

# Solid-phase microextraction fibre–water distribution constants of more hydrophobic organic compounds and their correlations with octanol–water partition coefficients

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## Abstract

Fibre coating–water distribution constants ( $K_{fw}$ ) of more hydrophobic chemicals were determined with six different solid-phase microextraction fibre types (including a polyoctylmethylsiloxane ( $C_8$ ) prototype) by fibre exposure to agitated large-volume water samples lasting several days. The results obtained are comparable with  $K_{fw}$  values obtained under dynamic conditions. Octanol–water partition coefficients ( $K_{ow}$ ) were measured with the mixture of distributing substances to examine  $\log K_{fw}$ – $\log K_{ow}$  relationships based on a consistent dataset.  $K_{fw}$  values obtained with liquid polymer fibre coatings correlate reasonably well with the hydrophobicity of the test compounds (with decreasing sensitivity in the following order: 7  $\mu$ m polydimethylsiloxane (PDMS) > 100  $\mu$ m PDMS >  $C_8$  > polyacrylate) whereas this is not the case with the PDMS–divinylbenzene (DVB) and Carbowax–DVB fibres, partially porous coatings which provide the highest  $K_{fw}$  values for all substances tested.

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## 1. Introduction

Solid-phase microextraction (SPME) is now widely used for preconcentration of organic micropollutants from water [1–3]. However, the extraction kinetics of more hydrophobic compounds seems to be very slow [4]. This makes optimization of SPME for these substances, especially the selection of a

suitable SPME fibre coating, an appropriate extraction time, and the sample agitation regime, difficult and time-consuming. When SPME is used for the estimation of octanol–water partition coefficients ( $K_{ow}$ ) [4,5] and bioavailable concentrations [6–9] of xenobiotics or for the study of their sorption processes to suspended particles, etc. [10–12], an incorrect determination of the fibre coating–water distribution constant ( $K_{fw}$ ) can lead to erroneous results. Published  $K_{fw}$  values are still incomplete or inconsistent. One can find, for example, for the hydrophobic 2,2',5,5'-tetrachlorobiphenyl  $K_{fw}$  values ranging from 3400 to 251 000 for fibres coated with 100  $\mu$ m

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polydimethylsiloxane [4,13–16]. These problems result partly from inappropriate experimental designs as discussed in several papers [17–22].

In continuing our former studies [4,23], we measured the long-term extraction time profiles of different groups of priority pollutants with six SPME fibre types, including a new polyoctylmethylsiloxane coating, and have calculated the  $K_{fw}$  values. We assumed that fibre exposure in a well-mixed water sample can yield results equivalent to those obtained under dynamic conditions in a more complicated flow-through system when two requirements are fulfilled. Firstly, it is necessary to prevent exhaustive extraction of analytes from the test solution. Therefore, a large sample volume must be used [17,18]. Secondly, a total mass balance for the analytes must be obtained which takes into account all possible losses of analytes due to adsorption and volatilisation. An additional important point, independent of the fibre exposure regime, is the choice of an appropriate method for the quantification of the absolute amounts of analytes extracted by the SPME fibre [24,25].

It has been found that the  $K_{fw}$  values for several fibre coatings correlate quite well with the hydrophobicity (i.e.  $K_{ow}$ ) of distributed analytes. Ref. [4] outlines the thermodynamic basis for such linear  $\log K_{fw}$ – $\log K_{ow}$  relationships and gives a summary of significant correlations for data sets reported before 1999. However, considerable uncertainties exist in the published  $K_{fw}$  and  $K_{ow}$  values of very hydrophobic substances (see, for example, the values for hexachlorobiphenyls to decachlorobiphenyl and for the higher condensed aromatic hydrocarbons listed unrated in Ref. [26] or the recent report [27] on the search for reliable  $K_{ow}$  data for hydrophobic organic compounds with DDT and DDE as a case study). Moreover, simultaneous distribution of several solutes between the contacting phases, which has been chosen as a more realistic and less time-consuming approach in our long-term SPME study, can cause differences compared to single-solute partitioning behaviour [28]. In order to be able to examine  $\log K_{fw}$ – $\log K_{ow}$  correlations based on a consistent dataset, we have determined  $K_{ow}$  values for our special solute mixture using the so-called slow-stirring method [29,30]. This technique has been validated recently in a ring test for more hydrophobic chemicals (with  $\log K_{ow}$  values ranging from 4.5 to 8.2 [31]).

