Solid-phase microextraction of volatile organic compounds Estimation of the sorption equilibrium from the Kováts index, effect of salinity and humic acids and the study of the kinetics by the development of an "agitated/static layer" model

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Abstract

The sorption equilibrium and kinetics of 11 chlorinated C_1- and C_2-hydrocarbons and monocyclic aromatic hydrocarbons on the poly(dimethylsiloxane) solid-phase microextraction coating was studied. A linear regression between the logarithm of the partitioning coefficients, corrected by Henry's law constant, and the Kováts indexes on a 100% poly(dimethylsiloxane) GC stationary phase was shown ($r=0.997$, $n=11$). The effect of salinity in artificial seawater on the sorption equilibrium was studied and compared to the salt effect on the solubility and on the air–water equilibrium partitioning. The effect of humic acids on the equilibrium partitioning in SPME was examined and compared to predictions from mass balances estimating the importance of the mass sorbed on the humic acid fraction. Kinetics of the mass transfer of the volatile organic compounds from the stirred aqueous phase into the organic phase were investigated. Equilibration times, i.e., the time at which 95% of the final sorbed mass is preconcentrated, varied between 0.77 (1,2-dichloroethane) and 35.0 min (tetrachloroethylene). These equilibration times were linearly related to the partitioning coefficients ($r=0.993$, $n=11$). A new model was developed in order to simulate the sorption process. In the model an agitated water body and an aqueous static layer at the water–polymer interface were considered. It was assumed that the mass transfer was limited by Fickian diffusion in the aqueous static layer and in the organic phase. Experimental results confirmed this approach and revealed a static water layer with a thickness between 3.0 and 5.5 μm for benzene, trichloroethylene and tetrachloromethane, indicating that the aqueous static layer is dependent on the sorption equilibrium coefficient.

Keywords: Extraction methods; Sorption equilibrium; Retention indices; Partition coefficients; Kinetic studies; Volatile organic compounds; Hydrocarbons; Humic acids

1. Introduction

The solid-phase microextraction (SPME) preconcentration technique is a method which is used to preconcentrate volatile organic compounds (VOCs)

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out of aqueous matrices [1–12]. Applications of solid-phase microextraction for liquid–(bounded) liquid extraction as well as for the headspace [7,9] is described. Briefly the SPME apparatus consists of a polymer coating on a fiber which is mounted on a syringe needle. In the procedure the analytes are allowed to diffuse into the bounded organic phase.

Subsequently they are thermally desorbed from the coating in a GC injector. Advantages are the absence of solvents, the simplicity, the low cost and the relative rapidity of the technique [13,14].

Some studies reported deal with applications of SPME in specific matrices like groundwater [3], air [6,8,10] or foods [15]. However, less information on the basic physicochemical background of the extraction is provided, i.e., on the sorption equilibrium and kinetics of the compounds into the organic phase. Usually equilibration times are approximated empirically from a plot of the extracted mass as a function of the exposure time [2–5,11,12]. Modelling of the process based on a physicochemical approach was done by Louch et al. [4] for direct liquid–liquid SPME extraction.

Louch et al. [4] developed two models in order to describe the sorption kinetics. Under unstirred conditions the "unagitated model" was based on a Fickian diffusion process both in the water phase and in the organic phase. Results from this approach fitted the experimental sorption profile very well. In practice however, stirring of the liquid is the preferred technique in order to accelerate the process. Therefore, Louch et al. [4] developed the "agitated" model. It was based on a perfectly mixed water body so that the process was only limited by Fickian diffusion in the organic phase. The experimental equilibration times were several times longer than the theoretical values so that it was concluded that the solution was not fully agitated to ensure that the sorption process was limited only by mass transport through the polymer.

In the present work the sorption of 11 chlorinated C_1- and C_2-hydrocarbons (CHCs) and monocyclic aromatic hydrocarbons (MAHs) out of water samples on the SPME stationary phase was studied. Equilibrium partitioning coefficients were determined and a relation with the Kováts indexes was examined. The effect of humic acids and artificial sea salt were evaluated. The salt effect on SPME was compared to the salt effect on solubility of organic compounds and on the gas–water equilibrium partitioning.

Next to the equilibrium partitioning, the kinetics of the sorption of the VOCs on the SPME coating were examined. A model based on an agitated aqueous zone and an aqueous static layer, adjacent to the SPME polymer, was developed in order to explain the experimental results.

2. Experimental

The CHCs chloroform, 1,1-dichloroethane, 1,2-dichloroethane, 1,1,1-trichloroethane, trichloroethylene (Janssen) and tetrachloroethylene (Merck) and the MAHs benzene, toluene (Merck), ethylbenzene and o-xylene (Aldrich) were used in the experiments without any preceding purification. Stock solutions were prepared by injection of 5 μl of each compound into 5 ml methanol (Merck, for chromatography, 99.8%).

In order to calibrate the SPME samples a mixture of the compounds was prepared in dichloromethane (Merck, for chromatography, 99.8%) at concentrations of 100 μl l^{-1}. Kováts indexes were determined by means of a 0.1% standard of C_5- to C_{18}-alkanes in CS_2. A water solution containing 1 μl ml^{-1} of this standard was prepared for extraction by SPME.

Artificial sea water was prepared from deionized water and artificial sea salt (Marine Sea Salt HW, Wiegandt, Germany). Solutions of 1.0%, 3.5%, 5.0% and 10.0% (w/w) were prepared by dissolving an appropriate amount of salt in 250 ml deionized water. The main elements of the salt were chlorine (54.93%), sodium (30.53%), sulphate (7.67%), magnesium (3.68%), calcium (1.18%) and potassium (1.11%).

The humic acids in the experiments were obtained from Aldrich (H 1675-2). Solutions of 20, 100 and 500 mg l^{-1} were prepared in deionized water.

