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# Study into the Equilibrium Mechanism between Water and Poly(dimethylsiloxane) for Very Apolar Solutes: Adsorption or Sorption?

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**Recently several publications appeared correlating octanol–water partitioning coefficients ( $K_{O/W}$ ) with solid-phase microextraction (SPME) extraction coefficients on poly(dimethylsiloxane) (PDMS) fibers. This correlation seems very good for medium–polar to polar compounds but cannot explain the observations for apolar compounds. It is shown that for polychlorinated biphenyls (PCBs) the published data are erroneous, because of system adsorption effects. PCB concentrations up to 10 times higher were measured on the stir bar compared to the SPME fiber. Using a short packed PDMS trap, it is shown that the true PDMS–water equilibrium constant is indeed proportional to literature  $K_{O/W}$  data.**

In solid-phase microextraction (SPME), knowledge of an accurate value for the equilibrium partitioning coefficients ( $K_{PDMS/W}$ ) of all compounds under investigation is most helpful. It would be very convenient if these coefficients could be directly deduced from octanol–water partitioning coefficients ( $K_{O/W}$ ), which are tabulated for numerous compounds.<sup>1</sup> In a number of publications,  $K_{PDMS/W}$  values have been correlated with  $K_{O/W}$  literature data.<sup>2,3,4</sup> It was found that over a certain range of compounds  $K_{O/W}$  and  $K_{PDMS/W}$  correlate very well, especially for low-molecular-weight analytes such as the BTXs (benzene, toluene, xylene, and related compounds).<sup>5,6</sup> This correlation should be very straightforward because the  $K_{O/W}$  value is a measure of analyte polarity; e.g., very apolar analytes have a very high  $K_{O/W}$  and are consequently almost exclusively present in the octanol phase. In the poly(dimethylsiloxane) (PDMS)–water equilibrium, the same mechanism occurs; very apolar analytes will partition virtually exclusively into the apolar PDMS phase and will thus consequently have a very high  $K_{PDMS/W}$  value.

Although this correlation seemed to hold for a wide range of solutes, for high-molecular-weight and very apolar solutes such as polyaromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs),<sup>7</sup> the correlation between  $K_{O/W}$  and  $K_{PDMS/W}$  was no longer valid. For PCBs it was found<sup>8</sup> that, with decreasing polarity (increasing  $K_{O/W}$  of a factor of  $4 \times 10^4$ ), the measured  $K_{PDMS/W}$  decreased by a factor of 40, which would mean a misprediction in  $K_{PDMS/W}$  of a factor  $2 \times 10^6$ . The authors explained their data by assuming surface adsorption on the PDMS fibers instead of bulk partitioning (sorption) and emphasized by comparison of data from two PDMS fibers (7 and 100  $\mu\text{m}$ ) the validity of this model. Despite their seemingly convincing results, we had serious doubts about this surface adsorption model and investigated the PDMS–water equilibrium of PCBs in more detail.

PCBs (and also PAHs) are among the compounds with the lowest water solubility<sup>9</sup> and are known to easily adsorb on glass or other surfaces (e.g., the stir bars used in SPME). We suspected this to be occurring in the experiments and data presented by Yang et al.<sup>8</sup> With increasing apolarity, compounds will adsorb more strongly on active surfaces and will increasingly be lost, which should explain the observed effect. It was already mentioned by Yang et al.<sup>8</sup> that the stir bars could not be reused since that causes contamination problems (by the adsorbed PCBs). Other surfaces accessible for PCB adsorption are the walls of the glass vial and the septum. Though these were deactivated glass and Teflon, respectively, this certainly cannot fully eliminate the adsorption of apolar solutes such as PCBs.

Recently, an alternative setup to SPME using cartridges packed with 100% PDMS particles for the extraction of compounds from water was presented.<sup>10</sup> The data using this approach were correlated with literature  $K_{O/W}$  data and good relationships were noted for a range of pesticides and PAHs. Only the highest molecular weight (6-ring) PAHs were found to perform poorly because of system adsorption effects caused by adsorption in the HPLC pump and tubing used to pump the sample through the cartridge. The PCBs, under investigation are even more apolar

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(1) Verschuere, K. *Handbook of Environmental Data on Organic Compounds*, van Nostrand Reinhold: New York, 1996.

