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Fluorous Membrane Ion-Selective Electrodes for Perfluorinated Surfactants: Trace-Level Detection and in Situ Monitoring of Adsorption

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S *Supporting Information*

ABSTRACT: Ion-selective electrodes (ISEs) with fluorous anion-exchanger membranes for the potentiometric detection of perfluorooctanoate (PFO⁻) and perfluorooctanesulfonate (PFOS⁻) were developed. Use of an anion-exchanger membrane doped with the tetraalkylphosphonium derivative $(R_{f8}(CH_2)_2)(R_{f6}(CH_2)_2)_3P^+$ and an optimized measurement protocol resulted in detection limits of 2.3×10^{-9} M (1.0 ppb) for PFO⁻ and 8.6×10^{-10} M (0.43 ppb) for PFOS⁻. With their higher selectivity for PFO⁻ over OH⁻, membranes containing the alternative anion exchanger $(R_{f6}(CH_2)_3)_3PN^+P((CH_2)_3-R_{f6})_3$ with a bis(phosphoranylidene)ammonium group further improved the detection limit for PFO⁻ to 1.7×10^{-10} M (0.070 ppb). These values are comparable with results obtained using well-established techniques such as gas chromatography−mass spectrometry (GC−MS), liquid chromatography−mass spectrometry (LC−MS), and liquid chromatography−tandem mass spectrometry (LC−MS−MS), but the measurement with ISEs avoids lengthy sample preconcentration, can be performed in situ, and is less costly. Even when eventual spectrometric confirmation of analyte identity is required, prescreening of large numbers of samples or in situ monitoring with ISEs may be of substantial benefit. To demonstrate a real-life application of these electrodes, in situ measurements were performed of the adsorption of PFOS⁻ onto Ottawa sand, which is a standard sample often used in environmental sciences. The results obtained are consistent with those from an earlier LC−MS study, validating the usefulness of these sensors for environmental studies. Moreover, PFOS⁻ was successfully measured in a background of water from Carnegie Lake.

Perfluorocarbon (PFC) surfactants are used for a wide range of applications, such as the production of polymers, lubricants, paints, polishes, cookware, and fire-retarding foams.[1] Because of their unique chemical stability,[2] they are not biodegradable, are persistent in the environment, and can be found worldwide in surface waters and animal tissues.[1,3−7] PFC surfactants with long alkyl chains, such as perfluorooctanoate (PFO⁻) and perfluorooctanesulfonate (PFOS⁻), are of particular environmental and health concern.[1,3,7−11] Currently available detection methods for PFO⁻ and PFOS⁻ include gas chromatography−mass spectrometry (GC−MS),[8,12] liquid chromatography−mass spectrometry (LC−MS),[13−16] and liquid chromatography−tandem mass spectrometry (LC−MS−MS). Each of these methods has some disadvantage, be it either an insufficient detection limit, the need for chemical derivatization prior to analysis, lengthy sample preparation, cost, or poor suitability for measurements in the field. With the purpose of developing a simple technique for fast prescreening of large numbers of samples and continuous on-site monitoring, we developed ion-selective electrodes (ISEs)[17,18]

with fluorous sensing membranes for the determination of PFO⁻ and PFOS⁻.

The selectivity of an ISE for different ions is determined by the free energy of transfer of the analyte ion from the aqueous sample into the hydrophobic sensing membrane.[19,20] Because of their long perfluoroalkyl chains PFO⁻ and PFOS⁻ favor fluorous media, which are immiscible with water and higher hydrocarbons and are the least polar and polarizable condensed phases known.[21,22] The hydrophobicities of PFO⁻ and PFOS⁻ are not only the direct result of the hydrophobic effect associated with the perfluoroalkyl groups. They are also indirectly enhanced by the strongly electron-withdrawing character of their perfluoroalkyl groups, which reduce the hydration energy of their oxoanion groups and, thereby, facilitate the phase transfer of PFO⁻ and PFOS⁻ out of the aqueous phase.[23] In contrast, the transfer of many other

environmentally relevant anions from aqueous samples into fluorous media is energetically much less favorable. Therefore, ISEs with fluorous sensing membranes are exceptionally selective to PFO⁻ and PFOS⁻.

In earlier work of our group, a fluorophilic methyltriarylphosphonium cation was synthesized, and fluorous anion-exchange membranes were prepared by doping of an inert liquid fluorous matrix with a salt of this cation.[24] The detection of PFO⁻ and PFOS⁻ with electrodes comprising such membranes was to the best of our knowledge the first demonstration of the potentiometric measurement of these analytes. The electrodes exhibited high selectivities for PFO⁻ and PFOS⁻ (log $K^{pot}_{Cl^-,PFO^-}$ = 7.4, log $K^{pot}_{Cl^-,PFOS^-}$ = 10.6; see Table 1).[24] While such selectivities were very promising, the

Table 1. Selectivities of ISE Membranes Consisting of Perfluoroperhydrophenanthrene Doped with Different Anion Exchangers

	PFO⁻ selectivity, log $K^{pot}_{PFO^-,J^-}$		
ion J	methyltriarylphosphonium[a]	anion-exchanger 1[b]	anion-exchanger 2[c]
PFOS⁻	3.2	1.8 ± 0.1	0.6 ± 0.1
Cl⁻	−7.4	−7.5 ± 0.3	−6.6 ± 0.1
OH⁻	d	−4.6 ± 0.1	−10.6 ± 0.2
NO₃⁻	−5.1	−6.0 ± 0.1	−5.8 ± 0.2

[a][3,5-(CH₂CH₂CH₂C₈F₁₇)₂C₆H₃]₃CH₃P⁺CH₃OSO₃⁻; data from ref 24. [b]Data from ref 25. [c]Determined with the fixed interference method. [d]Not reported.

decomposition of the methyltriarylphosphonium ion to a phosphine oxide in the presence of hydroxide caused slow sensor responses and drifts, even when the hydroxide ion was formed only in very small quantities in the presence of water and weak bases. Therefore, subsequent work developed the fluorophilic salts $(R_{f8}(CH_2)_2)(R_{f6}(CH_2)_2)_3P^+I^-$ and $(R_{f6}(CH_2)_3)_3PN^+P((CH_2)_3R_{f6})_3Cl^-$ with a tetraalkylphospho-

nium and bis(phosphoranylidene)ammonium group, respectively.[25,26] The higher chemical stabilities and excellent selectivities that were observed using sensing membranes doped with these anion exchangers were very promising in view of measurements of PFO⁻ and PFOS⁻ in environmental samples at very low concentrations.