## 2. Experimental

### 2.1. Materials

The following SPME fibre coatings were tested: 100  $\mu\text{m}$  polydimethylsiloxane (PDMS), 7  $\mu\text{m}$  PDMS, 85  $\mu\text{m}$  polyacrylate (PA), 65  $\mu\text{m}$  polydimethylsiloxane–divinylbenzene (PDMS–DVB), 65  $\mu\text{m}$  Carbowax–divinylbenzene (CW–DVB), and 65  $\mu\text{m}$  polyoctylmethylsiloxane ( $C_8$ ). All fibre assemblies (including the manual SPME holders) were purchased from Supelco (Taufkirchen, Germany) and were conditioned before use according to the manufacturer's instructions. In addition, new fibres were exposed for 1 h to vigorously stirred samples (5 ml) of double distilled water. In subsequent desorption/analysis steps, no compounds could be identified (blanks).

The test solutes included in the study are listed in Table 1 together with their abbreviated names, GC retention times, selected ions (for MS data acquisition) and their  $\log P^*$  values (i.e.  $K_{ow}$  recommended by the Medchem database [32]). The chemicals were obtained as neat substances from Sigma–Aldrich (Seelze, Germany), Promochem (Wesel, Germany) and Merck (Darmstadt, Germany). Three stock solutions of the test analytes were prepared gravimetrically in methanol. Aliquots of these stock solutions were used to spike the water samples (shortly before the start of the SPME experiments) by restricting the upper methanol concentration in the sample to 1% (v/v). The final aqueous concentration per test substance was adjusted between 100 and 200 ng/l, representing one-tenth of the solubility limit for the least soluble compounds (*p,p'*-DDD, BaP, PCB 153), and far below this limit for the others.

Methanol (for organic trace analysis), *n*-octanol (purity >99%), hexane and cyclohexane (for organic trace analysis), and nonane (“pro synthesis” grade) were obtained from Merck (Darmstadt, Germany). Double distilled water was prepared freshly before use from tap water by means of an automated laboratory distillation unit GFL 2102 (Gesellschaft für Labortechnik, Burgwedel, Germany).

### 2.2. SPME fibre exposure

A volume of 480 ml of a spiked water sample was filled into an Erlenmeyer flask. The remaining head-

Table 1

Test substances, their GC retention times, selected ions ( $m/z$ ) monitored in MS acquisition and  $\log P^*$  values (i.e.  $\log K_{ow}$  values recommended in Ref. [32])

Substance (abbreviated name)	$t_R$ (min)	$m/z$	Log $P^*$
1,2,3,4-Tetrachlorobenzene (TeCB)	14.28	216; 179	4.64
Pentachlorobenzene (PeCB)	17.13	250; 215	5.18
Hexachlorobenzene (HCB)	21.47	283.6; 142	5.73
$\alpha$ -Hexachlorocyclohexane ( $\alpha$ -HCH)	21.23	183; 219	3.80
$\beta$ -Hexachlorocyclohexane ( $\beta$ -HCH)	22.28	183; 219	3.78
$\gamma$ -Hexachlorocyclohexane ( $\gamma$ -HCH)	22.76	181; 219	3.72
$\delta$ -Hexachlorocyclohexane ( $\delta$ -HCH)	23.97	181; 219	4.14
1,1-Dichloro-2,2-bis( <i>p</i> -chlorophenyl)ethylene ( <i>p,p'</i> -DDE)	32.22	246; 176	6.96
1,1-Dichloro-2,2-bis( <i>p</i> -chlorophenyl)ethane ( <i>p,p'</i> -DDD)	34.17	165; 235	6.22
2,4,4'-Trichlorobiphenyl (PCB 28)	25.63	186; 258	5.62
2,2',5,5'-Tetrachlorobiphenyl (PCB 52)	26.97	220; 292	6.26
2,2',4,5,5'-Pentachlorobiphenyl (PCB 101)	30.94	326; 254	6.85
2,2',3,4,4',5'-Hexachlorobiphenyl (PCB 138)	35.99	360; 290	7.43
2,2',4,4',5,5'-Hexachlorobiphenyl (PCB 153)	34.74	360; 290	7.44
2,2',3,4,4',5,5'-Heptachlorobiphenyl (PCB180)	39.10	394; 324	8.14
Phenanthrene (PHE)	23.62	178; 152	4.47
Anthracene (ANT)	23.90	178; 152	4.45
Fluoranthene (FLU)	30.21	202; 150	5.16
Pyrene (PYR)	31.50	202; 150	4.88
Benzo[ <i>a</i> ]pyrene (BaP)	50.29	252; 224	6.13