(2) Dugay, J.; Miège, C.; Hennion, M.-C. *J. Chromatogr., A* **1998**, 795, 27.

(3) de Bruin, L. S.; Josephy, P. D.; Pawliszyn, J. B. *Anal. Chem.* **1998**, 70, 1986.

(4) Beltran, J.; Lopez, F. J.; Cepria, O.; Hernandez, F. *J. Chromatogr., A* **1998**, 808, 257.

(5) Arthur, C. L.; Pratt, K.; Motlagh, S.; Pawliszyn, J. B.; Belardi, R. L. *J. High Resolut. Chromatogr.* **1992**, 15, 741.

(6) Arthur, C. L.; Kilam, L. M.; Motlagh, S.; Lim, M.; Potter, D. W.; Pawliszyn, J. B. *J. Environ. Sci. Technol.* **1992**, 26, 979.

(7) Potter, D. W.; Pawliszyn, J. *J. Environ. Sci. Technol.* **1994**, 28, 298.

(8) Yang, Y.; Hawthorne, S. B.; Miller, D. J.; Liu, Y.; Lee, M. L. *Anal. Chem.* **1998**, 70, 1866.

(9) Erickson, M. D. *Analytical Chemistry of PCBs*, Butterworth Publishers: Newton, MA, 1986.

(10) Baltussen, E.; David, F.; Sandra, P.; Janssen, H.-G.; Cramers, C. A. *J. Chromatogr., A* **1998**, 805, 237.

Table 1. Ions Monitored for the Seven PCB Congeners<sup>a</sup>

compd	MS ion 1	MS ion 2	MS ion 3
PCB 28	259	261	287
PCB 52	291	293	319
PCB 101	291	293	319
PCB 118	327	329	353
PCB 138	327	329	353
PCB 153	361	365	389
PCB 180	395	397	399

<sup>a</sup> Systematic numbering according to Ballschmitter et al.<sup>11</sup>

than the six-ring PAHs and the system as it was described<sup>10</sup> will certainly not be directly applicable to the problem at hand. Instead of preparing a water sample containing the PCBs, which will result in adsorption problems, a small amount of PCB standard was injected with a syringe directly on the PDMS trap followed by pumping a certain volume of water through the trap. The analyte recovery as a function of sampled water volume allows one to determine the amount of analyte eluted out of the PDMS trap and thereby the  $K_{\text{PDMS/W}}$  constant. Since pure PDMS particles have too much retention for PCBs, fused-silica particles with different PDMS loadings were used. The SPME experiment of Yang et al.<sup>8</sup> was repeated, and not only the SPME fiber but also the stir bar were thermally desorbed.

## EXPERIMENTAL SECTION

**Test Solutions.** A mixture of seven PCBs (composition shown in Table 1) ranging from the trichloro- to heptachlorobiphenyls was obtained from NSI Environmental Solutions Inc. (Research Triangle Park, NC). This 10 ppm (ng/ $\mu\text{L}$ ) mixture in dichloromethane was diluted to 1 ppm for spiking of the packed PDMS traps. For SPME experiments, the standard was diluted to 0.1 ppm, and 5  $\mu\text{L}$  was used to spike 10 mL of bidistilled water to a concentration of 50 ppt.

**PDMS Traps.** For the work described in this report, it was impossible to use 100% PDMS particles since these exhibit too much retention for the high-molecular-weight PCBs. Instead of the pure PDMS phase, two GC stationary phases were used. These were either 5 or 20% PDMS coated on 100- $\mu\text{m}$  fused-silica beads (Restek, Bellefonte, PA). These two materials were packed in Optic-2 (Atas, Veldhoven, The Netherlands) liners with the following dimensions: length 81 mm; inner diameter 3 mm. A 50-mg sample of PDMS packing was placed on a glass frit positioned 15 mm from the bottom of the injector and was kept in place by a small plug of deactivated glass wool on top. The PDMS traps were conditioned up to 300 °C until no peaks are detected in blank chromatograms applying the positive chemical ionization (PCI)-selected ion monitoring (SIM) mode.