The SPME fiber coated with 100 μm of poly(dimethylsiloxane) (1 cm length) was obtained from Supelco. The inner diameter (110 μm) and the film thickness (100 μm) were measured by means of fluorescence microscopy. Before the extraction it was conditioned at 220°C during 10 min in a GC injector. The SPME organic phase was exposed to aqueous solutions (38.7 ml) in 40 ml cylindrical vials (inner diameter 2.5 cm), sealed by screw caps with PTFE/silicone septa (Supelco). The solutions were stirred by a magnetic stirring bar and a magnetic stirrer (IKA-Combimag RET, Janke and Kunkel) at 700 rpm.

The GC analyses of the VOCs preconcentrated on the SPME stationary phase, were carried out on a Varian gas chromatograph Model 3700, equipped with a flame ionization detector and a HP 3388A integrator. Injector temperature and detector temperature were 160°C and 220°C, respectively. The

carrier gas was helium (flow-rate 4.3 ml min^{-1}, inlet pressure 103 kPa). The detector was fed by air at 285 ml min^{-1} and H$_2$-gas at 33.8 ml min^{-1}. The compounds were separated on a 30 m×0.53 mm I.D. DB-1 capillary column (film thickness 5 μm, J and W Scientific). During the analysis the GC oven was kept at 40°C during 5 min and heated up to 150°C at a rate of 5°C min^{-1}. Kováts indexes were measured at 60°C (injector temperature 220°C).

Liquid solutions were analysed on the same GC system. Volumes of 1 μl were injected at 220°C. The GC oven temperature was kept at 24°C (by means of liquid nitrogen) during 17 min and the temperature was raised at a rate of 4°C min^{-1} up to 140°C and held for 2 min at this temperature.

In order to simulate the sorption kinetics of the VOCs on the SPME polymer a Microsoft FORTRAN Optimizing Compiler (version 5.00) was used.

3. Results and discussion

3.1. Sorption equilibrium of the VOCs on the SPME polymer

3.1.1. Experimental results

The partitioning coefficient K of 11 VOCs between the SPME polymer and (deionized) water was determined after a 45 min extraction time. The partitioning coefficient K was calculated from

$$K = \frac{RA}{VC_w} \qquad (1)$$

where K is the SPME organic phase–water equilibrium partitioning coefficient (dimensionless), C_w the concentration in the water phase (ng ml^{-1}), A the number of area units of the VOC in the GC analysis of the SPME coating (area unit), R the response factor for the VOC of the GC-detector [ng(area unit)$^{-1}$] and V the volume of the SPME organic phase (0.00066 ml). The results are given in Table 1. The aqueous concentrations of the VOCs at equilibrium were assumed to be equal to the initial concentrations because it was proven by the calculation of the mass balance that the aqueous concentration do not change substantially by the fraction sorbed on the stationary phase [equilibrium concentrations be-

Table 1
Experimental K values, relative deviations on K in % (R.S.D.%) ($n = 3$), Kováts retention indexes (I_k) ($n = 2$) and Henry's law constant (H)

VOC	K (–)	R.S.D.% on K	I_k	H^a
Chloroform	33±1	3.7	605.5±1.2	0.119
Tetrachloromethane	342±22	6.5	659.7±1.3	0.836
1,1-Dichloroethane	33±1	4.1	560.4±1.4	0.158
1,2-Dichloroethane	12±1	5.8	630.2±1.4	0.0334
1,1,1-Trichloroethane	207±12	5.5	638.9±1.3	0.480
Trichloroethylene	166±11	6.2	691.3±1.2	0.265
Tetrachloroethylene	841±59	9.4	803.3±1.2	0.450
Benzene	73±3	4.3	654.5±1.3	0.158
Toluene	225±12	5.2	758.1±1.2	0.179
Ethylbenzene	659±41	7.5	850.1±1.3	0.205
o-Xylene	543±36	7.3	880.2±1.2	0.130

The standard deviations on K values are calculated according to Eq. (3).
^{a} H (dimensionless) calculated from $\ln(H) = a \cdot T^{-1} + b$, where T is the absolute temperature (293 K) and a and b are obtained from Ref. [17].

tween 98.6% (tetrachloroethylene) and 99.8% (1,2-dichloroethane) of the initial concentration, depending on K].

The variance on the experimentally determined value for K is dependent on the variances on R, A, V and C_w:

$$\sigma^2(K) = \left(\frac{\partial K}{\partial R}\right)^2 \cdot \sigma^2(R) + \left(\frac{\partial K}{\partial A}\right)^2 \cdot \sigma^2(A)$$
$$+ \left(\frac{\partial K}{\partial V}\right)^2 \cdot \sigma^2(V) + \left(\frac{\partial K}{\partial C_w}\right)^2 \cdot \sigma^2(C_w) \quad (2)$$

The contributions to the variance of the preparation of the aqueous solution (C_w) (relative standard deviation ≤1%) can be neglected in comparison to the contribution to the variance of the gas chromatographic determination [relative standard deviation between 1.5 and 5.7% for R ($n = 5$) and between 5.0 and 8.3% for A ($n = 3$). And since V is constant, the latter equation can be written as

$$\sigma^2(K) = \left(\frac{\partial K}{\partial R}\right)^2 \cdot \sigma^2(R) + \left(\frac{\partial K}{\partial A}\right)^2 \cdot \sigma^2(A) \qquad (3)$$

From the data on $\sigma(R)$ and on $\sigma(A)$ together with the calculation of the partial derivatives, the standard deviations on K are calculated and presented in Table 1.

In the literature, K values are found for the CHCs

chloroform, tetrachloromethane, 1,1,1-trichloro-ethane and trichloroethylene. Chai and Pawliszyn [10] determined stationary phase–gas phase equilibrium partitioning constants so that their obtained values have to be corrected by the Henry's law constants provided in Table 1 in order to compare them with the results presented here. For chloroform values of 47.5 [10] and 398 [6] are mentioned, for tetrachloromethane 1052 [10] and 1000 [6], for 1,1,1-trichloroethane 303 [10] and 2512 [6] and for trichloroethylene 1259 [6]. It can be seen that the K values determined in this study are generally lower than the literature data. However, the data are limited and the scatter on the literature data is large, as can be seen for chloroform and 1,1,1-trichloroethane.

