in a rotavapor to coat the chromosorb homogeneously with the PCBs. Portions of 25 mg of coated chromosorb were placed into 10-mL vials. To each vial 3 mL of SDS solution was added, with concentrations ranging from 0.0 to 10.0 mM SDS. At the given experimental conditions, SDS critical micellar concentration is considered to be 1.15 mM (*19*). Solutions consist of SDS in a phosphate buffer of 0.02 M KH_2PO_4 and 0.15 M NaCl with pH 7. Experiments were conducted in triplicate at 25 ± 0.5 °C, and the vials were stirred continuously. Although the cmt of SDS is close to 25 °C (*19*), no precipitation of SDS crystals during the experiments was observed.

In order to determine the time to reach equilibrium, enhanced solubility plots at 5 mM SDS were made after 6, 24, 48, 72, and 96 h. After these periods, samples were taken and filtered using pipet filters leaving chromosorb behind. Chromosorb was rinsed three times, and the SDS micelle filtrate solutions were used for mass balance contol. Recoveries of the coating, rinsing, and filtering procedure showed to be between 81% and 104% depending on the PCB congener.

Since the chromosorb does not contain any impurities, cleanup of the samples is minimized, reducing losses and time during cleanup. Chromosorb was extracted during at least 6 h but usually overnight with 5 mL of acetone, and 1.5 μg of 1,2,3,5-tetrachlorobenzene was added as the recovery standard. From this sample, 100 μL was added to 3 mL of 2,2,4-trimethylpentane and analyzed by GC-ECD with 300 ng of pentachlorobenzene as the analytical internal standard for quantification of the PCBs and recovery standard. Chromosorb samples from the exposures to SDS concentrations below the cmc were extracted by 1 mL of acetone. After the addition of 300 ng of the recovery standard, the total sample was added to the 2,2,4-trimethylpentane. Under a flow of nitrogen, the acetone was evaporated, and the analytical standard was added. Spike recoveries usually were between 80% and 120% for the recovery standard and always higher than 95% for the analytical standard.

Sample analysis was performed on a 30-m DB-5 column with a diameter of 0.32 mm in a HP-5890 GC with ^{63}Ni electron capture detector and on-column injector. The carrier gas was helium (30 cm/s flow and 84 kPa pressure), and the makeup gas was argon/methane. All 14 PCBs were separated by the following *T* program: 80 °C-2 min-10 °C/min → 140 °C/5 min-3 °C/min → 240 °C-30 °C/min → 325 °C-5min; temperature of the detector was 350 °C.

Quantification of PCB peaks was done by integration of the peak surfaces and multilevel calibration consisting of six levels. Calibration levels ranged from 1 to 1000 pg/injection. Samples (0.5 μL) were injected in triplicate; standard deviations of the triplicate analysis of one sample were smaller than 3%. Standard deviations of the mean due to analytical error between triple samples were within 5%, except 4,4'-dichlorobiphenyl which possessed standard deviations up to 10% due to its irregular elution behavior. Standard deviations of the mean due to experimental error (chromosorb exposure and cleanup) ranged from 3% to 10% per triplicate sample. Determination of PCB solubilities in buffer and SDS solutions is based on PCB loss from chromosorb not containing impurities nor remainders of SDS. Hence limits of detection and limits of quantitation are comparable, ranging from 1.2 to 10 pg/mg of chromosorb depending on the PCB congener.

Results and Discussion

The experiments to determine the time required to reach equilibrium concentrations in SDS solution were conducted with all 14 PCBs, and the results were essentially the same for all PCBs. Solubilizing behavior of PCB 14, PCB 40, and PCB 128 in a micellar solution of 5 mM SDS from 0 to 96 h is plotted in Figure 1, with error bars expressing their standard deviations. Using a fluorescence quenching