**Experimental Setup.** The experimental setup consists of an HP 6890/5973 GC/MSD system (Hewlett-Packard, Little Falls, DE). The MS was operated in the PCI mode using methane as reagent gas. The electron multiplier voltage was set at a value 200 V above that recommended by the autotune program. The mass-selective detector (MSD) was operated in the time-scheduled SIM mode using three ions/component. The GC was fitted with

a 25-m-long, 250- $\mu\text{m}$ -inner diameter column coated with a film of 0.25- $\mu\text{m}$  HP-5MS (Hewlett-Packard). The oven was programmed from 40 °C at 20 °C/min to 325 °C.

For desorption of the PDMS traps, an Optic-2 (Atas) programmable temperature vaporizing (PTV) injector was used. The initial temperature was 40 °C, which was kept for 0.1 min; subsequently the injector was programmed at 12 °C/s to 310 °C, which was kept for 10 min. The split vent was continuously open at a flow of 25 mL/min.

SPME fibers coated with 100- $\mu\text{m}$  PDMS (Supelco, Bellefonte, PA) were desorbed in a Gerstel CIS-4 PTV injector (Müllheim a/d Ruhr, Germany). The initial temperature was 40 °C, programmed to 325 °C at 12 °C/s. Desorption was done in the splitless mode with the valve closed for 1.5 min.

Teflon-coated stir bars were desorbed in a Gerstel TDS-2 thermodesorption instrument for 5 min at 300 °C under a helium flow of 200 mL/min. Thermally released analytes were splitlessly transferred to a cold trap kept at -150 °C and were re-injected onto the analytical column in the splitless mode.

**Analytical Procedure.** The short packed PDMS traps were used in the following way. First, the cartridges were spiked with 1  $\mu\text{L}$  of the 1 ppm standard to introduce 1 ng of the PCBs. Subsequently, the trap was briefly purged with air to remove the solvent (dichloromethane) after which a volume of water was sampled (up to 10 L) by means of a vacuum pump to simulate the sampling of an actual water sample. Drying of the trap was performed by flushing with nitrogen for 25 min at a flow of 500 mL/min. Recoveries were calculated relative to a 1- $\mu\text{L}$  direct injection.

SPME experiments were performed as outlined by Yang et al.<sup>8</sup> SPME fibers were desorbed directly into the PTV injector. The stir bars were first briefly dried with a piece of tissue paper and then put in an empty thermal desorption tube (4 mm i.d., 17.8 cm length, Gerstel) which was inserted into the thermodesorption instrument.

## RESULTS AND DISCUSSION

After establishing proper operation of the analytical instrumentation, recovery experiments were started with the PDMS traps. Sample volumes were between 25 mL and 10 L, which were loaded at a rate of 100 mL/min by means of a vacuum pump. Recovery of the analytes was calculated relative to a 1- $\mu\text{L}$  direct injection. The ions selected for time-scheduled SIM are listed in Table 1. Figure 1 shows the recovery of the seven PCBs from water as a function of the sampled volume for (A) the 5% PDMS material and (B) the 20% PDMS material. As is clear from this figure, at higher sample volumes, PCBs are increasingly lost because of breakthrough from the PDMS trap. In principle, the shape of this curve is that of an error function (integrated Gaussian peak) of which the center corresponds to the retention volume ( $V_r$ ), which in turn can be calculated to a  $K_{\text{PDMS/W}}$  value by the formula where  $V_r$  and  $V_{\text{PDMS}}$  are the retention volume and the

$$V_r = K_{\text{PDMS/W}} V_{\text{PDMS}} \quad \text{or} \quad K_{\text{PDMS/W}} = V_r / V_{\text{PDMS}}$$

volume of PDMS material in the trap, respectively.  $V_r$  was determined as the volume at which the recovery is exactly 50%. For clarity, 50 mg of the 5% PDMS material contains 2.5 mg of

(11) Ballschmitter, K.; Schafer, W.; Buchert, H. *Z. Anal. Chem.* **1987**, 326, 253.