Besides the inherent selectivity of the ISE membrane, the design of the electrode is crucial when low detection limits are required. Both ISEs with inner filling solution in which the analyte ion is buffered at a low concentration[27−30] and electrodes with a solid contact rather than an inner filling solution were shown to permit ion detection in the nanomolar and lower concentration range.[31,32] For example, Ag⁺ detection at the low parts-per-trillion (4 ppt)[33] level was achieved by the combination of three-dimensionally ordered macroporous (3DOM) carbon as solid contact[34,35] and fluorous sensing membranes doped with a fluorophilic Ag⁺ ionophore. These sensors exhibited selectivities over many other heavy metal ions of 1:10¹⁰ and higher. With the same methodology, i.e., using 3DOM carbon-contacted electrodes with fluorous membrane matrixes, detection limits in the low-nanomolar range were obtained in this work for PFO⁻ and PFOS⁻.

As a demonstration of the usefulness of these ISEs for environmental studies, we also describe here the in situ detection of PFOS⁻ adsorption onto well-characterized standard sand samples. A quantitative understanding of PFOS⁻ adsorption onto mineral surfaces, such as silica, clay, and sand, is crucial to a better understanding of the transport and fate of PFCs in the environment.[36] Considerable effort was spent in the past to determine PFOS⁻ adsorption isotherms using ex situ techniques such as LC−MS.[37−39] With much simpler instrumentation and no need for sample preparation, we reproduced for Ottawa sand previously reported results within error and measured PFOS⁻ in lake water.
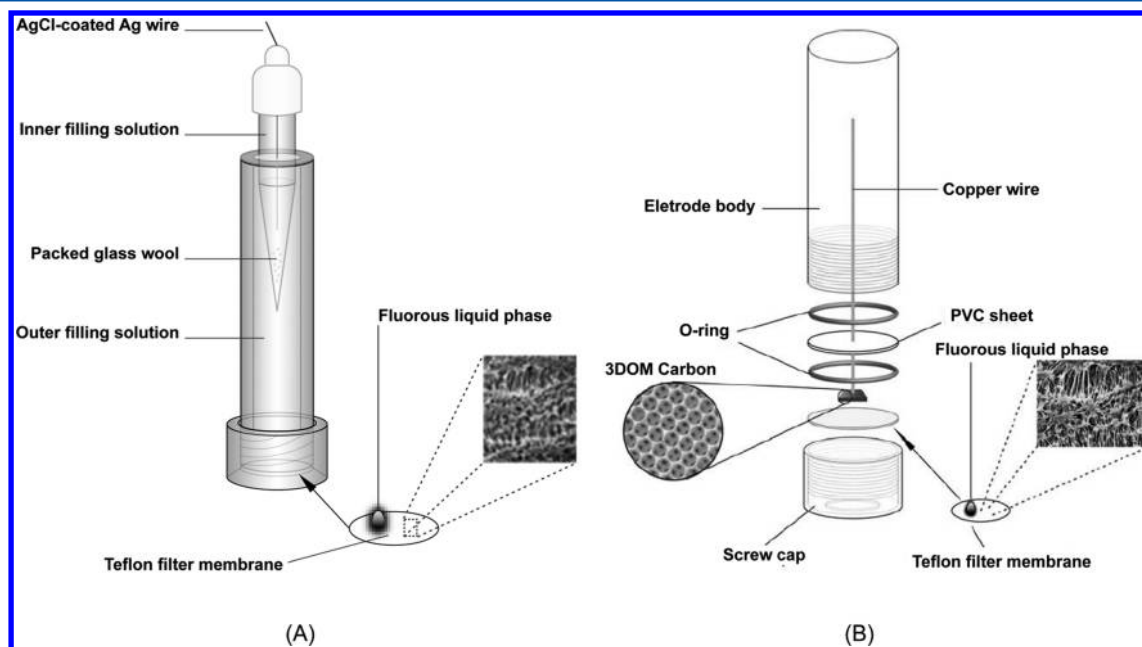

Figure 1. Schematics of ISEs based on fluorous sensing membranes with inner and outer filling solutions (ref 41, type A) and 3DOM carbon (ref 34) as solid contact (type B).

■ MATERIALS AND METHODS

The linear perfluorooligoether α-(heptafluoropropyl)-ω-(pentafluoroethoxy)-poly[oxy(1,1,2,2,3,3-hexafluoro-1,3-propanediyl)] (LPFPE) was purchased from Daikin Industries (Osaka, Japan). The iodide salt of $(R_{f8}(CH_2)_2)(R_{f6}(CH_2)_2)_3P^+$ (**1**) and the chloride salt of $(R_{f6}(CH_2)_3)_3PN^+P((CH_2)_3R_{f6})_3$ (**2**) (see the Supporting Information, Figure S1) were prepared according to previously reported procedures.[26,40] Ottawa sand standard was purchased from EMD Chemical (Gibbstown, NJ). The fluorophilic electrolyte salts $(R_{f8}(CH_2)_2)(R_{f6}(CH_2)_2)_3P^+$-$B(C_6H_3(C_6F_{13})_2)_4{}^-$ (**ES1**) and $(R_{f6}(CH_2)_3)_3PN^+P((CH_2)_3$-$R_{f6})_3B(C_6H_3(C_6F_{13})_2)_4{}^-$ (**ES2**) were prepared by metathesis (see the Supporting Information for structure formulas and synthesis).[24]

Two types of electrodes, i.e., two-compartment electrodes of type A and 3DOM carbon-contacted electrodes of type B, as shown in Figure 1, were prepared in the same way as described previously (see the Supporting Information for the sensing membrane preparation and the electrode assembly).[33,41] Detection limits were determined following the International Union of Pure and Applied Chemistry (IUPAC) recommendations by extrapolation of the linear response range to the value of the electromotive force (emf) in the absence of the target ion.[42,43] Selectivity coefficients were determined with both the fixed interference method (FIM)[44] and the separate solution method (SSM).[44] (See the Supporting Information for details of emf measurements.)