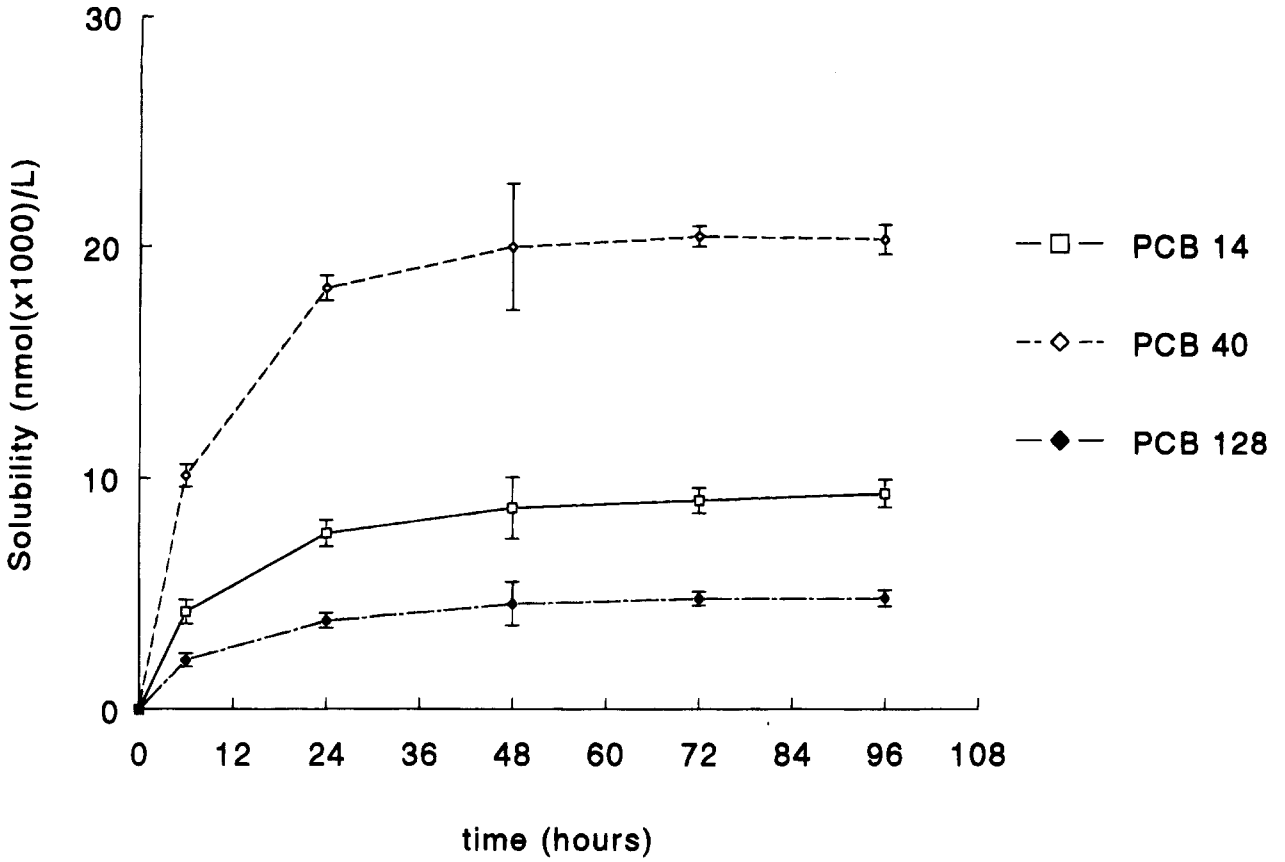

FIGURE 1. Equilibrium time of PCB 14, PCB 40, and PCB 128 in 5 mM sodium dodecyl sulfate.

TABLE 2

Experimental Solubilities (S in nmol/L) of Polychlorinated Biphenyls in Phosphate Buffered Solutions of 0.0, 1.0, 5.0, and 10.0 mM Sodium Dodecyl Sulfate