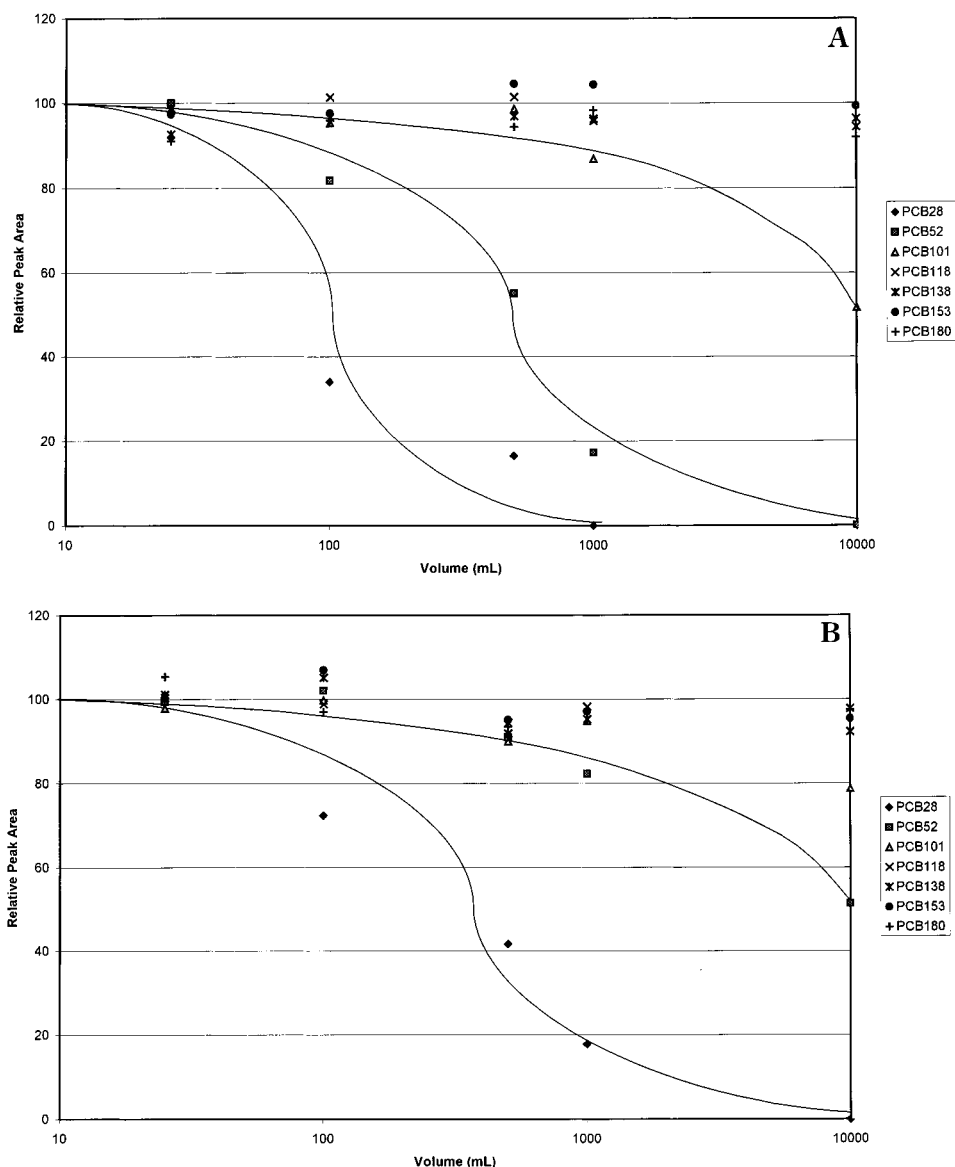


Figure 1. Recovery of the PCBs as a function of the sampled water volume. Trap was filled with 50 mg of 5% PDMS on fused silica. Amount of PCBs was 1 ng in all cases. B. Recovery of the PCBs as a function of the sampled water volume. Trap was filled with 50 mg of 20% PDMS on fused silica. Amount of PCBs was 1 ng in all cases.

Table 2. Experimentally Determined Retention Volumes and Calculated  $K_{\text{PDMS/W}}$  Values<sup>a</sup>