For GC conditions, see Section 2.4.

space was only 1–2 ml. The sample was stirred with a glass-coated stir bar by magnetic stirrer M 3000 D (Heidolph, Kehlheim, Germany), adjusted to 600 rpm. The SPME fibre was injected via a septum inlet at the side wall of the flask and placed in the well-agitated region so that the flow pattern passed the fibre coating approximately perpendicularly to the fibre axis. The fibre holder was clamped to a ring stand during exposure. The sample was neither thermostated separately (room temperature:  $24 \pm 2$  °C) nor exposed to sunlight.

### 2.3. Octanol–water partitioning, sampling and sample processing

The slow-stirring experiments [29,30] were carried out according to the revised procedure recently validated as a new guideline of the Organisation for Economic Co-operation and Development (OECD) for testing of chemicals [31]. Briefly, 800 ml water (presaturated with octanol) was filled in a water-jacketed glass cell (thermostated to  $25.0 \pm 0.2$  °C) with a total volume of ca. 1 liter into which a PTFE-coated stir bar was placed. Then, 20 ml water-

saturated octanol (spiked with the test chemicals) was pipetted slowly against the upper wall of the vessel to form a shallow surface layer on the water phase. The stirring speed was adjusted to ca. 180 rpm with magnetic stirrer M 3000 D. The solutes were allowed to distribute between the two phases for 1 week. Afterwards, 1 ml of the octanol-rich phase was withdrawn from the opening at the top of the cell and 300 ml of the water-rich phase was taken from a stop-cock at the bottom of the vessel. The former sample was aliquoted and diluted 10- to 1000-fold with cyclohexane before analysis. The aqueous sample was extracted using 30 ml cyclohexane in a separation funnel. The extract was concentrated in the presence of 50  $\mu$ l nonane (as retaining agent) to a final volume of 0.2 ml by solvent evaporation under a nitrogen stream in a TurboVap II (Zymak, Idstein, Germany). The analytical recovery of this sample processing had been checked previously [31] and no significant losses were detected for the less volatile compounds considered here.

The octanol–water partitioning experiments were carried out in triplicate and the results were averaged using the reciprocal individual variances as weights.

## 2.4. Instrumental analysis

All analyses were carried out with an HP 5890 II gas chromatograph equipped with a split/splitless injector, a 7673 autosampler and a 5971 MS detector. The analytes desorbed from the SPME fibres and those injected directly afterwards as standard solutions in hexane (1  $\mu$ l) for calibration of the GC response were separated on a 60 m $\times$ 0.25 mm I.D. DB-5MS column coated with 0.25  $\mu$ m film (J&W Scientific, Folsom, CA, USA). The injector was programmed to return to split mode 2 min after insertion of the SPME fibre and 1 min after liquid injection. Helium was used as carrier gas with a constant column flow-rate of 0.65 ml/min. The injector temperature was held constant at 250  $^{\circ}$ C. The GC oven temperature program was: 60  $^{\circ}$ C for 2 min, 30  $^{\circ}$ C/min to 150  $^{\circ}$ C, then 4  $^{\circ}$ C/min to 280  $^{\circ}$ C, hold for 20 min. The transfer line temperature was 280  $^{\circ}$ C.