To prepare a sand sample, a 100 ppm PFOS$^-$K$^+$ solution was prepared by dissolving 10 mg of PFOS$^-$K$^+$ in 100 mL of a 0.010 M KNO$_3$ solution. The resulting solution was then diluted stepwise with 0.010 M KNO$_3$ to give a series of 100 mL solutions with PFOS$^-$K$^+$ concentrations in the range from 0.10 to 12 ppm. These diluted solutions were added into polyethylene bottles loaded with 1.0 g of Ottawa sand, and the bottles were sealed and shaken for more than 24 h to allow the PFOS$^-$/solid suspensions to reach equilibrium.

■ RESULTS AND DISCUSSION

Response and Selectivity of PFO$^-$/PFOS$^-$ ISEs. To respond to anions, an ISE membrane must exhibit anion-exchange capacity.[19,20,45,46] This is achieved by incorporating anion exchangers into an inert water-immiscible matrix. In the case of a fluorous sensing membrane, these anion exchangers are fluorophilic cations. However, because fluorous phases have the lowest polarity of all condensed phases known,[21] only very few fluorophilic salts soluble in fluorous phases are known. For this project, our selection of fluorophilic cations suitable for the preparation of PFO$^-$ and PFOS$^-$ sensor membranes was limited to the two cations **1** and **2**, which were recently introduced for the development of fluorous membrane ISEs.[25,26]

For the initial characterization of potentiometric responses and PFO$^-$ and PFOS$^-$ selectivities, fluorous phases consisting of perfluoroperhydrophenanthrene doped with 2.0 mM **1** were prepared and used as sensing membranes in electrode bodies of the type A, as shown in Figure 1. The outer filling solutions of these electrodes contained 1.0 μM PFO$^-$Na$^+$ or PFOS$^-$K$^+$, depending on which ion was being detected. Calibration curves were obtained by successive dilution of PFO$^-$Na$^+$ or PFOS$^-$K$^+$ samples with water. As shown in Figure 2, these electrodes exhibited the expected theoretical (Nernstian) response, with a decrease of 59.2 mV per 10-fold increase of the PFO$^-$ or
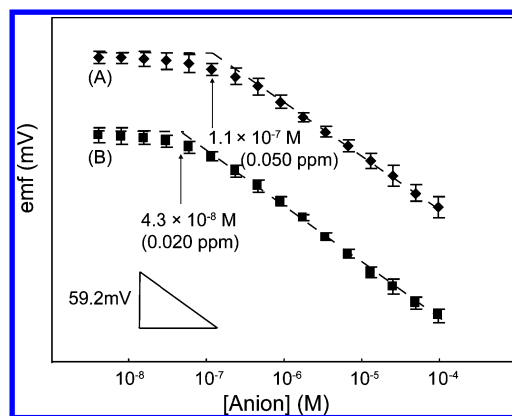

Figure 2. Potentiometric response curves for (A) PFO$^-$ and (B) PFOS$^-$ with ISEs based on membranes consisting of the tetraalkylphosphonium cation **1** (2.0 mM) in perfluoroperhydrophenanthrene. The response curves were obtained by averaging responses of three electrodes.

PFOS$^-$ concentration in the sample solution. The observed response times were on the order of a few seconds at high PFO$^-$/PFOS$^-$ concentrations (above 1.0 μM) and on the order of a few minutes at low PFO$^-$/PFOS$^-$ concentrations. Such response times are typical for ISEs and are limited by the speed of complete sample change[47] at higher concentrations and the kinetics of analyte diffusion to the sensor surface at lower concentrations.

As expected, membranes doped with the anion-exchanger **1** provided high selectivities[19,20] for PFO$^-$ and PFOS$^-$ (log $K^{pot}_{PFO^-,Cl^-} = -7.5$, log $K^{pot}_{PFOS^-,Cl^-} = -9.3$). On the basis of these selectivities, no significant interference from Cl$^-$ is expected for PFO$^-$ concentrations higher than $10^{-10.5}$ M or PFOS$^-$ concentrations higher than $10^{-12.3}$ M when measuring in surface water or groundwater samples, in which the Cl$^-$ concentration is typically less than 1.0 mM.[48] In samples such as seawater (Cl$^-$ concentration $\approx$19 g/L, i.e., 0.54 M),[48] chloride would start to interfere when PFO$^-$ or PFOS$^-$ concentrations are lower than 10^{-8} or 10^{-10} M, respectively.

The selectivities for PFO$^-$ and PFOS$^-$ provided by these ISE membranes doped with anion-exchanger **1** were similar to those reported earlier for ISE membranes doped with a fluorophilic methyltriarylphosphonium derivative (log $K^{pot}_{PFO^-,Cl^-} = -7.4$, log $K^{pot}_{PFOS^-,Cl^-} = -10.6$; see Table 1).[24] However, as mentioned above, the fluorophilic cation **1** is a better choice as an anion exchanger because the methyltriarylphosphonium cation used earlier exhibited limited chemical stability, resulting in slow changes of the emf over time.[24] Unfortunately, even though decomposition of **1** to a phosphine oxide is much slower than in the case of the methyltriarylphosphonium cation, decomposition of **1** could still be observed spectroscopically at high pH, as reported previously.[25] Possibly because of anion–dipole interactions between OH$^-$ and a phosphine oxide decomposition product of anion-exchanger **1**,[25] the sensors with membranes doped with **1** exhibited an unusually high preference for OH$^-$ over chloride (log $K^{pot}_{Cl^-,OH^-} = 2.9$), which is not expected for an ionophore-free ion-exchanger electrode (as defined on p 1595 of ref 49).