	5% PDMS on fused silica		20% PDMS on fused silica		literature data	
	$V_r$ (mL)	$K_{\text{PDMS/W}}$	$V_r$ (mL)	$K_{\text{PDMS/W}}$	$K_{\text{PDMS/W}}$ (SPME) <sup>7</sup>	$K_{\text{O/W}}$ <sup>1</sup>
PCB 28	79	$3.9 \times 10^4$	$3.9 \times 10^2$	$4.7 \times 10^4$	$8.7 \times 10^3$	$5.5 \times 10^5$
PCB 52	$5.7 \times 10^2$	$2.8 \times 10^5$	$1.0 \times 10^4$	$1.3 \times 10^5$	$7.3 \times 10^3$	$1.8 \times 10^6$
PCB 101	$1.0 \times 10^4$	$5.1 \times 10^6$	$>10^4$	$>10^6$	$3.8 \times 10^3$	$7.1 \times 10^6$
PCB 118	$>10^4$	$>10^7$	$>10^4$	$>10^6$	$3.3 \times 10^3$	$2.5 \times 10^6$
PCB 138	$>10^4$	$>10^7$	$>10^4$	$>10^6$	$2.3 \times 10^3$	$1.0 \times 10^7$
PCB 153	$>10^4$	$>10^7$	$>10^4$	$>10^6$	$2.5 \times 10^3$	$2.8 \times 10^7$
PCB 180	$>10^4$	$>10^7$	$>10^4$	$>10^6$	$8.7 \times 10^2$	

<sup>a</sup> Additionally  $K_{\text{O/W}}$  literature data are included

PDMS, which converts to (density 825 g/L) 2.06  $\mu\text{L}$ . A 50-mg sample of the 20% PDMS material contains 8.25  $\mu\text{L}$  of PDMS liquid phase. Table 2 shows the data calculated from Figure 1 and the resulting estimates for  $K_{\text{PDMS/W}}$ .

From Table 2 it can be deduced that calculated  $K_{\text{PDMS/W}}$  data are in good agreement between 5 and 20% PDMS. This is a first

(but strong) indication that PCB retention is a bulk, dissolution process (sorption) rather than a surface adsorption phenomenon. The  $K_{\text{PDMS/W}}$  values increase with increasing  $K_{\text{O/W}}$ , or in other words, more apolar analytes are partitioned more strongly into the (apolar) PDMS phase, which is exactly what is expected. Comparing these results with the  $K_{\text{PDMS/W}}$  data reported by Yang

Table 3. Recovery (%) of the PCBs from the SPME Experiments

compd <sup>11</sup>	SPME fiber	stir bar	total
PCB 28	16	40	56
PCB 52	18	52	70
PCB 101	16	57	73
PCB 118	5	83	88
PCB 138	9	59	68
PCB 153	9	80	89
PCB 180	8	75	83

et al.<sup>8</sup> (Table 2), a remarkable dissimilarity is noted. The data show a decrease of  $K_{\text{PDMS/W}}$  with increasing apolarity which is the opposite of that observed in our experiments. To find the cause of these differences, the SPME experiment was repeated analyzing not only the SPME fiber itself but also the Teflon stir bar.

Water samples (10 mL) were prepared as described in Test Solutions. SPME fibers were exposed to the water sample for 1 h under stirring at a speed of 1000 rpm. After this the fiber was retracted and desorbed in the PTV injector. The stir bar was dried and inserted into an empty thermal desorption tube, which was desorbed after completion of the SPME run. Table 3 lists the results of these analyses, and the recoveries on both the SPME fiber and on the stir bar expressed as the amount present relative to the totally introduced amount are given. From these data it is clear that a significant amount of PCBs is present on the stir bar.

In fact, all PCBs are present in higher amounts on the stir bar than on the SPME fiber. Additionally, it is clear that compounds with a high PCB number (more polar) are present in lower amounts on the SPME fiber than those with a lower PCB number (more polar), which is the same effect as observed by Yang et al.<sup>8</sup> This is, however, counteracted by the amount of PCB present on the stir bar so that the most apolar solutes are still extracted in the highest amount (overall). It has to be noted that, in addition to the stir bar and the SPME fiber, PCBs can also be present adsorbed on the glass wall. This was not investigated in this study.

## CONCLUSIONS

It is shown that published  $K_{\text{PDMS/W}}$  data are erroneous because of system adsorption effects. The data are biased by adsorption onto stir bars used in the SPME procedure and probably the glass vial. Ten times more compound can be present on stir bars than on the SPME fiber itself. Using a short packed PDMS trap, it was shown that the true PDMS–water equilibrium constant is indeed proportional to literature  $K_{\text{O/W}}$  data. It can be concluded that the water–PDMS contact is definitely a sorption mechanism instead of an adsorption effect.

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