The same observation is found for the MAHs. K values for benzene in the literature are 125 [4], 126 [3], 199 [10] and 200 [5], and for toluene 294 [4], 340 [3], 357 [10] and 759 [5]. Also, the data of Chai and Pawliszyn [10] are calculated from the stationary phase–gas phase equilibrium partitioning constants. For ethylbenzene partitioning coefficients of 528 [3] and 2138 [5] and for o-xylene coefficients of 654 [4] and 1820 [5] are mentioned.

3.1.2. Relation between the partitioning coefficients and the Kováts indexes

The SPME organic phase in our experiments is poly(dimethylsiloxane). Since this type of polymer is also used as a stationary phase in GC, a relationship between the experimental K values and the retention of the VOCs on this type of stationary phase was examined.

In isothermal GC the logarithm of the stationary phase–gas phase equilibrium distribution constant K_g (dimensionless) is linearly related to the Kováts index I_k [16]:

$$\ln K_g \sim I_k \qquad (4)$$

If in SPME the K values are divided by the Henry's law constant (H, dimensionless), the new parameter K/H expresses the equilibrium between the organic phase and air. Since the free energy of a VOC in the gaseous phase can be assumed to be independent of the bulk gas, whether it is air or helium, then both parameters K/H and K_g are similar organic phase–gas phase equilibrium distribution

constants so that a linear relationship between the logarithm of K/H and I_k can be expected:

$$\ln(K/H) = aI_k + b \qquad (5)$$

For all compounds the Kováts index was determined experimentally (Table 1). The Henry's law constant was calculated at 20°C from the relation between H and the absolute temperature given by Dewulf et al. [17] (Table 1). The linear regression between ln (K/H) and I_k showed a slope and an intercept of 0.00975 and −0.2477, respectively. A correlation coefficient of 0.997 was observed ($n = 11$). A plot of the experimental results and the regression line are given in Fig. 1.

In conclusion, the relationship between the equilibrium partitioning coefficients in SPME and the Kováts indexes allows the estimation of the partitioning coefficients K in SPME from the retention indexes in GC.

3.1.3. Effects of salinity and humic acids on the sorption equilibrium

Salinity

The partitioning coefficients were determined for salt water concentrations with salinities of 0, 1, 3.5 (= sea water concentration), 5 and 10% (w/w). In Table 2 the experimental K_{salt} values are given and compared to the K values for deionized water. It can be seen that the partitioning coefficients increased by a factor of 1.66 (1,2-dichloroethane) to 2.01 (1,1,1-trichloroethane) at salt concentrations of 10%.

The salt effect on the equilibrium partitioning expressed by a factor of increase is mentioned for sodium chloride solutions by Arthur and Pawliszyn [1] and by Page and Lacroix [15]. At a salt concentration of 10.19% Arthur and Pawliszyn [2] found a factor of increase of 2.15, 4.04 and 3.07 for 1,1,1-trichloroethane, trichloroethylene and tetrachloroethylene, respectively. The factor for 1,1,1-trichloroethane is close to the factor determined in our study at a salinity of 10.0%. Page and Lacroix [15] determined the factors at NaCl saturation for a series of CHCs, including 1,1,1-trichloroethane (3.64), trichloroethylene (4.53) and tetrachloroethylene (2.27). This latter factor of increase is even lower than the factor at a salinity of 10.19% (3.07),
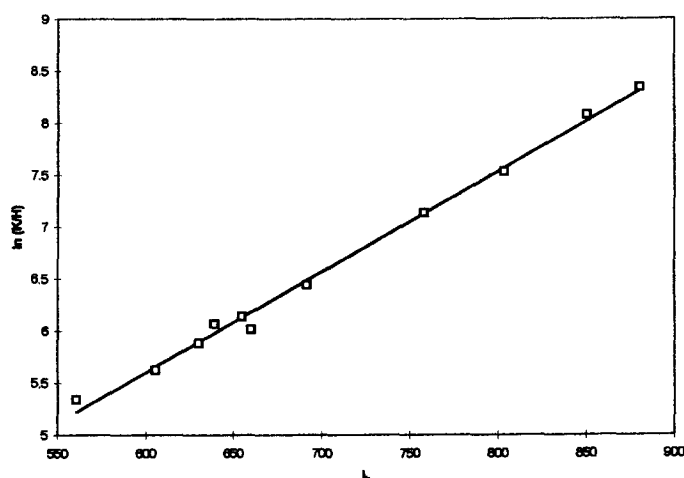
Fig. 1. Plot illustrating the relation between the partitioning coefficient K and the Kováts index I_k. H is Henry's law constant.

mentioned by Arthur and Pawliszyn [1]. In conclusion, the literature data do not agree on the magnitude of the salt effect in SPME.

When the thermodynamical background of the effect of salinity on the equilibrium partitioning is considered, a relation with the effect of salinity on the solubility can be assumed. The decrease in solubility of an organic compound is explained by the Setschenow constant or salting out constant [18]:

$$\log C^{sat}_{w,salt} = \log C^{sat}_{w} - K^{s}[salt] \qquad (6)$$

where $C^{sat}_{w,salt}$ and C^{sat}_{w} are the concentrations at

saturation of the VOCs in water without and with a salt addition, K^{s} is the Setschenow constant (1 mol^{-1}) and [salt] is the salinity in mol l^{-1}. The heat of solution affects the sorption equilibrium constant K in a same way as it affects the solubility so that a linear relationship between K_{salt} and the salt concentration is expected:

$$\log K_{salt} = \log K + K^{s'}[salt] \qquad (7)$$

From the composition of the artificial sea salt, the salinity was calculated as 0.158 mol l^{-1} for a 1% concentration. The results of the linear regression

Table 2
Relative factors of increase of K at salinities of 0.0 (deionized water), 1.0, 3.5, 5.0 and 10.0%; salt effect constants ($K^{s'}$, in l mol^{-1}) and the regression coefficient (r) of the salt effect ($n = 5$)