Since the fluorophilic cation $(R_{f6}(CH_2)_3)_3PN^+P((CH_2)_3$-$R_{f6})_3$, **2**, shows no sign of deterioration even when exposed to strongly alkaline solutions,[26] the PFO$^-$ and PFOS$^-$ response of electrodes of type A (Figure 1) based on liquid sensing membranes consisting of 2.0 mM **2** in perfluoroperhydrophe-

Table 2. Improved Detection Limits for Solid-Contact Electrodes of Type B Based on Optimized Conditioning Procedures

		detection limit (M)	
membrane composition	analyte	1.0 μM (2 days)[a]	1.0 nM (2 days)[b]
anion-exchanger **1** (0.25 mM), electrolyte salt **ES1** (5.0 mM)	PFO$^-$	$(3.4 \pm 0.7) \times 10^{-8}$	$(2.3 \pm 0.7) \times 10^{-9}$
anion-exchanger **1** (0.25 mM), electrolyte salt **ES1** (5.0 mM)	PFOS$^-$	$(3.1 \pm 0.2) \times 10^{-9}$	8.6×10^{-10}
anion-exchanger **2** (2.0 mM)	PFO$^-$	$(5.1 \pm 1.6) \times 10^{-9}$	$(1.7 \pm 0.2) \times 10^{-10}$
anion-exchanger **2** (1.0 mM), electrolyte salt **ES2** (0.25 mM)	PFO$^-$	$(4.3 \pm 0.9) \times 10^{-9}$	$(2.2 \pm 0.3) \times 10^{-10}$

[a]Obtained after conditioning in 1.0 μM solution for 2 days. [b]Obtained after conditioning in 1.0 nM solution for 2 days.

nanthrene were tested. Nernstian responses were confirmed for both anions. The selectivities for PFO$^-$ and PFOS$^-$ over Cl$^-$ were slightly smaller (log $K^{pot}_{PFO^-,Cl^-}$ = −6.6, log $K^{pot}_{PFOS^-,Cl^-}$ = −7.2) than in the case of ISEs based on **1**, but the selectivities over OH$^-$ were much improved (log $K^{pot}_{PFO^-,OH^-}$ = −10.6, log $K^{pot}_{PFOS^-,OH^-}$ = −11.2; see Table 1).[25]

Optimization of Detection Limits for PFO$^-$. Detection limit optimization was initially performed for electrodes based on the fluorophilic anion-exchanger **1**. As can be seen from Figure 2, the detection limit of electrodes with perfluoroperhydrophenanthrene as fluorous matrix and an outer filling solution containing 1.0 μM PFO$^-$Na$^+$ was 1.1×10^{-7} M for PFO$^-$, as determined according to IUPAC recommendations.[42,43] It was expected that replacement of perfluoroperhydrophenanthrene as the fluorous inert matrix with the more viscous linear perfluorooligoether LPFPE (0.099 Pa s)[50] would favor lower detection limits since it is well-known that decreases of ionic mobilities in ISE membranes diminish transmembrane ion fluxes and, thereby, affect detection limits.[19] LPFPE offers the additional benefit that its vapor pressure is lower than that of perfluoroperhydrophenanthrene, which is desirable for long-term use.[51] However, the iodide salt of the fluorophilic anion-exchanger **1** was found to have a rather low solubility in LPFPE (<0.25 mM), resulting in very high electrical resistances of the sensing membranes of several hundred gigaohms, impeding the reliable measurement of potentiometric responses. Therefore, LPFPE membranes were doped with anion-exchanger **1** (0.25 mM) and, in addition, 5.0 mM of the fluorophilic electrolyte salt **ES1**, which was prepared by metathesis to consist of **1** as the cation and the fluorophilic tetrakis[3,5-bis(perfluorohexyl)phenyl]borate as the anion. The use of this electrolyte salt decreased the resistance of the ISE membranes from hundreds to a few gigaohms. Membranes with added electrolyte salt were used for all further experiments.

To achieve a low detection limit, electrodes with LPFPE membranes containing anion-exchanger **1** and electrolyte salt **ES1** were optimized with a two-step conditioning protocols. As described in the literature,[27,32,52,53] conditioning of ISE membranes prior to their use is important to achieve low detection limits. On one hand, exposure of freshly prepared ISEs to a conditioning solution with a high concentration of target analyte is necessary to ensure that enough analyte ions are available in this solution to replace the counterions of the anion exchangers originally present in the sensing membrane. Conditioning in a solution with too low of an analyte concentration results in an incomplete exchange of the counterions of the anion exchangers in the sensing membrane, which in subsequent experiments causes ion fluxes from the sample into the ISE membrane and, thereby, worsens detection limits. However, the initial conditioning causes unfavorable detection limits due to coextraction of analyte ions into the sensing membrane and possible adsorption of analyte ions onto the electrode body during the conditioning process. Therefore,

in the second conditioning step, the electrodes need to be exposed to a solution with a much lower concentration of the target ion (1.0 or 10 nM) to remove from the bulk of the sensing membrane excess target anions not paired with the anion exchanger.

With these considerations in mind, freshly prepared electrodes (type A, 0.25 mM **1** and 5.0 mM **ES1** in LPFPE, 1.0 μM PFO$^-$Na$^+$ in the outer filling solution) were first conditioned in 1.0 μM PFO$^-$Na$^+$ solution for 1 day. At this point, the detection limit for PFO$^-$ was determined to be 4.9×10^{-8} M. After a change of their outer filling solution to 10 nM PFO$^-$Na$^+$ and conditioning in 10 nM PFO$^-$Na$^+$ solution for another 2 days, the detection limit was lowered slightly to 3.0×10^{-8} M. For ISEs with an inner and outer filling solution (separated from one another as shown in Figure 1A), attempts to further lower the detection limit were not successful. However, the same type of LPFPE membranes was also tested in solid-contact electrodes of type B (shown in Figure 1), again using a multistep conditioning procedure. After conditioning in 1.0 μM, 10 nM, and 1.0 nM solution for 2 days each, a detection limit of 2.3×10^{-9} M was achieved (Table 2). This demonstrates the advantages of 3DOM carbon as solid contact.

Lowering Detection Limits with Anion-Exchanger 2. Even though **1** is more stable than the fluorophilic methyltriarylphosphonium cation, its slow decomposition may not only affect the selectivity over hydroxide but, because of a very slow decrease in ion-exchanger capacity, also causes a concomitant continuous loss of low levels of PFO$^-$ from the sensing membrane into samples. This contaminates the latter with PFO$^-$ and, in so doing, worsens the detection limit for this analyte.[25] To further improve the detection limit for PFO$^-$, use of the fluorophilic anion exchanger $(R_{f6}(CH_2)_3)_3PN^+P$-$((CH_2)_3R_{f6})_3$, **2**, which is more chemically stable and provides a higher selectivity of PFO$^-$ over OH$^-$ (log $K^{pot}_{PFO^-,OH^-}$ = −10.6), was indicated.

