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Ion exchange membranes as novel passive sampling material for organic ions: Application for the determination of freely dissolved concentrations

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ABSTRACT

Many studies in pharmacology, toxicology and environmental science require a method for determining the freely dissolved concentration of a target substance. A recently developed tool for this purpose is equilibrium passive sampling with polymeric materials. However, this method has rarely been applied to ionic organic substances, primarily due to limited availability of convenient sorption materials. This study introduces ion exchange membranes (IEMs) as a novel passive sampling material for organic ions. The partitioning of 4-ethylbenzene-1-sulfonate, 2,4-dichlorophenoxyacetic acid and pentachlorophenol to one anion exchange membrane (FAS) and of difenzoquat, nicotine and verapamil to one cation exchange membrane (FKS) was investigated. All test substances exhibited a sufficiently high affinity for the respective IEM with logarithmic IEM–water partition coefficients >2.3. Sorption equilibrium was established quickly, within several hours for the FAS membrane and within 1–3 days for the FKS membrane. For permanently charged substances the partitioning to the IEMs was independent of pH, but was influenced by the salt composition of the test solution. For all test substances sorption to IEM was dependent on the substance concentration. Bovine serum albumin–water partition coefficients determined by passive sampling with IEMs agree well with those determined by the conventional dialysis method. The results of this study indicate that IEMs exhibit the potential to measure freely dissolved concentrations of organic ions in a simple and time-saving manner.

1. Introduction

Measuring the freely dissolved concentration of a target substance is of high relevance for pharmacological, toxicological and environmental studies. In pharmacology it is assumed that only the free fraction of a drug can cross biological membranes and is active at the target site [1]. Likewise, only the free concentration of a contaminant in aquatic environments is bioavailable for organisms and therefore responsible for potential adverse effects [2–4]. Moreover, the freely dissolved concentration is an important parameter for assessment of transport and distribution of environmental contaminants [5], because the mobility of contaminants strongly depends on the materials to which they are associated. Equilibrium dialysis is a well-established standard method for the determination of the freely dissolved concentration in binding experiments with dissolved and colloidal organic materials such as humic matter, phospholipid liposomes and proteins. Dialysis experiments are inexpensive and easy to perform, but involve several disadvantages. First, depending on the test substance and experimental setup of the dialysis cells, the equilibration time can be very long. Previous studies reported that equilibration needs several to 48 h [6–9], but longer equilibration times are also sometimes required [10,11]. Second, a significant loss of substance can occur due to sorption to the dialysis membrane. Third, the potential volume shift caused by osmotic pressure can also be an error source for dialysis experiments [12]. In addition, for substances with strong binding to the dissolved organic material, a sensitive measurement technique is required to determine the remaining, low freely dissolved concentrations.

Equilibrium passive sampling with a polymeric sorbent such as solid phase microextraction (SPME) fibers is a useful tool for the determination of freely dissolved concentrations. In this method, the polymer is exposed to an aqueous solution containing the target substance and the dissolved organic material such as protein.

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After equilibrium is established, the polymer phase is removed and the concentration in the polymer is measured. From the concentration in the polymer ($C_{polymer}$ [mmol kg^{-1}]) and the pre-determined polymer–water partition coefficient ($K_{polymer/water}$ [L kg^{-1}]), the freely dissolved concentration of the target substance in the aqueous phase at the final equilibrium state (C_{water} [mmol L^{-1}]) can be calculated according to the following equation:

$$C_{water} = \frac{C_{polymer}}{K_{polymer/water}} \quad (1)$$

The approach has been widely investigated and applied for neutral organic substances [9,13–16]. Nevertheless, only a few attempts have been made so far to adapt this technique to ionic organic substances, mainly because convenient sorption materials are not available. Previous studies used polyacrylate (PA) coated SPME fibers for passive sampling of weak acids and bases such as phenols [17,18], anilines [18], and pharmaceuticals [19,20]. These studies demonstrated that sorption by PA fibers is only significant for the neutral species of the studied weak acids and bases. This means that under pH conditions where the substances are present predominantly as ions, the sorption by PA is generally weak. Moreover, the low affinity of PA for ionic species suggests that it cannot effectively extract strong acids and bases which are fully ionized in water, unless the molecule contains a very large hydrophobic moiety in its structure (e.g., linear alkylbenzene sulfonates [21] and quaternary ammonium surfactants) [22]. Very recently, "mixed-mode" SPME fibers that combine hydrophobic and ion exchange properties have been applied for untargeted metabolomic profiling [23] and the passive sampling of amphetamine [24] as well as cationic surfactants such as lauryl diethanolamine [25]. These studies suggest that polymers with ion exchange properties have reasonably high affinity for ionic species. However, the main disadvantages of using SPME fibers for passive sampling of organic ions are the lack of commercially available ion exchange fibers, the small volume of the sorption material and thus a low sorption capacity.