VOC	0.0%	1.0%	3.5%	5.0%	10.0%	$K^{s'}$	r
Chloroform	1.00	1.08	1.16	1.44	1.73	0.153	0.976
Tetrachloromethane	1.00	1.07	1.24	1.41	1.96	0.185	0.999
1,1-Dichloroethane	1.00	1.06	1.21	1.41	1.83	0.169	0.995
1,2-Dichloroethane	1.00	1.10	1.17	1.41	1.66	0.138	0.975
1,1,1-Trichloroethane	1.00	1.09	1.24	1.48	2.01	0.192	0.995
Trichloroethylene	1.00	1.09	1.19	1.43	1.94	0.182	0.991
Tetrachloroethylene	1.00	1.05	1.09	1.40	1.69	0.150	0.962
Benzene	1.00	1.12	1.20	1.49	1.89	0.173	0.982
Toluene	1.00	1.15	1.21	1.56	2.04	0.192	0.977
Ethylbenzene	1.00	1.14	1.15	1.57	1.94	0.181	0.956
o-Xylene	1.00	1.16	1.18	1.6	2.00	0.187	0.960

between log K_{salt} and the salt concentration are presented in Table 2. Schwarzenbach et al. [18] reported Setschenow constants from the literature of 0.18 and 0.19 for benzene (NaCl solutions) and of 0.17 for toluene (sea water).

Another physicochemical equilibrium which is affected by the salinity is the air–water equilibrium partitioning [17,19]. A relation with the salinity was established similarly [17]. From the literature data at 25°C a salt effect constant is calculated as 0.19 and 0.20 l mol^{-1} for benzene and toluene, respectively. In conclusion, the data for benzene and toluene on the equilibirium partitioning in SPME, on the solubility and on the gas–water equilibirium partitioning indicate that these three processes are affected in a similar degree by the salt effect.

Humic acids

The effect of humic acids in the aqueous solution on the sorption equilibrium was examined at concentrations of 20, 100 and 500 mg l^{-1} of humic acids and compared to the sorption experiments with deionized water. The results (each value is the average of three measurements) are presented in Table 3. An *F*-test was carried out in order to investigate the influence of the humic acid concentrations on the equilibrium distribution constant. At 100 mg l^{-1} only tetrachloromethane showed a significant decrease (at 0.05 significance level),

whereas at 500 mg l^{-1} tetrachloromethane (92%), tetrachloroethylene (88%), toluene (95%), ethylbenzene (91%) and *o*-xylene (91%) showed a significant decrease. These compounds have log K_{ow} (K_{ow}, the octanol–water partitioning coefficient) above 2.69 (toluene) (see Table 3).

The effect of humic acids can be estimated from the mass balance:

$$M = C_w(V_w + V_h K_{ow} + V_s K) \qquad (8)$$

where M is the total mass in the vial, V_w, V_h and V_s are the volumes of water, humic acids and the SPME polymer, and K_{ow} the octanol–water partitioning coefficient. In this approach the humic acid–water equilibrium distribution constant is estimated by the K_{ow} distribution constant. For the experiments at concentrations of 500 mg l^{-1}, the calculated change in the mass sorbed relative to the experiment without humic acid addition is given in Table 3. The compounds for which the *F*-test revealed a significant difference, showed in the calculations changes of more than 5% for K. The other compounds with log K_{ow} data equal to or lower than 2.48 (1,1,1-trichloroethane), have changes for K below 3%.

Most environmental samples are not expected to have humic acid concentrations up to 500 mg l^{-1}. Therefore, it can be concluded that for the measurements of the VOCs in environmental samples the sorption equilibrium in SPME will not be affected

Table 3
Relative factor of increase of K at humic acid concentrations (C_H, in mg l^{-1}) of 0, 20, 100, 500 mg l^{-1}; expected relative factor of increase based on the mass balance (C_{calc}) and the logarithm of the octanol–water partitioning coefficient (log K_{ow}) applied in the mass balance

VOC	$C_H = 0$	$C_H = 20$	$C_H = 100$	$C_H = 500$	C_{calc}	log K_{ow}[a]
Chloroform	1.00	1.00	1.01	0.96	0.99	1.93
Tetrachloromethane	1.00	0.98	0.95[b]	0.92[b]	0.95	2.73
1,1-Dichloroethane	1.00	1.01	1.00	0.99	0.99	1.79
1,2-Dichloroethane	1.00	1.02	1.01	1.00	1.00	1.47
1,1,1-Trichloroethane	1.00	1.00	0.98	0.98	0.97	2.48
Trichloroethylene	1.00	0.97	1.02	1.01	0.97	2.42
Tetrachloroethylene	1.00	0.98	0.96	0.88[b]	0.93	2.88
Benzene	1.00	1.00	0.98	0.96	0.99	2.13
Toluene	1.00	1.00	0.98	0.95[b]	0.95	2.69
Ethylbenzene	1.00	1.00	0.98	0.91[b]	0.88	3.15
o-Xylene	1.00	1.01	0.98	0.91[b]	0.88	3.12

[a] Data from Refers. [18] and [20].
[b] Significant difference from the factor at $C_H = 0$ at a 0.05 significance level.

substantially by the presence of organic polymeric substances.

3.2. Sorption kinetics of the VOCs on the SPME polymer

3.2.1. Experimental results

For the 11 VOCs the amount sorbed on the SPME coating was measured as a function of the exposure time. The results are given in Table 4. It can be seen that for the compounds with lower sorption equilibrium constants the equilibrium is reached quickly. The sorption profile is of an exponential shape. If the mass sorbed is expressed relative to the mass sorbed after 45 min of exposure:

$$f = \frac{\text{mass sorbed at time } t}{\text{mass sorbed at 45 min}} \quad (9)$$

then f can be written as

$$f = a[1 - \exp(bt)] \quad (10)$$

where a and b are constants. These constants are estimated by nonlinear regression and are presented in Table 5, together with the correlation coefficients r. It can be seen that the regression coefficients vary between 0.966 (1,2-dichloroethane) and 0.999 (1,1,1-trichloroethane, benzene and toluene). For tetrachloromethane, trichloroethylene and benzene the experimental results and the regression curves are presented in Fig. 2.