Samples from the octanol–water partitioning experiments were analysed by direct injection via the autosampler (1  $\mu$ l) in the same GC system using the aforementioned temperature program, except that the capillary column (of the same type) was only 30 m long. The retention times were approximately half those listed in Table 1.

## 2.5. Calculation of $K_{fw}$ values and their variance

For the determination of the absolute amounts extracted by the SPME fibres ( $m_f$ ), calibration curves must be generated for the GC response. We used direct liquid injection of analytes in hexane at 5–7 concentration levels (via the autosampler). When the GC peak areas versus mass injected shows good linearity and sensitivity, one can calculate  $m_f$  by inversion of the calibration functions for all analytes. In the calculation of the fibre coating–water distribution constant, it is necessary to account for the evaporated amount ( $m_h$ ) and the adsorbed amount ( $m_a$ ) of the test substance. The final equation for  $K_{fw}$  is:

$$K_{fw} = \frac{C_f^{\infty}}{C_w^{\infty}} = \frac{m_f/V_f}{(m_{w(0)} - m_f - m_h - m_a)/V_w} \quad (1)$$

where  $C^{\infty}$  values are the equilibrium concentrations in the respective phases and  $V$  values are the volumes

of the phases. The initial amount of substance [ $m_{w(0)}$ ] in the water sample is known from spiking and the extracted amount ( $m_f$ ) will be determined. The evaporated amount of analyte ( $m_h$ ) can be estimated using tabulated Henry's law constants if the headspace volume is known. For the actual set of test substances in the minimal headspace left, this fraction is negligible [4]. Quantification of the amount of substance adsorbed on the glass walls during fibre exposure ( $m_a$ ) is time-consuming. Thus, we treat it as an experimental uncertainty of the initial water concentration  $C_{w(0)}$ . With these assumptions, we obtain the following simplified equation for  $K_{fw}$ :

$$K_{fw} = \frac{m_f/V_f}{C_{w(0)} - m_f/V_w} \quad (2)$$

Using the law of error propagation, the following equation is obtained from Eq. (2) for the variance of  $K_{fw}$ ,  $s_K^2$ :

$$s_K^2 = \left( \frac{\partial K_{fw}}{\partial m_f} \cdot s_{m_f} \right)^2 + \left( \frac{\partial K_{fw}}{\partial V_f} \cdot s_{V_f} \right)^2 + \left( \frac{\partial K_{fw}}{\partial C_{w(0)}} \cdot s_{C_{w(0)}} \right)^2 + \left( \frac{\partial K_{fw}}{\partial V_w} \cdot s_{V_w} \right)^2 \quad (3)$$

We assumed the following realistic estimates for the standard deviation of the parameters describing the fibre geometry: 5  $\mu$ m for the diameter of the silica fibre without coating, 10  $\mu$ m for the O.D. of the fibre, 1 mm for the length of coated fibre tip. The error in  $V_w$  is set to 1 ml. For  $C_{w(0)}$ , the directly injected amount of analyte, and the peak areas after fibre desorption and calibration, we assumed a relative standard error of 5%.

## 3. Results and discussion

### 3.1. Extraction time profiles

The extraction time profiles are obtained in each case from seven experiments lasting for 1 h to 7 days. One can differentiate between fibres coated with a liquid stationary phase and those with a partially porous (i.e. DVB-blended) coating. With the former type of coatings, the HCH isomers, TeCB and PeCB and most of the polyaromatic hydrocarbons

(PAHs) reach their maximum amount extracted after 17–20 h of fibre exposure, whereas this takes about 3 days with the porous fibres. This delay indicates that substances must pass a longer diffusion pathway to the adsorbing sites due to the porous nature of the coating. In almost all cases, we found distinct maxima in the extraction time profiles. These are difficult to interpret because there are wider gaps between the data and they should be the object of a separate study.