Electrodes of type A with an LPFPE membrane containing 2.0 mM $(R_{f6}(CH_2)_3)_3PN^+P((CH_2)_3R_{f6})_3PFO^-$, 1.0 μM PFO$^-Na^+$ in their outer filling solution, and 1.0 mM KCl in the inner filling solution gave a detection limit of 5.3×10^{-9} M. After replacing the outer filling solution with 10 nM PFO$^-$Na$^+$ and conditioning in 10 nM PFO$^-$Na$^+$ solution, this detection limit was lowered to 3.6×10^{-9} M. 3DOM carbon-contacted electrodes with the same sensing membranes were also prepared. Initial conditioning of the electrodes in 1.0 μM PFO$^-$Na$^+$ solutions gave a detection limit of 5.1×10^{-9} M, which was lowered to 1.7×10^{-10} M (0.070 ppb) upon conditioning in 1.0 nM PFO$^-$Na$^+$ (Table 2 and Supporting Information Figure S2).

However, response times of these ISEs with membranes doped with **2** were very long due to their high electrical resistances. To lower the latter, electrolyte salt **ES2** was added into sensing membranes doped with **2**. Because this initially worsened the detection limit, different concentrations of anion-

exchanger **2** and electrolyte salt **ES2** were investigated. A detection limit comparable to that of the electrodes based on LPFPE doped with 2.0 mM **2** but no electrolyte salt **ES2** was eventually obtained with membranes based on **2** (1.0 mM) and **ES2** (0.25 mM), lowering the membrane resistance 10 times with respect to membranes without electrolyte salt (see Table S1, Supporting Information). Solid-contact electrodes with 3DOM carbon solid contacts and sensing membranes containing **2** (1.0 mM) and **ES2** (0.25 mM) exhibited an optimized detection limit of 2.2×10^{-10} M (0.091 ppb) for PFO$^-$ (Table 2).

Detection Limits for PFOS$^-$. Similar experiments as for PFO$^-$ were carried out also for the detection of PFOS$^-$. Table 2 shows that initial electrode conditioning in 1.0 μM PFOS$^-$K$^+$ resulted in a 3.1×10^{-9} M detection limit, and additional conditioning in 1.0 nM PFOS$^-$ further improved the detection limit to 8.6×10^{-10} M (0.43 ppb). Since the anion-exchanger **2** provided similar selectivities for PFO$^-$ and PFOS$^-$, the detection limit for PFOS$^-$ was not studied using sensor membranes doped with anion-exchanger **2**.

The detection limits of direct measurements of PFO$^-$ and PFOS$^-$ with these ISEs are higher than the reported detection limits of LC–MS–MS methods (0.010–10 ng/L, i.e., 0.010 ppt to 0.010 ppb, respectively), the currently most accepted approach to PFO$^-$ and PFOS$^-$ analysis.[10] However, the lowest reported detection limits with LC–MS–MS are achieved using preconcentration, such as solid-phase extraction. It remains to be seen to what extent preconcentration can improve the detection limit of analysis methods using these ISEs. Moreover, the much simpler and field-deployable ISEs are more suitable for in situ and on-site measurements of PFO$^-$ and PFOS$^-$, as shown in the following.

Adsorption of PFO$^-$ and PFOS$^-$ as Studied in Situ with ISEs. In this section it is shown how the PFO$^-$/PFOS$^-$ sensors described above can be applied to study the absorption of PFO$^-$ or PFOS$^-$ onto solids. Adsorption of PFO$^-$ and PFOS$^-$ onto glass is well-known[54] and indeed was readily observed by us when using glass beakers. When attempts to measure calibration curves for PFO$^-$ were performed using successive dilution of a PFO$^-$Na$^+$ sample in a glass beaker, excessive drifts in the potentiometric response were observed after each dilution step. Apparently, PFO$^-$ adsorbed onto the glass walls of the beaker, and PFO$^-$ release back into the solution occurred after each dilution step, affecting the concentration of PFO$^-$ in the sample. This also resulted in biased response slopes of approximately −36 mV/decade (see the Supporting Information). When polypropylene beakers were used instead, theoretical response slopes were obtained, and no drifts of this type were observed. Similar observations were made for PFOS$^-$. These observations not only indicate the necessity to use polypropylene containers and pipets to store and transfer PFO$^-$ and PFOS$^-$ samples, but also demonstrate the feasibility of in situ monitoring of PFO$^-$ and PFOS$^-$ with these ISEs.

Adsorption of PFO$^-$ and PFOS$^-$ onto surfaces of materials such as sand, clay, and minerals is a major factor in the fate and transport of these compounds in a natural environment. While a quantitative study of PFO$^-$ adsorption has yet to be reported, PFOS$^-$ adsorption was investigated in several research groups using LC–MS.[37–39] In order to validate our ISE method, we therefore investigated the adsorption of PFOS$^-$ onto Ottawa sand using the same experimental system as used earlier in the groups of Penn and Simcik,[37] but using ISEs for in situ monitoring of PFOS$^-$ rather than LC–MS for ex situ analysis.

Ottawa sand was selected because it is well-characterized and because it has been widely used as a standard material in environmental chemistry.[37]

Since PFOS$^-$ adsorption depends on the ionic strength of the ambient solution, the LC–MS work in the groups of Penn and Simcik was performed with a 0.010 M KNO$_3$ background in all samples.[37] Using the same conditions for this ISE study, NO$_3^-$ became the most relevant interfering species. Table 1 shows that ISE membranes doped with the anion-exchanger **1** exhibit a better PFOS$^-$ selectivity over NO$_3^-$ than those doped with **2**. Therefore, sensing membranes consisting of LPFPE containing **1** (0.25 mM) and electrolyte salt **ES1** (5.0 mM) were used. Also, since the PFOS$^-$ concentrations studied in the Penn and Simcik groups fell in the range from 0.12 to 10 ppm (2.4×10^{-7} to 2.0×10^{-5} M PFOS$^-$), 3DOM carbon-contacted electrodes with their particularly low detection limit were not required, and adsorption onto sand was studied using electrodes with inner and outer filling solutions (electrode setup A in Figure 1). To minimize transmembrane ion fluxes, the outer filling solutions contained 0.010 M KNO$_3$ and 0.010 ppm PFOS$^-$K$^+$ (20 nM PFOS$^-$K$^+$), resulting in a linear response in a range from 0.020 to over 10 ppm PFOS$^-$ (for a calibration curve, see the Supporting Information, Figure S4). By reducing the PFOS$^-$K$^+$ concentration in the outer filling solution to a value as low as 0.0010 ppm (2.0 nM), the lower end of the working range could be further lowered to 0.0080 ppm, which was good enough to measure the concentrations of dissolved PFOS$^-$ in equilibrium with sand samples.