The aim of this work was to test the applicability of ion exchange membranes (IEMs) for passive sampling of ionic organic substances. Organic ions are expected to have a high affinity for IEMs of opposite charge due to ionic interactions. Because of their industrial use for electrodialysis, IEMs are generally thin and highly permeable for ions with the opposite charge. Both features could contribute to a fast establishment of sorption equilibrium. Another advantage of the IEMs is that they are durable in general. Furthermore, various options for ion exchange materials are at hand, because many different types of inexpensive IEM are commercially available.

In this study, the sorption characteristics of two IEMs, a cation exchange membrane and an anion exchange membrane, were investigated using six ionic organic substances with different ionizable groups. Specifically, the equilibration time, sorption isotherms and the influence of pH and salt concentration on the partition coefficients were investigated experimentally. Subsequently, the IEMs were tested for their suitability for the determination of the freely dissolved concentration in binding experiments with bovine serum albumin (BSA). The BSA–water partitioning was also investigated with a standard equilibrium dialysis method for all test substances to validate the IEM-passive sampling approach.

2. Materials and methods

2.1. Materials

Water was purified with a Milli-Q Gradient A10 system from Millipore. Methanol (Suprasolv) and acetonitrile (Lichrosolv) were obtained from Merck. Unless otherwise noted below, for all sorption experiments Hanks' balanced salt solution (HBSS) (without phenol red and sodium bicarbonate, Sigma–Aldrich) buffered with 10 mM tris(hydroxymethyl)aminomethane (Tris) from Carl Roth was used. HBSS is a simulated physiological solution and has the following constituents: 140 mM Na^+, 6.14 mM K^+, 1.26 mM Ca^{2+}, 0.81 mM Mg^{2+}, 154 mM Cl^-, 4.2 mM HCO_3^-, 0.78 mM HPO_4^{2-}, 0.81 mM SO_4^{2-}, 5.55 mM D-glucose. The pH value of the buffer was adjusted to 7.4 with 1 N HCl or NaOH solution from Merck. Glacial acetic acid, NH_4OH solution (28–30% NH_3), H_3PO_4, ammonium acetate, bis(2-hydroxyethyl)amino-tris(hydroxymethyl)methane (Bis-Tris), 1,3-bis[tris(hydroxymethyl)methylamino]propane (Bis-Tris propane), Na_2CO_3, $NaHCO_3$, NaCl, NaN_3, $Na_2HPO_4{\cdot}2H_2O$ and $NaH_2PO_4{\cdot}H_2O$ were from Sigma–Aldrich, Carl Roth or Merck. Bovine serum albumin (essentially fatty acid free) and Bradford reagent were purchased from Sigma–Aldrich. The test substances were from the following providers: Dr. Ehrenstorfer GmbH (pentachlorophenol and difenzoquat methyl sulfate), Alfa Aesar ((S)-(−)-nicotine), TCI Deutschland GmbH (sodium 4-ethylbenzene-1-sulfonate (EBS)), and Sigma–Aldrich (2,4-dichlorophenoxyacetic acid (2,4-D) and (±)-verapamil hydrochloride). All substances had a purity of at least 98%; for their molecular structure and pK_a values, see Figure S-1 and Table S-1, respectively, in the Supporting information. These chemicals were selected to cover differing structures of ionic functional groups. As indicated by their pK_a values, all substances studied here are present primarily as ions in aqueous solutions at neutral pH. Solid phase extraction (SPE) cartridges (Oasis WAX) were purchased from Waters.

2.2. Ion exchange membranes

The IEMs applied for this study were obtained from FuMA-Tech GmbH (St. Ingbert, Germany) and are typically used for standard demineralization processes in electrodialysis. The anion exchange membrane "FAS" used for anionic test substances contains quaternary amines as ion exchange groups, Br^- as preloaded counterion and has an ion exchange capacity of 1.5 meq g^{-1}. The cation exchange membrane "FKS" for use with cationic analytes contains sulfonic acids as ion exchange groups, H^+ as preloaded counterion and has an ion exchange capacity of 1.2 meq g^{-1}. Both membranes were provided with a nominal thickness of 20 and 30 μm. The 20 μm thick membranes (FAS-20 and FKS-20) were preferred because of expected faster equilibration. However, the 20 μm thick membranes do not belong to the standard assortment of the provider and their quantity was limited. Therefore, some substances had to be measured with the 30 μm membranes (FAS-30 and FKS-30), which are commercially available. For each substance a consistent membrane thickness was used. The type of IEM used for the different test substances is shown in Table 1. For all experiments, discs (approximately 9 mm in diameter) were cut out of the IEMs with dissecting scissors, weighed on an analytical balance (1.5–3.5 mg, depending on membrane type and thickness) and conditioned in HBSS (unless otherwise noted below) for at least 3 h. For FAS membranes, the buffer was replaced once to assure the complete removal of bromide.

To allow a complete extraction of the test substances from the IEMs after the passive sampling experiments, different extraction solutions were checked out in preliminary experiments. Either pure solvent or solvent–water mixtures, all containing inorganic acid, base or salt, were used. More details on the extraction solutions are provided in the Supporting information – Section 2.

2.3. Characterizing sorption properties of IEMs

2.3.1. Equilibration time

The equilibration time for the determination of IEM–water partition coefficients ($K_{IEM/water}$) was investigated for all test