### 3.2. Fibre–water distribution constants

The determined maxima in  $m_f$  were used for the calculation of  $K_{fw}$  values. We have chosen these maximum amounts because we cannot exclude analyte losses during longer experiments which may have caused the observed decrease in the extraction time profiles. The obtained distribution constants are summarized in Table 2. Their relative standard errors calculated according to Eq. (3) range from 10 to 15%. These are conservative estimates due to the

assumptions made for the standard deviations of the experimental parameters (cf. Section 2.5).

Comparisons of our results with  $K_{fw}$  data obtained by other researchers are possible for all fibres except for the  $C_8$  prototype. The available literature data can be rated in the following way: the values published by Yang et al. [14] and Valor et al. [13] as well as our former results [4] fall short by 1–2 orders of magnitude, at least for the substances with a  $\log K_{ow} > 5$ . The reasons for that are certainly the short equilibration times and/or the small sample volumes used in these batch experiments. Otherwise, the distribution constants determined in such batch SPME mode but with larger sample volumes [15,21] are comparable with those obtained under dynamic sampling conditions [16,20,22]. Our actual results fit these data quite well as shown in Fig. 1 for the 100  $\mu\text{m}$  PDMS fibre. Exceptions are only  $\delta$ -HCH ( $\log K_{ow} = 4.25$ ) and BaP ( $\log K_{ow} = 6.35$ ), for which we found approximately one order of magnitude lower  $K_{fw}$  values than expected.

In general, it can be concluded from Table 2 that

Table 2

Fibre coating–water distribution constants,  $K_{fw}$ , calculated according to Eq. (2) based on the maximum amount extracted ( $K_{fw}$  values are rounded to three digits; their relative standard errors are between 10 and 15%). The last column contains the octanol–water partition coefficients,  $K_{ow}$ , which have standard errors between 1 and 5%

Substance	$K_{fw}$						$K_{ow}$
	7 $\mu\text{m}$ PDMS	100 $\mu\text{m}$ PDMS	85 $\mu\text{m}$ PA	65 $\mu\text{m}$ $C_8$	65 $\mu\text{m}$ PDMS–DVB	65 $\mu\text{m}$ CW–DVB	
TeCB	1600	4030	14 200	5680	304 000	189 000	41 800
PeCB	8400	11 100	38 500	33 200	468 000	281 000	138 000
HCB	21 500	27 500	81 100	89 600	407 000	281 000	481 000
$\alpha$ -HCH	n.d.*	461	4540	917	120 000	253 100	7590
$\beta$ -HCH	n.d.	392	24 400	606	74 100	266 300	8100
$\gamma$ -HCH	n.d.	387	5300	1371	158 000	24 000	6760
$\delta$ -HCH	n.d.	106	4360	424	52 500	11 000	17 700
$p,p'$ -DDE	247 000	183 000	349 000	226 000	275 000	457 000	1 179 000
$p,p'$ -DDD	27 900	35 700	200 000	84 500	256 000	226 000	1 440 000
PCB 28	44 200	57 000	286 000	127 000	516 000	620 000	708 000
PCB 52	96 500	137 000	445 000	146 000	477 000	674 000	986 000
PCB 101	303 000	299 000	350 000	351 000	494 000	860 000	3 520 000
PCB 138	952 000	445 000	846 000	421 000	427 000	769 000	7 600 000
PCB 153	1 030 000	468 000	1 010 000	442 000	504 000	942 000	4 710 000
PCB 180	2 320 000	355 000	693 000	297 000	320 000	367 000	14 000 000
PHE	1780	2810	29 800	6130	275 000	238 000	48 800
ANT	1580	2880	28 200	6430	227 000	206 000	48 300
FLU	5280	6110	70 700	24 700	240 000	240 000	158 000
PYR	6370	6650	78 200	21 100	206 000	212 000	166 000
BaP	45 900	13 900	27 800	28 700	20 000	27 500	2 240 000

\*n.d., not determined, that means that the amount of analyte desorbed from the fibre was below LOQ and thus  $K_{fw}$  calculation was impossible.