After calibration, the electrodes were inserted into 100 mL standard solutions that had the same composition as the outer filling solution of the electrodes. With such a symmetric setup, signal drift caused by ion fluxes can be minimized. Aliquots of the sand suspensions equilibrated with PFOS$^-$ for 24 h were then spiked into these 100 mL standard solutions,[37] and potentiometric responses were recorded. The equilibrium concentrations of PFOS$^-$ in the aqueous suspensions and the amount of PFOS$^-$ adsorbed onto the sand were calculated from these responses using calibration curves.

A thus obtained isotherm for PFOS$^-$ adsorption onto Ottawa sand is shown in Figure 3, along with corresponding values
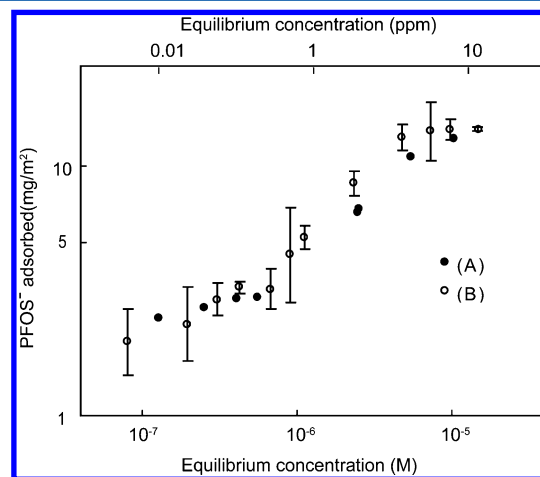

Figure 3. Isotherm of PFOS$^-$ adsorption onto sand (A) from ref 37 and (B) measured with ISE membranes consisting of a linear perfluorooligoether doped with anion-exchanger **1** (0.25 mM) and electrolyte salt **ES1** (5.0 mM). Data are averages for measurements with three or more electrodes.

measured with LC−MS from the literature. It shows a close correlation between the literature and the ISE data. As reported, this isotherm can be interpreted as a two-step phenomenon: a first level of saturation is reached near 0.50 ppm, and a second one occurs at 5.7 ppm. Considering the limited number of data points reported in ref 37, our values are acceptably close to the 0.40 ppm and 8.0 ppm thresholds reported there. Our observations are consistent with an explanation discussed in ref 37, which proposed that PFOS⁻ monolayer formation on sand may occur at lower concentrations, while hemimicelles[55] are formed at high concentrations. Moreover, the PFOS⁻ solid/liquid distribution coefficient, K_d, calculated from the data of this study is 2.46 ± 0.25 L/kg, which agrees well with the reported value from the literature.[37] To obtain a standard deviation for the latter, we refitted the data in Figure 3 from ref 37 and obtained 2.72 ± 0.35 L/kg.

Lake Water Application. To assess the usefulness of the developed method for PFO⁻/PFOS⁻ analysis in a real sample, the ISEs with LPFPE membranes doped with **1** (0.25 mM) and electrolyte salt **ES1** (5.0 mM), 10 nM PFOS⁻K⁺ in their outer filling solution, and 1.0 mM KCl in the inner filling solution (i.e., electrode setup A in Figure 1) were applied to detect PFOS⁻ in water samples collected from Carnegie Lake. This New Jersey lake has an average depth of only 9 ft and a history of nutrient pollution. The United States Environmental Protection Agency lists the water status of Carnegie Lake as impaired.[56] PFOS⁻ levels of the samples were found to be below the detection limit of the electrodes, which was not unexpected because Carnegie Lake is not near a major source of PFO⁻ and PFOS⁻ pollutants. To assess if compounds commonly present in these natural water samples—such as natural organic matter—interfere with the sensors' response, spiking with PFOS⁻ was performed. Because water collected from Carnegie Lake contains sand and other particulate matter and because surface adsorption of PFOS⁻ is known to occur (see previous section), the samples were filtered before use. The images of an unfiltered and a filtered sample along with an image of the filter after use illustrate the high level of undissolved matter (see the Supporting Information, Figure S5). Upon filtration, PFOS⁻ was spiked into the samples, and calibration curves for PFOS⁻ in the background provided by the lake samples were determined. Six replicate measurements were performed, and the PFOS⁻ calibration curves in the lake water matrix overlapped well with the ones measured in pure water. The switch from pure water to lake water resulted in changes in slopes and intercepts (E^0) of the calibration curves of only 0.01% ± 1.69% and 1.26% ± 5.22%, respectively (see the Supporting Information, Table S2). These differences are not statistically significant and show that these sensors can be used successfully for measurements in natural water samples. To assess the accuracy of the PFOS⁻ measurements in the spiked samples, PFOS⁻ recovery was determined by calculating PFOS⁻ concentrations from the emf values measured in the spiked lake water samples and the calibration curves determined in pure water. The measured PFOS⁻ concentrations were then compared to the concentrations expected from spiking. The average recovery was 95.5% ± 2.8% (see the Supporting Information, Table S3), which confirms the successful application of these sensors in lake water. As expected, interferences from anions commonly present in lake water, such as ClO_4^-, NO_3^-, Cl^-, HCO_3^-, and CH_3COO^-, were not observed since these sensors provide high selectivities

for PFOS⁻ (log $K_{PFOS^-,ClO_4^-}^{pot}$ = −6.0, log $K_{PFOS^-,NO_3^-}^{pot}$ = −7.8, log K_{PFOS^-,Cl^-}^{pot} = −9.3, log $K_{PFOS^-,HCO_3^-}^{pot}$ = −9.6, log $K_{PFOS^-,CH_3COO^-}^{pot}$ = −11.6).[25]

The interference from other perfluorinated anions differing only by the number of carbon atoms in their perfluoroalkyl group, such as perfluorohexanesulfonate (PFHxS⁻) and perfluorobutanesulfonate (PFBS⁻), needs to be taken into consideration when applying these sensors for real-sample analysis. Therefore, the potentiometric selectivity for PFOS⁻ over PFHxS⁻ and PFBS⁻ was determined, giving log $K_{PFOS^-,PFHxS^-}^{pot}$ as −1.91 ± 0.01 and log $K_{PFOS^-,PFBS^-}^{pot}$ as −3.19 ± 0.02. As expected on the basis of their higher hydrophobicity,[21] anions with a longer perfluoroalkyl chain were detected selectivity over anions with a shorter perfluoroalkyl chain. Therefore, interference from short-chain homologues of PFO⁻ and PFOS⁻ (which are commonly present in environmental samples at similar concentration levels)[57] and longer-chain homologues of PFO⁻ and PFOS⁻ (which are commonly present in samples at lower concentration levels)[57] is expected to be often minor.