Table 5
Regression coefficients a and b and correlation coefficient r of the empirical relation $f = a[1 - \exp(bt)]$, where f is the mass sorbed at time t relative to the mass sorbed at $t = 45$ min and $t =$ exposure time (min); and the time at which 95% of the final mass is sorbed (t 95%, min)

VOC	a	b	r	t 95%
Chloroform	0.993	−1.893	0.971	1.66
Tetrachloromethane	0.988	−0.185	0.998	17.6
1,1-Dichloroethane	1.022	−1.913	0.993	1.38
1,2-Dichloroethane	1.008	−3.702	0.966	0.77
1,1,1-Trichloroethane	0.995	−0.372	0.999	8.32
Trichloroethylene	1.001	−0.421	0.998	7.07
Tetrachloroethylene	1.012	−0.0796	0.997	35.0
Benzene	0.998	−0.970	0.999	3.13
Toluene	0.992	−0.328	0.999	9.63
Ethylbenzene	0.992	−0.104	0.997	30.3
o-Xylene	0.985	−0.121	0.998	27.4

It is clear that the equilibration time depends on the sorption equilibrium constant K. If the equilibration time is defined as the time at which 95% of the final concentration is reached:

$$t\,95\% = \frac{\ln(1 - 0.95/a)}{c} \quad (11)$$

then the t 95% values can be plotted as a function of K, as presented in Fig. 3. A linear relationship is found with a correlation coefficient of 0.993 ($n = 11$). The dependency of the equilibration time on the distribution constant is explained by a static water

Table 4
Sorbed masses (ng) of the VOCs on the SPME polymer at 0.5, 1.0, 5.0, 30.0 and 45.0 min of exposure time

| VOC	0.5	1.0	5.0	15.0	30.0	45.0
Chloroform	–	15.1	17.5	18.2	17.5	17.9
Tetrachloromethane	18.5	33.4	104	157	174	175
1,1-Dichloroethane	8.0	11.4	13.3	13.5	13.0	12.9
1,2-Dichloroethane	5.1	5.9	6.1	6.2	5.9	6.0
1,1,1-Trichloroethane	16.9	31.2	77.7	94.4	94.9	95.0
Trichloroethylene	18.0	32.2	75.7	90.2	89.4	89.0
Tetrachloroethylene	24.4	47.7	177	321	436	478
Benzene	8.9	14.4	22.7	23.4	23.1	23.2
Toluene	11.8	22.2	58.3	73.1	74.4	74.6
Ethylbenzene	12.8	25.1	90.2	155	197	208
o-Xylene	11.8	22.8	80.3	134	163	170
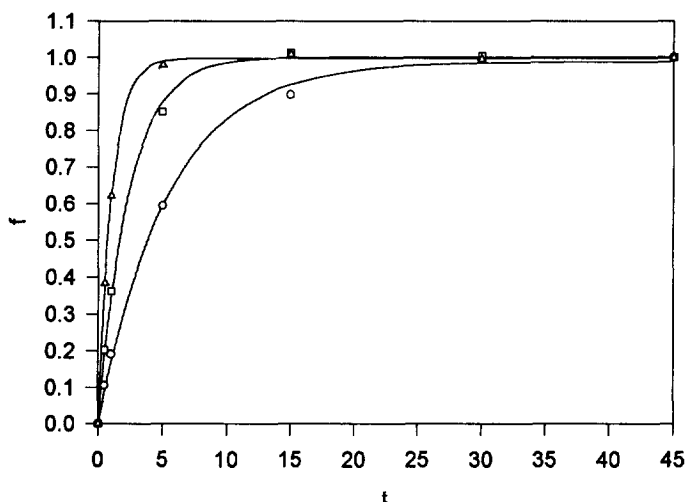
Fig. 2. Relative fraction sorbed in the organic phase as a function of the exposure time. Triangles, squares and circles are the experimental results for benzene, trichloroethylene and tetrachloromethane, respectively. The solid lines are the regression curves

layer next to the stationary phase [4]. For compounds with a higher K value a larger amount has to be transported into the polymer. The flux through the static water layer and the fiber is considered to be almost independent of K for VOCs so that the equilibrium time is longer for compounds with higher K values [4].

In the literature, equilibration times for CHCs of 5 (chloroform, tetrachloroethylene) to 15 min (tetra-chloromethane) [6] and between 4 and 6 min [11] are mentioned. When the data on the equilibration time of benzene are compared, times of 2 min (100 μm film thickness) [2,3] and 2.5 to 5 min (56 μm film thickness, time dependent on the stirring speed) [4] and of 14 min (100 μm film thickness) [5] are mentioned. In general, for the other MAHs longer
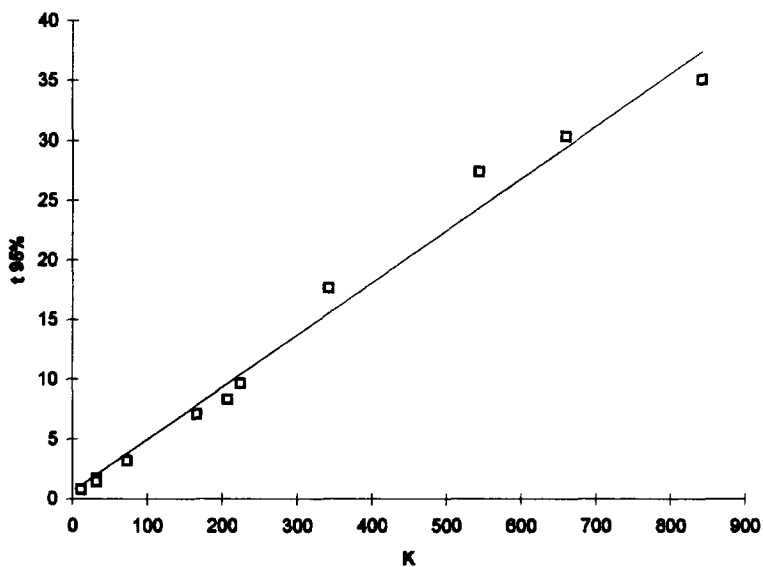

Fig. 3. Plot of the equilibration time (time at which 95% of the final sorbed mass is reached, t 95%) as a function of the equilibrium partitioning constant K.

equilibration times are needed [2,3]. It has to be emphasized that most equilibration time data in the literature are based on the graphical interpretation of the sorbed mass vs. exposure time plot so that the times at which 90 or 95% of the final mass sorbed are not exactly quantified.

