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Using solid phase micro extraction to determine salting-out (Setschenow) constants for hydrophobic organic chemicals

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ABSTRACT

With increasing ionic strength, the aqueous solubility and activity of organic chemicals are altered. This so-called salting-out effect causes the hydrophobicity of the chemicals to be increased and sorption in the marine environment to be more pronounced than in freshwater systems. The process can be described with empirical salting-out or Setschenow constants, which traditionally are determined by comparing aqueous solubilities in freshwater and saline water. Aqueous solubilities of hydrophobic organic chemicals (HOCs) however are difficult to determine, which might partly explain the limited size of the existing data base on Setschenow constants for these chemicals. In this paper, we propose an alternative approach for determining the constants, which is based on the use of solid phase micro extraction (SPME) fibers. Partitioning of polycyclic aromatic hydrocarbons (PAHs) to SPME fibers increased about 1.7 times when going from de-ionized water to seawater. From the log-linear relationship between SPME fiber–water partition coefficients and ionic strength, Setschenow constants were derived, which measured on average 0.35 L mol^{-1}. These values agreed with literature values existing for some of the investigated PAHs and were independent of solute hydrophobicity or molar volume. Based on the present data, SPME seems to be a convenient and suitable alternative technique to determine Setschenow constants for HOCs.

1. Introduction

Hydrophobic organic chemicals (HOCs), such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls bind more extensively to solid phases in the marine environment then they do in the freshwater environment (Hegeman et al., 1995; Means, 1995; Brunk et al., 1997; Tremblay et al., 2005). This so-called salting-out phenomenon is mainly driven by an increase in the compounds' aqueous activity coefficients in the presence of dissolved inorganic salts (Schwarzenbach et al., 2003; Turner, 2003). Salting-out causes increased levels or "trapping" of the chemicals in sediments from in particular estuarine systems (Brunk et al., 1997; Turner, 2003), with a subsequent elevated potential for local ecotoxicological effects. In order to describe the salting-out effect, Setschenow (1889) proposed an empirical equation quantifying the change in a chemical's aqueous solubility as a function of the ionic strength of the medium. When combining the original Setschenow equation with a linear partitioning equation (i.e., describing sorption of compounds between a solid phase and water), the following equation is obtained (Brunk et al., 1997):

$$K^s = K^0 10^{k_s I} \tag{1}$$

in which K^s is the solid phase–water distribution coefficient in salt water (L kg^{-1}), K^0 is the solid phase–water distribution coefficient in salt-free water (L kg^{-1}), k_s is the salting-out or Setschenow constant (L mol^{-1}), and I is the ionic strength of the water (mol L^{-1}).

Because the majority of sorption studies are performed in freshwater systems, Setschenow constants are required for accurate fate and effect assessments of HOCs in marine and estuarine environments. Attempts have been made to correlate Setschenow constants to chemical properties such as molecular surface area (Whitehouse, 1985) and molar volume (Xie et al., 1997), but these have not been very successful. Hence, the constants cannot easily be modeled and the need for experimentally-determined values has been expressed (Xie et al., 1997), all the more since Setschenow constants are available only for a very limited number of chemicals (Xie et al., 1997). One reason for this lack of data might be that the determination of the constants traditionally involves aqueous solubility measurements at different ionic strengths (Setschenow, 1889; Whitehouse, 1985). For HOCs these measurements are rather difficult, which is clearly reflected by the broad range in experimental values produced by different laboratories and methods. Reported values for the aqueous solubility of high molecular weight PAHs for instance may cover more than two orders of magnitude (Mackay et al., 1992). The development of alternative, simple techniques for determining Setschenow constants might facilitate an expansion of the existing data set and thereby

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an improvement of the risk assessment of chemicals in saline environments.

In the present study, we propose an alternative method with which Setschenow constants for HOCs can be determined in a relatively simple and inexpensive way. The proposed method uses solid phase micro extraction (SPME), an extraction technique currently widely applied in environmental research (Heringa and Hermens, 2003). SPME fiber–water partition coefficients were determined at different salinity levels and Setschenow constants were subsequently derived by curve-fitting the log-linear version of Eq. (1) to the obtained partitioning data. The polymer phase applied on the SPME fibers (polydimethylsiloxane) is expected not to change structurally or chemically in the presence of dissolved salts, which obviously is a requirement when determining the effects of solution chemistry on solute behavior. Using this SPME approach, Setschenow constants were determined for thirteen PAHs, comprising an octanol–water partition coefficient (K_{ow}) range of $10^{4.6}$–10^{7}. For some of the tested compounds, Setschenow constants were available in the literature, allowing a validation of the proposed method. Because Setschenow constants probably are not or hardly dependent on the concentration of the test chemical (Schwarzenbach et al., 2003), the experiments were performed at a single concentration per compound. As opposed to most previous determinations, which were generally performed at solubility levels (Xie et al., 1997), the concentrations in the present experiment were in the environmentally-low concentration range (ng L^{-1}), in order to ascertain environmentally-relevant data.