CONCLUSION

By combining the advantages of fluorous membrane matrixes and 3DOM carbon solid contacts, i.e., enhanced selectivities and minimized transmembrane ion fluxes, respectively, detection limits for PFO⁻ and PFOS⁻ in the low-nanomolar range and below were achieved. The successful application of these ISEs to investigate in situ adsorption of PFOS⁻ onto sand and the detection of PFOS⁻ in water samples collected from Carnegie Lake represent the first uses of potentiometric PFOS⁻ sensors in real-life samples and demonstrate the usefulness of this method for environmental studies. This opens a venue to monitor PFO⁻ and PFOS⁻ continuously on site to study their transport and fate in the environment. Alternatively, quick and uncomplicated prescreening of large numbers of samples on site may be performed with these electrodes prior to the tedious and time-consuming off-site analysis of much smaller numbers of selected samples with conventional methods of analysis, such as LC−MS−MS. The latter would be indicated in particular in case of samples suspected to contain multiple perfluoroalkyl homologues differing in their chain length.

ASSOCIATED CONTENT

Ⓢ Supporting Information
(1) Structure formulas of **1**, **2**, **ES1**, and **ES2**, (2) materials and methods, (3) calibration curves and detection limits of electrodes based on **2** after conditioning in solutions with different concentrations of PFO⁻Na⁺, (4) detection limits and resistances for different fluorous membranes, (5) PFO⁻ responses measured with glass and polypropylene beakers, (6) potentiometric responses to PFOS⁻ in solutions with a 0.010 M KNO_3 background, (7) pictures of lake water samples and a used water filter, (8) (lack of) effect of lake water exposure on emf slope and intercept, and (9) mean recoveries and standard deviations for analyses of PFOS⁻ in Carnegie Lake water samples. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Giesy, J. P.; Kannan, K. *Environ. Sci. Technol.* **2001**, *35*, 1339.

(2) Kissa, E. *Fluorinated Surfactants and Repellants*, 2nd ed.; Marcel Dekker Inc.: New York, 2001.

(3) Kannan, K.; Koistinen, J.; Beckmen, K.; Evans, T.; Gorzelany, J. F.; Hansen, K. J.; Jones, O. P. D.; Helle, E.; Nyman, M.; Giesy, J. P. *Environ. Sci. Technol.* **2001**, *35*, 1593.

(4) Moody, C. A.; Martin, J. W.; Muir, D. C. G.; Mabury, S. A. *Environ. Sci. Technol.* **2002**, *36*, 545.

(5) Boulanger, B.; Vargo, J.; Schnoor, J. L.; Hornbuckle, K. C. *Environ. Sci. Technol.* **2004**, *38*, 4064.

(6) Houde, M.; De Silva, A. O.; Muir, D. C. G.; Letcher, R. J. *Environ. Sci. Technol.* **2011**, *45*, 7962.

(7) Huset, C. A.; Chiaia, A. C.; Barofsky, D. F.; Jonkers, N.; Kohler, H.-P. E.; Ort, C.; Giger, W.; Field, J. A. *Environ. Sci. Technol.* **2008**, *42*, 6369.

(8) Scott, B. F.; Moody, C. A.; Spencer, C.; Small, J. M.; Muir, D. C. G.; Mabury, S. A. *Environ. Sci. Technol.* **2006**, *40*, 6405.

(9) Kuklenyik, Z.; Reich, J. A.; Tully, J. S.; Needham, L. L.; Calafat, A. M. *Environ. Sci. Technol.* **2004**, *38*, 3698.

(10) Voogt, P. d.; Sáez, M. *Trends Anal. Chem.* **2006**, *25*, 326.

(11) Larsen, B. S.; Kaiser, M. A. *Anal. Chem.* **2007**, *79*, 3966.

(12) Alzaga, R.; Bayona, J. M. *J. Chromatogr., A* **2004**, *1042*, 155.

(13) Berger, U.; Langlois, I.; Oehme, M.; Kallenborn, R. *Eur. J. Mass Spectrom.* **2004**, *10*, 579.

(14) Risha, K.; Flaherty, J.; Wille, R.; Buck, W.; Morandi, F.; Isemura, T. *Anal. Chem.* **2005**, *77*, 1503.

(15) Furdui, V. I.; Crozier, P. W.; Reiner, E. J.; Mabury, S. A. *Chemosphere* **2008**, *73*, S24.

(16) Saito, K.; Uemura, E.; Ishizaki, A.; Kataoka, H. *Anal. Chim. Acta* **2010**, *658*, 141.

(17) Morf, W. E. *The Principles of Ion-selective Electrodes and of Membrane Transport*; Elsevier: New York, 1981.

(18) Bobacka, J.; Ivaska, A.; Lewenstam, A. *Chem. Rev.* **2008**, *108*, 329.

(19) Bühlmann, P.; Chen, L. D. Ion-Selective Electrodes With Ionophore-Doped Sensing Membranes. In *Supramolecular Chemistry: From Molecules to Nanomaterials*; Gale, P. A., Steed, J. W., Eds.; Wiley: New York, 2012; p 2539.

(20) Bakker, E.; Bühlmann, P.; Pretsch, E. *Chem. Rev.* **1997**, *97*, 3083.

(21) Gladysz, J. A.; Curran, D. P.; Horváth, I. T. *Handbook of Fluorous Chemistry*; Wiley/VCH: Weinheim, Germany, 2004.

(22) Horváth, I. T.; Rábai, J. *Science* **1994**, *266*, 72.