3.2.2. Modelling

Approach

The sorption profiles observed in the previous section (Section 3.2) can be approached by a physicochemical interpretation of the sorption process. As discussed in the introduction, Louch et al. [4] developed two models. The authors suggested that the discrepancy between their "agitated" model and the experiments could be due to a static water layer surrounding the SPME coating. In this work a model was constructed which involves a mixed water body and a static zone.

Model equations and boundary conditions

The developed "agitated/static layer" model is presented in Fig. 4. The system is considered in cylindrical coordinates so that the central fused-silica fiber is located at radii between $r=0$ and $r=r_f$. The SPME stationary phase coated on this central fiber is located at radii between $r=r_f$ and $r=r_c$. The stationary aqueous layer, adjacent to this polymeric coating, begins at $r=r_c$ and ends at $r=r_s$ where the water bulk phase starts. Finally $r=r_v$ is the radius of the bottle.

In the water bulk phase, i.e., at heights above and under the SPME polymer and at radii from $r=r_s$ to $r=r_v$ at heights of the SPME polymer, the water concentration is constant. In the aqueous static layer around the SPME fiber and in the organic phase, a differential equation for the diffusion can be established:

$$\frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \cdot \frac{\partial C}{\partial r} = \frac{1}{D} \cdot \frac{\partial C}{\partial t} \tag{12}$$

where C is the concentration in the static layer $(r_c < r < r_s)$ and in the stationary phase (for $r_f < r < r_c$), t = time and D = diffusion coefficient of the VOC in the respective phases. The differential method of Crank–Nicolson [21] is suited for the modelling of
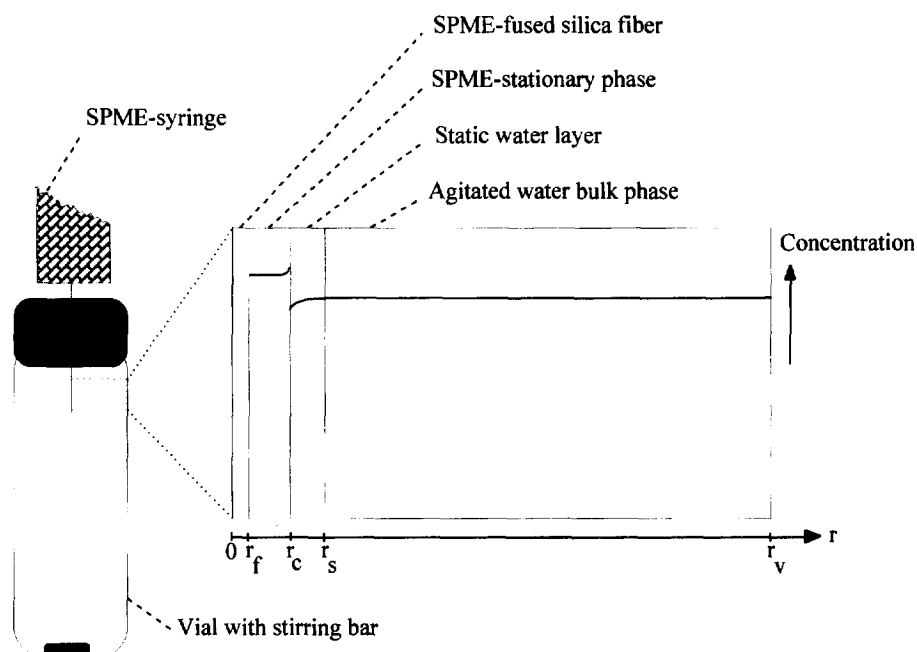

Fig. 4. Schematic representation of the "agitated/static layer" model. r is the distance from the center of SPME fiber and c is the concentration.

the process. The whole system is divided in N radial layers with a radius from r to $r+\Delta r$ so that

$$\frac{\partial C}{\partial t} = \frac{C_n^{t+\Delta t} - C_n^t}{\Delta t} \tag{13}$$

$$\frac{\partial C}{\partial r} = \frac{1}{2} \cdot \frac{C_{n+1}^t - C_{n-1}^t}{2\Delta r} + \frac{1}{2} \cdot \frac{C_{n+1}^{t+\Delta t} - C_{n-1}^{t+\Delta t}}{2\Delta r} \tag{14}$$

where C is the concentration in the SPME coating ($r_f < r < r_c$) or in the static layer ($r_c < r < r_s$). $C_{w,n}^{t+\Delta t}$ and C_n^t are the concentrations in layer n at time $t+\Delta t$ and t, respectively, C_{n+1}^t and C_{n-1}^t are the concentrations at time t in the layers $n+1$ and $n-1$, respectively. Finally $C_{n+1}^{t+\Delta t}$ and $C_{n-1}^{t+\Delta t}$ are the concentrations at time $t+\Delta t$ in the layers $n+1$ and $n-1$. So for the second order differential one obtains

$$\frac{\partial^2 C_n}{\partial r^2} = \frac{1}{2} \cdot \frac{C_{n-1}^t + C_{n+1}^t - 2C_n^t}{(\Delta r)^2}$$
$$+ \frac{1}{2} \cdot \frac{C_{n-1}^{t+\Delta t} + C_{n+1}^{t+\Delta t} - 2C_n^{t+\Delta t}}{(\Delta r)^2} \tag{15}$$