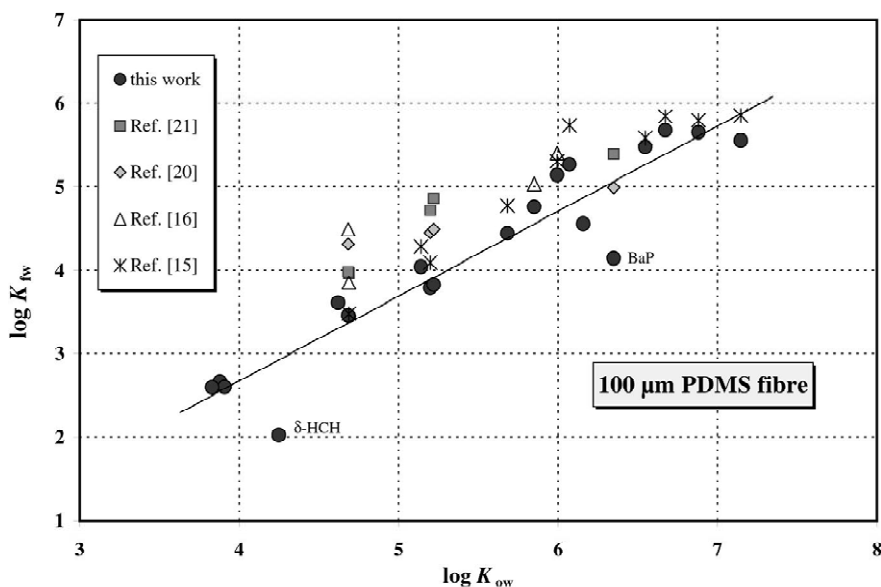


Fig. 1. Measured and selected reported  $\log K_{fw}$  with the 100  $\mu\text{m}$  polydimethylsiloxane fibre versus  $\log K_{ow}$  of the distributing substances (the regression line drawn is based on the actual measured values only).

the partially porous fibres PDMS–DVB and CW–DVB yield the highest  $K_{fw}$  values for all substance groups investigated. This finding is especially pro-

nounced for the chlorobenzenes, the HCH isomers (in some cases with the exception of  $\delta$ -HCH) and the PAHs (except for BaP). For the PCBs, we did not obtain such drastic differences. This fact can perhaps be associated with their higher lipophilicity which may primarily influence the fibre–water distribution with the liquid-type coatings (see the following section).

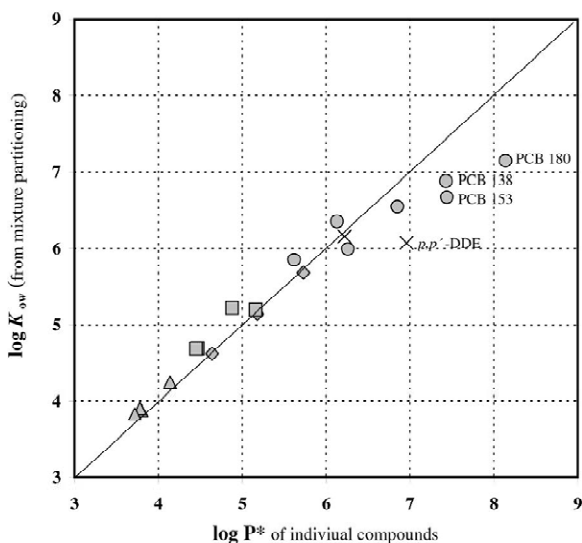


Fig. 2. Experimentally determined octanol–water partition coefficients of the test compounds (determined after mixture partitioning) versus their  $\log P^*$  values (i.e. the  $\log K_{ow}$  recommended for the individual compounds taken from Ref. [32]). Symbols: triangle, HCHs; square, PAHs; circle, PCBs; diamond, chlorobenzenes; cross, DDD and DDE.