IUPAC no.	$S_{0.0}$ [a] (nmol/L)	$S_{1.0}$ [a] (nmol/L)	$S_{5.0}$ [a] (nmol/L) (×1000)	$S_{10.0}$ [a] (nmol/L) (×1000)
14	426.2 (± 14.2)	517.2 (± 27.8)	9.33 (± 0.60)	21.68 (± 1.87)
30	1476 (± 47)	1451 (± 138)	111.2 (±2.7)	233.4 (± 14.1)
15	479.5 (± 91.9)	672.3 (± 138.9)	23.96 (± 2.28)	65.69 (± 4.09)
29	831.6 (± 71.8)	877.0 (± 198.9)	70.68 (± 2.58)	137.79 (± 9.16)
49	32.00 (± 8.91)	89.16 (± 16.03)	24.49 (± 1.93)	49.88 (± 2.83)
40	97.31 (± 19.21)	194.9 (± 30.2)	20.34 (± 0.64)	45.42 (± 0.30)
61	54.80(± 7.06)	121.9 (± 20.1)	23.00 (± 1.38)	55.92 (± 3.33)
155	3.45 (± 0.60)	4.02 (± 0.67)	3.95 (±0.17)	9.00 (±0.52)
116	12.27 (± 2.87)	81.40 (± 23.42)	24.35 (± 1.50)	45.46 (± 2.76)
136	4.48 (± 1.17)	10.29 (± 1.82)	3.76 (± 0.15)	9.03 (± 0.50)
128	3.91 (± 0.50)	5.28 (± 1.16)	4.81 (± 0.35)	10.90 (± 0.85)
180	1.97 (± 0.58)	3.92 (± 0.95)	7.06 (± 0.85)	15.53 (± 1.58)
198	0.56 (± 0.16)	0.89 (± 0.16)	1.38 (± 0.05)	1.98 (± 0.12)
209	0.01 (± 0.002)	0.08 (± 0.01)	0.18 (± 0.02)	0.42 (± 0.004)

[a] Values and standard deviations (between parentheses) are for the means of triplicate samples.

technique, Grätzel and Thomas concluded that it takes about 40 h after preparation before SDS micelles are stabilized (*17*). As our time exposure experiments show, the chemical concentration in the solution reaches its maximum after 48 h and stays constant at that level. Since the standard deviations of the concentration measurements at 72 and 96 h are somewhat smaller than at 48 h, 72 h was chosen as the minimum time to achieve equilibrium, and 96 h was chosen as the experimental exposure time throughout the course of the experiment. During the course of the experiments described in this study no signs of biodegradation have been observed.

Experimentally determined solubility data (nmol/L) at different SDS concentrations below and above the cmc are listed in Table 2 for all 14 PCB congeners. Aqueous solubility data of relevant PCBs from the literature are listed in Table 1. Data from Mackay et al. (*15*) are determined values based on data from cited literature, data from Dunnivant et al. (*14*) were obtained by a generator column, and the PCB 198 data point from Brodsky and Ballschmiter (*24*) was derived from reversed-phase liquid chromatography. The experimental solubility data were determined in a saline phosphate buffer containing phosphate and sodium salt but fit very well in the same order of magnitude of aqueous solubility literature data in pure water. Concentrations of dissolved electrolytes under the experimental conditions do not seem to have a major influence on aqueous solubilities of the hydrophobic chemicals used in this study.