2. Materials and methods

2.1. Chemicals, SPME fibers, and glassware

Testing chemicals used were phenanthrene, anthracene, fluoranthene, pyrene, benz[*a*]anthracene, chrysene, benzo[*e*]pyrene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, benzo[*ghi*]perylene, dibenz[*ah*]anthracene, and indeno[1,2,3-*cd*]pyrene (all >98%; Aldrich, Steinheim, Germany). Other organic chemicals used were 2-methylchrysene (99.2%; BCR, Geel, Belgium), methanol (HPLC super gradient grade; Lab-Scan, Dublin, Ireland), and acetonitrile and hexane (HPLC grade; Lab-Scan). Salts used were sodium chloride (NaCl), sodium sulfate (Na_2SO_4), sodium tetraborate ($Na_2B_4O_7$), calcium chloride ($CaCl_2 \times 2H_2O$), strontium chloride ($SrCl_2 \times 6H_2O$), sodium carbonate ($NaHCO_3$), potassium chloride (KCl), potassium bromide (KBr), magnesium chloride ($MgCl_2 \times 6H_2O$), and sodium azide (NaN_3). They were obtained from Merck (Darmstad, Germany), Riedel-de Haën (Seelze, Germany), Aldrich, or Fluka (Steinheim, Germany) and were of analytical or extra pure grade. Polydimethylsiloxane (PDMS)-coated, disposable SPME fiber (glass fiber core diameter 110 μm, PDMS coating thickness 28.5 μm) was obtained from Poly Micro Industries (Phoenix, AZ, USA). Prior to use, the fiber was cut into pieces of 5 cm length, which were washed two times with acetonitrile and two times with Millipore water, respectively. Photodegradation of PAHs during experimental measurements was prevented by using amber-colored glassware or glassware covered with aluminum foil. All glassware was rinsed with acetone before use.

2.2. Preparation of artificial seawater solutions

Artificial seawater was prepared by dissolving NaCl (21.03 g L^{-1}), Na_2SO_4 (3.52 g L^{-1}), KCl (0.61 g L^{-1}), KBr (0.088 g L^{-1}), $Na_2B_4O_7 \times 10H_2O$ (0.034 g L^{-1}), $MgCl_2 \times 6H_2O$ (9.5 g L^{-1}), $CaCl_2 \times 2H_2O$ (1.32 g L^{-1}), $SrCl_2 \times 6H_2O$ (0.02 g L^{-1}), and $NaHCO_3$ (0.17 g L^{-1}) in Millipore water (composition adopted from Spotte et al. (1984)). The resulting solution was then diluted 2:3 and 1:3 with Millipore water. A fourth solution consisted of 0.01 M $CaCl_2 \times 2H_2O$ in Millipore water (background solution). To prevent biodegradation of PAHs, NaN_3 (50 mg L^{-1}) was added to all of these solutions. Final total salt concentrations were 0.45, 0.30, 0.15, and 0.01 M, respectively, translating to ionic strengths of 0.62, 0.41, 0.21, and 0.062 M, respectively.

2.3. PDMS–water partitioning experiments

PDMS-coated SPME fiber–water partition coefficients (K_f) were determined in fivefold for each of the four salinity levels as follows. Amber-colored full glass bottles of 110 mL were filled with one of the four above-mentioned solutions, leaving about 10 mL of headspace, and two 5 cm pieces of SPME fibers were added. Subsequently, the systems were spiked with 50 μL of a cocktail solution of 13 PAHs in acetone (each at a concentration of about 0.7 mg L^{-1}). Bottles were closed and put on a horizontal shaker for 6 weeks in the dark; at 120 rpm and 20 °C. PAH concentrations in the aqueous phase were then determined by carefully transferring about 100 mL of solution to 100 mL cylinders, containing 4 mL of hexane. The solution volume was accurately determined by using a balance and an experimentally-determined solution-specific density. The cylinders were closed with glass stoppers and shaken for 2 h at 120 rpm. Then, the hexane layer was transferred to a calibrated pointed flask. The remaining water phase was extracted additionally two times with 3 mL of hexane. The hexane phases were pooled, evaporated to 0.5 mL, and solvent-exchanged to 0.45 mL of acetonitrile. Fifty μL of internal standard solution (10 mg L^{-1} of 2-methylchrysene in acetonitrile) was added and after vortexing, the extracts were transferred to autosampler vials and stored at −18 °C until analysis. Recoveries of the water phase extraction procedure were 92–100% (depending on the PAH). SPME fibers were also collected from the bottles, wiped with a wet tissue, and cut into pieces of about 1.25 cm, while holding them vertically in amber-colored autosampler vials filled with 180 μL of acetonitrile in a 250 μL insert. Then, 20 μL of internal standard solution was added, the vials were vortexed for 1 min and stored at −18 °C. Recoveries of this fiber extraction procedure were 99.6 ± 0.1%. Prior to the analysis, vials were defrosted and vortexed again. PAH concentrations in all extracts were then analyzed on a HPLC system, consisting of a Varian Prostar 420 autosampler, a Gynkotec P580HPG HPLC pump, a Jasco FP-2020 Plus fluorescence detector, and a Vydac 201TP54 C_{18} column (25 cm; d.i. 4.2 mm; d.f. 5 μm; kept at 27.0 °C). The mobile phase consisted of methanol and water (mixture changing from 30:70 to 100:0, and flow increasing from 0.7 to 1.5 mL min^{-1} over time), which were degassed by a Shimadzu DGU-14A degasser.

2.4. Data analysis

HPLC chromatograms were integrated with Chromcard 1.21 integration software (CE instruments, Milano, Italy). Resulting peaks were corrected for the internal standard peaks and converted into concentrations based on a four-point calibration curve. Subsequently, PAH concentrations in fibers (C_f) and water (C_w) were calculated, which were corrected for recoveries and blank measurements (average of triplicate unspiked systems). SPME fiber–water partition coefficients (K_f values) were then determined according to $K_f = C_f/C_w$. The resulting coefficients for the four different salinity levels were log-transformed ($\log K_f^{s,i}$), plotted against the respective ionic strength values (I), and the obtained linear relationships were extrapolated with GraphPad Prism (version 4.00, GraphPad Software, Inc.) to an ionic strength of 0 in order to obtain K_f^0 values. Finally, k_s values were determined by curve-fitting (GraphPad Prism) to the log-linear form of Eq. (1):