From the latter equation the concentrations in the layer n, $n-1$ and $n+1$ at time $t+\Delta t$ are written as a function of the concentrations at time t:

$$PC_{n-1}^{t+\Delta t} + Q_L C_n^{t+\Delta t} + RC_{n+1}^{t+\Delta t} =$$
$$- PC_{n-1}^t + Q_R C_n^t - RC_{n+1}^t \tag{16}$$

where the coefficients P, Q_L, Q_R and R are

$$P = \frac{1}{2(\Delta r)^2} - \frac{1}{4r(\Delta r)} \tag{17}$$

$$Q_L = -\frac{1}{(\Delta r)^2} - \frac{1}{D(\Delta)t} \tag{18}$$

$$Q_R = \frac{1}{(\Delta r)^2} - \frac{1}{D(\Delta t)} \tag{19}$$

$$R = \frac{1}{2(\Delta r)^2} + \frac{1}{4r(\Delta r)} \tag{20}$$

In order to calculate the concentrations at time $t+\Delta t$, a matrix notation is suitable:

$$[A][C^{t+\Delta t}] = [B][C^t] \tag{21}$$

In order to simulate the sorption process, boundary conditions must be formulated. First, the concen-

tration in the static water layer adjacent to the water bulk phase is equal to the water bulk phase concentration:

$$C_{w, r=r_s}^{t+\Delta t} = C_{w, bulk}^{t+\Delta t} \tag{22}$$

and at the water–polymer interphase equilibrium is assumed:

$$C_{w, r=r_c}^{t+\Delta t} = \frac{C_{s, r=r_c}^{t+\Delta t}}{K} \tag{23}$$

Further on, the flux from the static water layer adjacent to the SPME stationary phase into the SPME-polymer must be equal to the flux the first layer of the SPME-polymer receives:

$$D_w \cdot \frac{C_{w, r=r_c+\Delta r}^{t+\Delta t} - C_{w, r=r_c}^{t+\Delta t}}{\Delta r} =$$
$$D_s \cdot \frac{C_{s, r=r_c}^{t+\Delta t} - C_{s, r=r_c-\Delta r}^{t+\Delta t}}{\Delta r} \tag{24}$$

The third condition is that the slope of the concentration profile at $r=r_f$ must be zero or

$$\frac{\partial C_{s, r=r_f}}{\partial r} = 0 \tag{25}$$

If $C_{s, r=r_f}$ is noted in a Taylor series:

$$C_{s, r=r_f} = C_{s, r=r_f+\Delta r} + \frac{\Delta r}{1!} \cdot \frac{\partial C_{s, r=r_f+\Delta r}}{\partial r} \tag{26}$$

then the condition becomes

$$\frac{\partial C_{s, r=r_f+\Delta r}}{\partial r} + \Delta r \cdot \frac{\partial^2 C_{s, r=r_f+\Delta r}}{\partial r^2} = 0 \tag{27}$$

In the Crank–Nicolson differential method the equation can be written as

$$C_{s, r_f+2\Delta r} - 4C_{s, r_f+\Delta r} + 3C_{s, r_f} = 0 \tag{28}$$

The initial concentration for the bulk water phase and the static water layer at time $t=0$ is the initial water concentration $C_{w, r}^{t=0}$. Instantaneous equilibrium between the aqueous phase and the outer layer of the SPME stationary phase is considered whereas the concentration in all other layers of the SPME polymer were initially set equal to zero.

Application of the developed model

From the simulations it was found that the optimal finite intervals of time Δt and of interval Δr to obtain a good accuracy were 1 ms and 0.5 μm, respectively. The model parameters $C_w^{t=0}$, K, the thickness of the static layer δ and the diffusion coefficients D_w and D_s in water and in the stationary phase, respectively, have to be filled in. Three parameters are known a priori. $C_w^{t=0}$ is the initial water concentration, K has been determined experimentally (Table 1) and D_w (m^2 s^{-1}) is estimated from the Othmer–Thakar equation [18]. Data on the diffusion coefficients in poly(dimethylsiloxane) of the VOCs studied in this work are scarce. A coefficient at 25°C of $2.8 \cdot 10^{-10}$ m^2 s^{-1} for benzene is mentioned [22]. However, the diffusion is determined by the density of poly(dimethylsiloxane) which is dependent on the degree of polymerisation and on the branching of the polymer [23]. So this means that the value of $2.8 \cdot 10^{-10}$ m^2 s^{-1} is only a valuable starting value for the simulation of the sorption process. Next to the diffusion coefficient in the polymer, the thickness of the static water layer (δ) has to be estimated.

A least sum of relative deviations was applied in order to obtain an optimal fit:

$$\sum_i \frac{|X_{\text{model},\,i} - X_{\text{exp},\,i}|}{|X_{\text{model},\,i}|} \qquad (29)$$

The parameters $C_w^{t=0}$, D_w and the optimized K values together with the estimated parameters δ and D_s from the simulations of tetrachloromethane, trichloroethylene and benzene are given in Table 6, while the simulation together with the experimental results are presented in Fig. 5. It can be seen from the plots that the model fits the experimental data very well. The model estimations fall within the error of the experimental results. Moreover, no systematic deviations at the beginning or at the end of the curve are noticed.

The diffusion coefficients D_s are of the same order of magnitude as the literature value of $2.8 \cdot 10^{-10}$ m^2 s^{-1} [22]. Tetrachloromethane proves to have a diffusion coefficient of $1.5 \cdot 10^{-10}$ m^2 s^{-1} whereas trichloroethylene and benzene have a coefficient $3.0 \cdot 10^{-10}$ m^2 s^{-1}. Similarly, at a temperature of 60°C, the diffusion coefficient of tetrachloromethane ($0.7 \cdot 10^{-10}$ m^2 s^{-1}) was half the diffusion coefficient of trichloroethylene ($1.45 \cdot 10^{-10}$ m^2 s^{-1}) and chloroform ($1.4 \cdot 10^{-10}$ m^2 s^{-1}) for a polydimethylsiloxane polymer [24].