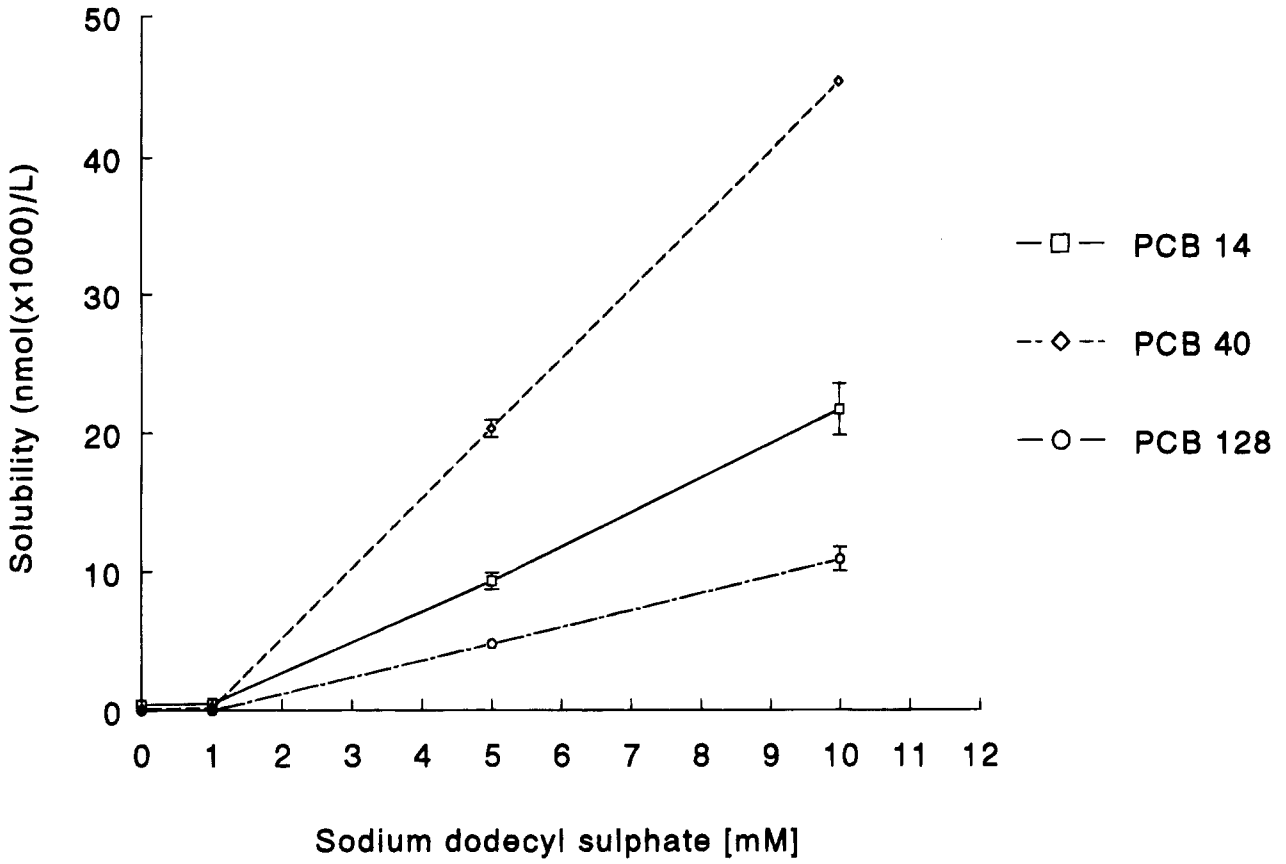

FIGURE 2. Solubilities of PCB 14, PCB 40, and PCB 128 in solutions of 0.0, 1.0, 5.0, and 10.0 mM sodium dodecyl sulfate.

At SDS concentrations of 5 and 10 mM PCB, solubilities are enhanced by several orders of magnitude, ranging from 100 to 10 000 times the aqueous solubility. Standard deviations for aqueous solubilities range from 3% up to 30%; this range of errors is quite commonly achieved with the generator column technique (*13–16*). At SDS concentrations above the cmc these standard deviations are between 0.7% and 10%. Due to the fact that only the pure solid that remained on the chromosorb is analyzed instead of solute extracted from the water, the percentage of error of the experimental solubility data is not correlated to the order of magnitude of these data. If aqueous solubility data are based on analyses of the chemical that is extracted from the water, impurities do interfere more severely with solutes that have to be extracted from larger volumes of water, yielding higher inaccuracies for compounds possessing lower aqueous solubities. In Figure 2, the solubility of PCB 14, PCB 40, and PCB 128 is plotted as a function of the SDS concentration. As this figure illustrates, the enhancement of the solubility above the cmc depends linearly on the SDS concentration, indicating that this phenomenon is due indeed to the process of dissolving in the expanding hydrophobic micellar phase. This observation is in agreement with the results of other authors (*2–5*). From Table 2, it can be seen that even at SDS concentrations below the cmc a small but significant ($P < 0.01$) solubility enhancement occurs, a phenomenon that is also described by Kile and Chiou for DDT (log $K_{ow} = 6.19$) in solutions of non-ionics but not with SDS (*1*). This enhanced solubility below the cmc is probably due to the presence of surfactant monomers and to the hemimicelles sorbed to the chromosorb. Based on the surface area of the chromosorb present in the vials, the amount of SDS sorbed to the chromosorb in terms of hemimicelles in the solution at 1 mM SDS is expected to be less than 1% (*23*).