### 3.3. Correlation of $K_{fw}$ values with the hydrophobicity of the distributing substances

The octanol–water partition coefficients determined from a mixture using the slow-stirring procedure (cf. Section 2.3) are in most cases comparable with the  $K_{ow}$  values for the individual compounds as can be seen in Fig. 2. A substantial decrease in  $K_{ow}$  values obtained from mixture experiments was found only for  $p,p'$ -DDE and three higher chlorinated PCBs. An explanation for this discrepancy could be cosolute effects, which might affect the activities of the solutes in the water phase to a different extent [28].

In the following regression analysis, we used the  $K_{ow}$  values determined from the mixture whereby we did not exclude single points, i.e.  $\delta$ -HCH or BaP, from the dataset. The parameters of the linear log

Table 3  
Linear relationships  $\log K_{fw} = A + B \log K_{ow}$  values

Fibre type	A	B	r
7 $\mu\text{m}$ PDMS	-2.6098	1.2394	0.9643
100 $\mu\text{m}$ PDMS	-1.4012	1.0177	0.9436
85 $\mu\text{m}$ PA	1.3308	0.6501	0.8968
65 $\mu\text{m}$ C <sub>8</sub>	-0.4353	0.8922	0.9421
65 $\mu\text{m}$ PDMS–DVB	Not significant	Not significant	0.3917
65 $\mu\text{m}$ CW–DVB	3.0552	0.4058	0.7148

$K_{fw}$ – $\log K_{ow}$  relationships (based on our actual data only) are given in Table 3. Relatively strong correlations are obtained for the liquid-type coatings. The sensitivity of  $\log K_{fw}$  with respect to the hydrophobicity of the distributing substances decreases in the following order: 7  $\mu\text{m}$  PDMS > 100  $\mu\text{m}$  PDMS > C<sub>8</sub> > PA. Comparable relationships with PAHs and/or chlorobenzenes and PCBs have already been published for the 100  $\mu\text{m}$  PDMS and the PA fibre [15,21]. A close inspection of the actual data indicates, in some cases, a progressive deviation in the upper range of the data points. Similar effects have been noticed by Dong and Chang [21]. Future investigations should clarify whether these are measurement artefacts or of fundamental nature, for example, in terms of a loss of the presumed linearity in the relationship between the compound's activity coefficient in the polymeric fibre coating and the water-saturated octanol phase [4].

A very poor correlation was found for the porous CW–DVB fibre; the PDMS–DVB data do not correlate with  $\log K_{ow}$ . We tend to assign these findings to the fact that here the accessibility of the adsorbing sites for the solute molecules in the pores of the coating is the controlling factor for the distribution behavior, rather than the hydrophobicity. But this is another challenging task which makes it necessary to determine the porosity and specific internal surface area of the coating and, most critically, the molecular surface area occupied per analyte molecule in this competitive adsorption process.

#### 4. Conclusions

Our results demonstrate that determination of fibre–water distribution constants of more hydrophobic substances is feasible by the SPME fibres exposed to a well-mixed and large-volume water

sample, for 1 day (for compounds with  $\log K_{ow} < 5$ ) or 3 days (for substances with  $\log K_{ow} > 5$ ). A more detailed interpretation of the observed maxima in the extracted amount requires recording of the extraction time profiles in shorter time intervals, additional experiments under varied hydrodynamic conditions, quantification of adsorption losses onto the glass walls and knowledge of relevant substance- and coating-specific properties (diffusivities, porosity, etc.).

The C<sub>8</sub> fibre prototype tested did not provide any advantage over the commercially available liquid polymer coatings, either with respect to the extraction efficiency or the correlation of  $K_{fw}$  with hydrophobicity. In this regard, we have thus revised the conclusions drawn in our former work [4].

When  $K_{fw}$  measurements are used for indirect determination of  $K_{ow}$  values, care must be taken in the extreme hydrophobicity range due to the possible loss of linearity in the  $\log K_{fw}$ – $\log K_{ow}$  relationship and the uncertainties in the reference  $K_{ow}$  values or the deviations resulting from differences between single- and multicomponent partitioning behavior.

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