The static water layer for the compounds proves to be 5.5, 3.5 and 3.0 μm for tetrachloromethane, trichloroethylene and benzene, respectively. The layer has to be regarded as a zone in which depletion of the VOC occurs. The thickness of this zone is dependent on the partitioning coefficient K: the higher the K value the thicker the layer in which depletion occurs. In conclusion the "agitated/static layer" approach of the sorption process proves to be a good physicochemical interpretation of sorption process.

4. Conclusion

The partitioning coefficients of 11 VOCs for a poly(dimethylsiloxane) coating in SPME were determined and varied between 12 ± 1 (1,2-dichloroethane) and 841 ± 59 (tetrachloroethylene). The coefficients, which could be compared to literature data, were generally lower, though it has to be mentioned that a large variation on the available data is noticed.

A clear relationship between the partitioning coefficients and the Kováts indexes on a poly(dimethylsiloxane) GC stationary phase was established, involving a correction by Henry's law constant (regression coefficient 0.997, $n = 11$). The

Table 6

Parameters in the "agitated/static layer" model: $C_w^{t=0}$ = initial water concentration; K = distribution coefficient; D_w = diffusion coefficient in water; D_s = diffusion coefficient in the stationary phase and δ = thickness of the static layer

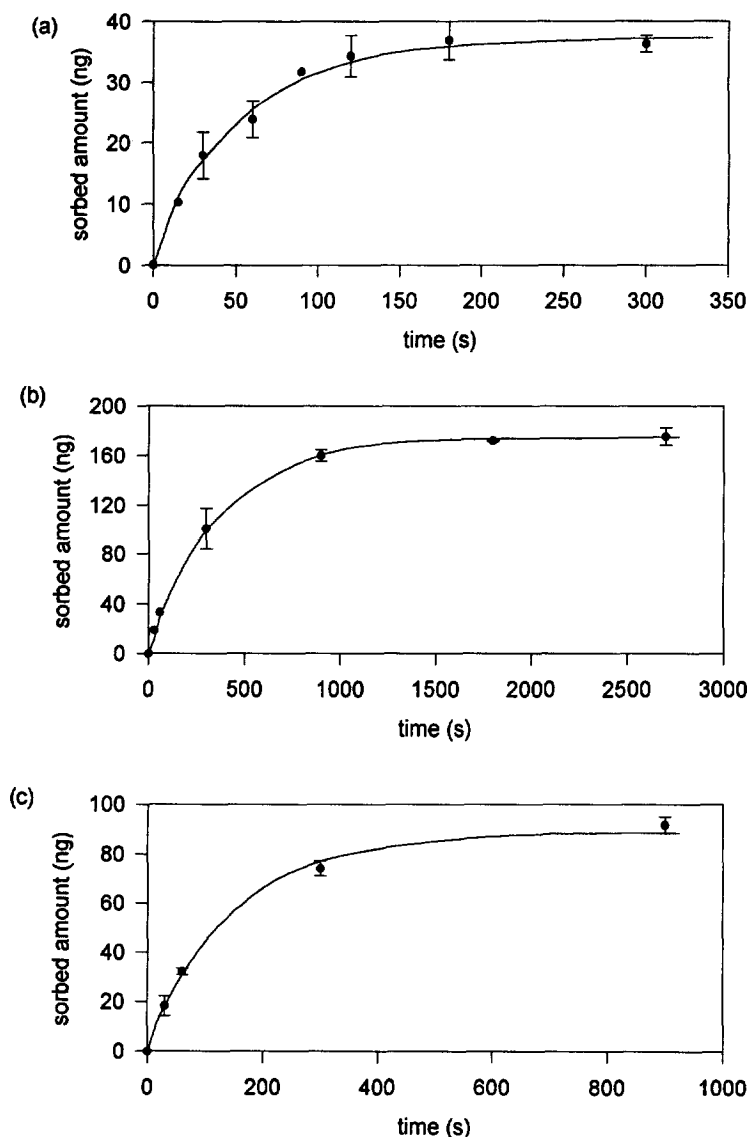| VOC	$C_w^{t=0}$ (μg l^{-1})	K (–)	D_w (m^2 s^{-1})	D_s (m^2 s^{-1})	δ (μm)
Benzene	832	70	$8.9 \cdot 10^{-10}$	$3.0 \cdot 10^{-10}$	3.0
Trichloroethylene	736	183	$7.9 \cdot 10^{-10}$	$3.0 \cdot 10^{-10}$	3.5
Tetrachloromethane	803	331	$9.0 \cdot 10^{-10}$	$1.5 \cdot 10^{-10}$	5.5

Fig. 5. Plot of the experimental results in the exposure experiments and of the curves from the "agitated/static layer" model for (a) benzene, (b) tetrachloromethane and (c) trichloroethylene. Experimental points are provided with 95% confidence intervals ($n=2$).

relation indicates the possibility to use the Kováts index as a tool to estimate the K values.

The effect of salinity on the equilibrium partitioning coefficient was examined and showed that correction factors between 1.09 (tetrachloroethylene) and 1.24 (tetrachloromethane, 1,1,1-trichloroethane) have to be introduced for marine sea water (salinity 3.5%) compared to deionized water. The salt effect in SPME proved to be comparable to the salt effect

on the solubility and on the air–water equilibrium partitioning. Values for benzene and toluene were similar to values mentioned in the literature.

The sorption kinetics showed that equilibration times ranged from 0.77 (1,2-dichloroethane) to 35.0 min (tetrachloroethylene) and were linearly related to the partitioning coefficient ($r=0.994$, $n=12$). The new developed model, i.e., the "agitated/static layer" model, fitted the experimental results very

well. It was shown that the thickness of the static water layer ranged between 3.0 and 5.5 μm for benzene, tetrachloromethane and trichloroethylene. The model confirmed the suggestion of Louch et al. [4] who stated that the underestimation of the equilibration time from their (fully) agitated model was due to the presence of a static water layer. However, the model showed that the thickness of the layer is dependent on the partitioning coefficient so that the static layer is to be considered as a zone in which the depletion of the analytes occurs.

Acknowledgments

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