Table 3 shows the micelle/water partition coefficients for PCB 14, PCB 15, PCB 198, and PCB 209 as determined by eq 4. It can been seen that the log K_{mw} for these PCBs in solutions of 5 and 10 mM SDS are essentially equal. Differences in log K_{mw} between solutions of 5 and 10 mM SDS are in the same range or even smaller than their individual standard deviations. Standard deviations range from 0.03 to 0.14 log unit and differences between K_{mw} in 5 and 10 mM SDS are in the range of 0.01 to 0.1 log unit for the whole series of PCBs. Based on this criterium, the decision was made to select the mean log K_{mw} of both SDS concentrations. The values obtained are also listed in Table 3. Constant micelle/water partition coefficients over a wide range of micellar concentrations were also observed by Park and Jaffé (*6*). The only known data point in the range of log K_{ow} values of our PCBs is the log K_{mw} value of 5.38 of DDT from the work of Kile and Chiou (*1*). Their reported log K_{mw} value of 5.38 is 0.32 log unit smaller than the value of 5.70 as expected from our eq 5 with the log K_{ow} value of 6.19. In their paper no measure for the standard error is given, hence it is hard to say whether this difference is systematical or not (*1*).

The enhancement of the chemical solubility above the cmc is linearly dependent on the SDS concentration and can completely be explained by the enlarged solubility capacity of the expanding micellar volume. In addition, PCB activity coefficients in the micellar phase were calculated from their K_{mw} following eq 1 with the PCB activity coefficients at 1 mM SDS. Standard deviations of the activity coefficients in 5 and 10 mM SDS can completely be explained by the standard deviations in 1 mM SDS. The

TABLE 3

Experimental Micelle/Water Partition Coefficients (log K_{mw}) and Chemical Activity Coefficients (log γ) for Polychlorinated Biphenyls

IUPAC no.	log K_{mw} [a] 5 mM	log K_{mw} [a] 10 mM	log K_{mw} [b]	log $\gamma_{1.0}$ [a]	log $\gamma_{10.0}$ [a]
14	4.59 (± 0.03)	4.63 (± 0.03)	4.61 (± 0.03)	7.97 (± 0.02)	2.13 (± 0.02)
30	5.21 (± 0.05)	5.24 (± 0.05)	5.22 (± 0.05)	7.21 (± 0.04)	0.76 (± 0.04)
15	4.94 (± 0.14)	5.04 (± 0.11)	4.99 (± 0.12)	6.69 (± 0.08)	0.44 (± 0.08)
29	5.25 (± 0.05)	5.21 (± 0.04)	5.23 (± 0.04)	7.28 (± 0.09)	0.86 (± 0.09)
49	5.77 (± 0.05)	5.78 (± 0.05)	5.77 (± 0.05)	8.41 (± 0.07)	1.43 (± 0.07)
40	5.36 (± 0.06)	5.42 (± 0.06)	5.39 (± 0.06)	7.51 (± 0.06)	0.88 (± 0.06)
61	5.62 (± 0.05)	5.67 (± 0.04)	5.65 (± 0.04)	8.20 (± 0.07)	1.12 (± 0.07)
155	6.32 (± 0.05)	6.36 (± 0.04)	6.34 (± 0.04)	9.26 (± 0.07)	1.69 (± 0.07)
116	5.80 (± 0.04)	5.76 (± 0.03)	5.78 (± 0.04)	7.86 (± 0.11)	0.89 (± 0.11)
136	5.88 (± 0.09)	5.96 (± 0.09)	5.92 (± 0.09)	8.87 (± 0.07)	1.70 (± 0.07)
128	6.31 (± 0.03)	6.33 (± 0.03)	6.32 (± 0.03)	8.79 (± 0.09)	1.25 (± 0.09)
180	6.59 (± 0.11)	6.64 (± 0.11)	6.62 (± 0.11)	9.31 (± 0.09)	1.46 (± 0.09)
198	6.48 (± 0.09)	6.40 (± 0.09)	6.44 (± 0.09)	9.58 (± 0.07)	1.96 (± 0.07)
209	6.67 (± 0.09)	6.72 (± 0.09)	6.70 (± 0.09)	9.06 (± 0.07)	1.13 (± 0.07)

[a] Values and standard deviations (between parentheses) are for the mean of triplicate samples. [b] Values are the mean of log K_{mw} values in 5.0 and 10.0 mM SDS solutions. Standard deviations (between parentheses) are pooled from the individual samples.