(23) Jing, P.; Rodgers, P. J.; Amemiya, S. *J. Am. Chem. Soc.* **2009**, *131*, 2290.

(24) Boswell, P. G.; Anfang, A. C.; Bühlmann, P. *J. Fluorine Chem.* **2008**, *129*, 961.

(25) Chen, L. D.; Mandal, D.; Gladysz, J. A.; Bühlmann, P. *New J. Chem.* **2010**, *34*, 1867.

(26) Chen, L. D.; Mandal, D.; Pozzi, G.; Gladysz, J. A.; Bühlmann, P. *J. Am. Chem. Soc.* **2011**, *133*, 20869.

(27) Ceresa, A.; Bakker, E.; Hattendorf, B.; Günther, D.; Pretsch, E. *Anal. Chem.* **2001**, *73*, 343.

(28) Sokalski, T.; Ceresa, A.; Zwickl, T.; Pretsch, E. *J. Am. Chem. Soc.* **1997**, *119*, 11347.

(29) Qin, W.; Zwickl, T.; Pretsch, E. *Anal. Chem.* **2000**, *72*, 3236.

(30) Ceresa, A.; Radu, A.; Peper, S.; Bakker, E.; Pretsch, E. *Anal. Chem.* **2002**, *74*, 4027.

(31) Crespo, G. A.; Macho, S.; Rius, F. X. *Anal. Chem.* **2008**, *80*, 1316.

(32) Lai, C.-Z.; Joyer, M. M.; Fierke, M. A.; Petkovich, N. D.; Stein, A.; Bühlmann, P. *J. Solid State Electrochem.* **2009**, *13*, 123.

(33) Lai, C.-Z.; Fierke, M. A.; Correa da Costa, R.; Gladysz, J. A.; Stein, A.; Bühlmann, P. *Anal. Chem.* **2010**, *82*, 7634.

(34) Lai, C.-Z.; Fierke, M. A.; Stein, A.; Bühlmann, P. *Anal. Chem.* **2007**, *79*, 4621.

(35) Fierke, M. A.; Lai, C.-Z.; Bühlmann, P.; Stein, A. *Anal. Chem.* **2010**, *82*, 680.

(36) Plassmann, M. M.; Meyer, T.; Lei, Y. D.; Wania, F.; McLachlan, M. S.; Berger, U. *Environ. Sci. Technol.* **2011**, *45*, 6872.

(37) Johnson, R. L.; Anschutz, A. J.; Smolen, J. M.; Simcik, M. F.; Penn, R. L. *J. Chem. Eng. Data* **2007**, *52*, 1165.

(38) McNamee, C. E.; Matsumoto, M.; Hartley, P. G.; Mulvaney, P.; Tsujii, Y.; Nakahara, M. *Langmuir* **2001**, *17*, 6220.

(39) Xiao, F.; Zhang, X. R.; Penn, L.; Gulliver, J. S.; Simcik, M. F. *Environ. Sci. Technol.* **2011**, *45*, 10028.

(40) Mandal, D.; Jurisch, M.; Consorti, C. S.; Gladysz, J. A. *Chem.— Asian J.* **2008**, *3*, 1772.

(41) Lai, C.-Z.; Reardon, M. E.; Boswell, P. G.; Bühlmann, P. *J. Fluorine Chem.* **2010**, *131*, 42.

(42) Guilbault, G. G.; Durst, R. A.; Frant, M. S.; Freiser, H.; Hansen, E. H.; Light, T. S.; Pungor, E.; Rechnitz, G. A.; Rice, N. M.; Rohm, T. J.; Simon, W.; Thomas, J. D. R. *Pure Appl. Chem.* **1976**, *48*, 127.

(43) Buck, R. P.; Lindner, E. *Pure Appl. Chem.* **1994**, *66*, 2527.

(44) Bakker, E.; Pretsch, E.; Bühlmann, P. *Anal. Chem.* **2000**, *72*, 1127.

(45) Bühlmann, P.; Yajima, S.; Tohda, K.; Umezawa, Y. *Electrochim. Acta* **1995**, *40*, 3021.

(46) Bühlmann, P.; Yajima, S.; Tohda, K.; Umezawa, K.; Nishizawa, S.; Umezawa, Y. *Electroanalysis* **1995**, *7*, 811.

(47) Lindner, E.; Tóth, K.; Pungor, E. *Dynamic Characteristics of Ion-Selective Electrodes*; CRC Press: Boca Raton, FL, 1988.

(48) Feth, J. H. *Chloride in Natural Continental Water—A Review*; U.S. Geological Survey Water Supply Paper 2176; United States Government Printing Office: Washington, DC, 1981.

(49) Bühlmann, P.; Pretsch, E.; Bakker, E. *Chem. Rev.* **1998**, *98*, 1593.

(50) *Demnum data sheet*; Daikin Industries: Osaka, Japan, May 2009.

(51) Lai, C.-Z.; Koseoglu, S. S.; Lugert, E. C.; Boswell, P. G.; Rábai, J.; Lodge, T. P.; Bühlmann, P. *J. Am. Chem. Soc.* **2009**, *131*, 1598.

(52) Chumbimuni-Torres, K. Y.; Rubinova, N.; Radu, A.; Kubota, L. T.; Bakker, E. *Anal. Chem.* **2006**, *78*, 1318.

(53) Konopka, A.; Sokalski, T.; Lewenstam, A.; Maj-Zurawska, M. *Electroanalysis* **2006**, *18*, 2232.

(54) Martin, J. W.; Berger, U.; Voogt, P. D.; Field, J. A.; Franklin, J.; Giesy, J. P.; Harner, T.; Muir, D. C. G.; Scott, B.; Kaiser, M.; Järnberg, U.; Jones, K. C.; Mabury, S. A.; Schroeder, H.; Simcik, M.; Sottani, C.; van Bavel, B.; Kärrman, A.; Lindstrom, G.; Leeuwen, S. V. *Environ. Sci. Technol.* **2004**, *38*, 248A.

(55) Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*, 2nd ed.; John Wiley & Sons: New York, 2003.

(56) U.S. Environmental Protection Agency. http://www.epa.gov/waters/305b/index.html (accessed Aug 11, 2012).

(57) Furdui, V. I.; Crozier, P. W.; Reiner, E. J.; Mabury, S. A. *Chemosphere* **2008**, *73*, S24.