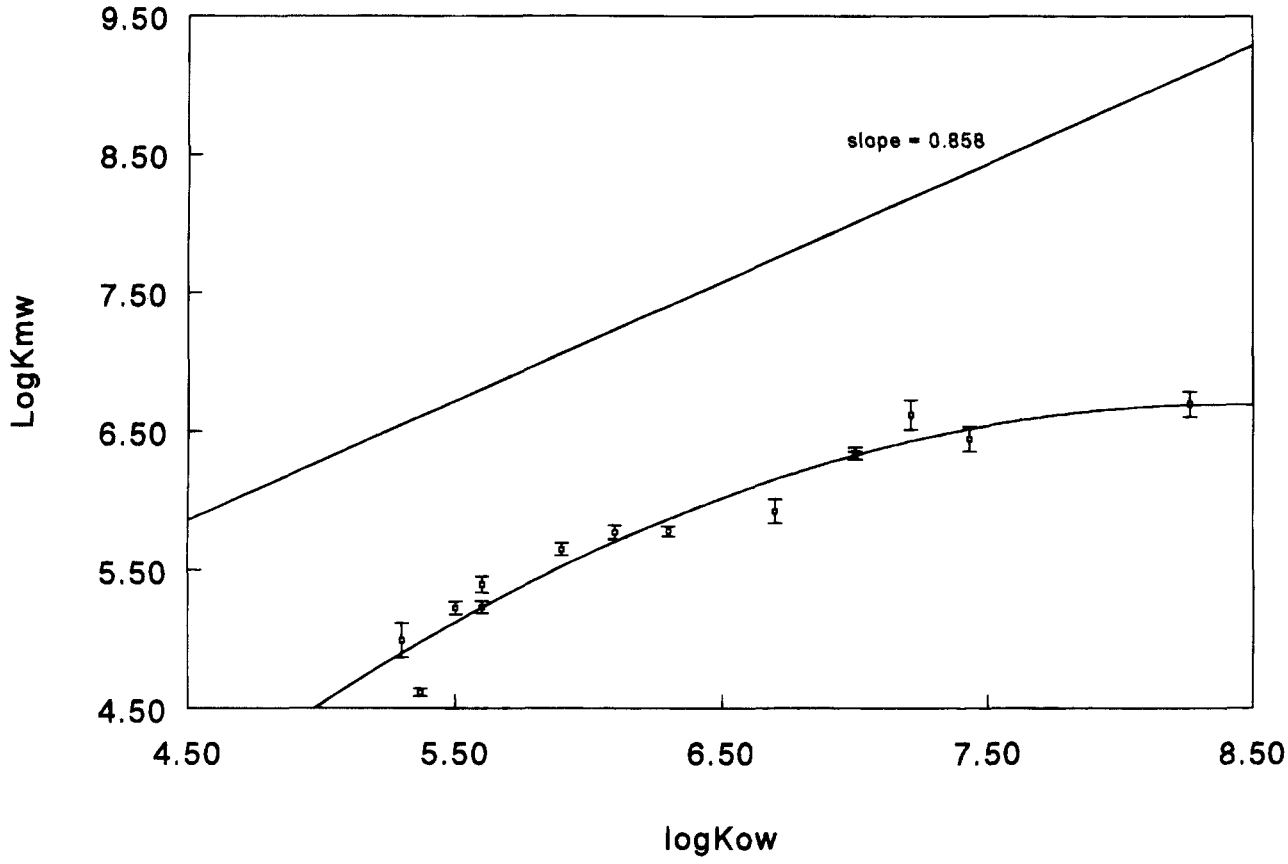

FIGURE 3. Relationship between the 1-octanol/water partition coefficient (log K_{ow}) and the SDS micelle/water partition coefficient (log K_{mw}). The straight line shows the slope of 0.858 of the linear relationship from the work of Edwards et al. and the work of Valsaraj and Thibodeaux (refs 2 and 4).

values of the activity coefficients are independent of micellar concentration, and PCB mole fractions in both aqueous and micellar phases remain small enough to allow activity coefficients to stay constant.

Log K_{mw} values were compared to the log K_{ow} data collected from the literature that are listed in Table 1. Data on log K_{ow} are selected by Mackay et al. (*15*) except for PCB 14, PCB 180, and PCB 198 that are obtained from RP-HPLC experiments by Brodsky and Ballschmiter (*24*). The best fit of the relationship between log K_{ow} and log K_{mw} of the PCBs used in this study with log K_{ow} values of 5–8.5 is a second-order polynomial as shown in Figure 3 and eq 5:

$$\log K_{mw} = -0.19\ (\pm 0.05) \log K_{ow}^2 + 3.12\ (\pm 0.78) \log K_{ow} - 6.45\ (\pm 2.53) \quad (5)$$

$$n = 14 \qquad r^2 = 0.94 \qquad \text{SER} = 0.17 \qquad F = 92$$

In Figure 3, a straight line with a slope of 0.858, similar to the relationship as demonstrated by Valsaraj and Thibodeaux (*4*) and Edwards et al. (*2*) in their studies in SDS is drawn to show the deviation between log K_{ow} and

log K_{mw} for the PCBs studied here. Above a log K_{ow} of about 5 this linear relation curves off. Applying a second-order polynomial improves both the standard error of regression and the regression coefficient. The breakdown of the linear relation between log K_{mw} and log K_{ow} at very high log K_{ow} values agrees with recent observations on the relatively low partitioning between water and artificial membranes and bioconcentration levels of extreme hydrophobics (*25–27*).

The observed nonlinearity of the relationship between log K_{ow} and log K_{mw} partly may be explained by the hydration of the polar headgroups of the SDS micelles and their polar pallisade layer (*1, 2*). The influence of the polar region by screening off the hydrophobic core will be stronger for the more hydrophobic chemicals. Another explanation may be the more structured nature of the micellar core in comparison to bulk solvents such as 1-octanol. Relatively more energy is required to form a cavity in more structured phases for larger and more hydrophobic molecules in comparison to smaller ones, and the gain in terms of entropy is less than in bulk solvents, resulting in lower partition coefficients and a loss of linearity between log K_{ow} and log K_{mw}. This explanation is supported by the results of Park and Jaffé that demonstrated relatively higher partitioning of non-ionic organics into micelles than in the more structured hemimicelles with increasing molecular size of the solute (*6*).

Conclusions

The method described here is an indirect one, based on the differences in PCB mass that is left behind on the chromosorb after exposure to solutions of SDS at different concentrations. Therefore, the error in the final results is an accumulation of the errors from the samples of the coated chromosorb, the chromosorb after aqueous exposure, and the chromosorb after exposure with the micellar solution. Still, the analyses themselves were so accurate that the final results show the same range of errors that is achieved with the well-established generator column technique for solubility measurements and the slow stirring technique for determining partition coefficients in well defined 1-octanol/water systems. An advantage of the method described in this study is that its accuracy is high, and many experiments can be conducted at the same time since no large equipment is required such as a generator column.

A proper understanding of the thermodynamics and mechanisms of partitioning of hydrophobics in micelle/water and membrane/water systems is decisive in the study of transport kinetics and fate of these compounds in environmental systems and living organisms. In our future work, we will try to elucidate this matter further.

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List of Symbols

K_{mw}	micelle/water partition coefficient
K_{ow}	1-octanol/water partition coefficient
C_m	compound concentration in the micellar phase
$C_{w(cmc)}$	compound concentration in the aqueous phase at the cmc
$\bar{V}_m$	molar volume of the micellar phase
$\bar{V}_w$	molar volume of the aqueous phase
V_m	volume of the micellar phase
V_w	volume of the aqueous phase
γ_m	compound chemical activity coefficient in the micellar phase
$\gamma_{w(cmc)}$	compound chemical activity coefficient in the aqueous phase at the cmc
M_{total}	total mass of the solute
$M_{w(0)}$	mass of the solute present in the aqueous phase before surfactant is added
$M_{p(0)}$	mass of the pure solute before surfactant is added
$M_{w(x)}$	mass of the solute present in the aqueous phase after the addition of surfactant
$M_{p(x)}$	mass of the pure solute after the addition of surfactant
M_m	mass of solute present in the micellar phase
$M_{p(cmc)}$	mass of the pure solute at the cmc
X	solute mole fraction
F	fugacity ratio
$S_{(0.0)}$	compound aqueous solubility
$S_{(cmc)}$	compound solubilty at the cmc

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