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Remediation of Perfluorooctylsulfonate Contamination by in Situ Sequestration: Direct Monitoring of PFOS Binding to Polyquaternium Polymers

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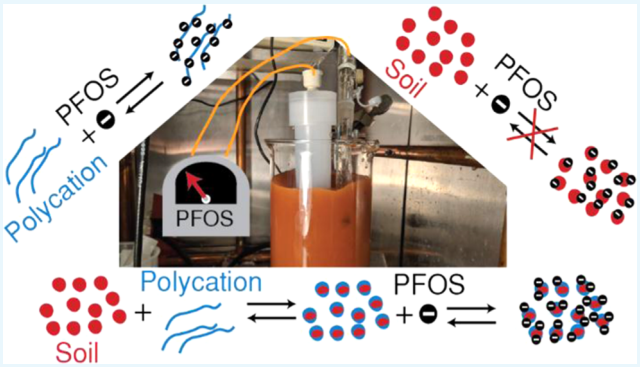
Supporting Information

ABSTRACT: In situ methods for the sequestration of perfluorooctyl-1-sulfonate (PFOS) that are based on PFOS binding to polyquaternium polymers were reported previously, providing an approach to immobilize and concentrate PFOS in situ. To apply these methods in real life, the concentrations of polymers that permit efficient sequestration must be determined. This is only possible if the stoichiometry and strength of PFOS binding to polyquaternium polymers are known. Here, we report on the use of fluorous-phase ion-selective electrodes (ISEs) to determine the equilibrium constants characterizing binding of PFOS to poly(dimethylamine-*co*-epichlorohydrin) and poly(diallyldimethylammonium) in simulated groundwater and in soil suspensions. We introduce a new method to interpret potentiometric data for surfactant binding to the charged repeat unit of these polyions by combining a 1:1 binding model with the ISE response model. This allows for straightforward prediction and fitting of experimental potentiometric data in one step. Data fit the binding model for poly(diallyldimethylammonium) and poly(dimethylamine-*co*-epichlorohydrin) chloride in soil-free conditions and in the presence of soil from Tinker Air Force Base. When the total PFOS concentration in a soil system is known, knowledge of these PFOS binding characteristics permits quantitative prediction of the mobile (free) and polymer-bound fractions of PFOS as a function of the concentrations of the polyquaternium polymer. Because the technique reported here is based on the selective in situ determination of the free ionic surfactant, we expect it to be similarly useful for determining the sequestration of a variety of other ionic pollutants.



INTRODUCTION

Per- and polyfluoroalkyl substances (PFASs) are compounds in which all or the majority of the hydrogen atoms are replaced by fluorine.[1] They typically comprise a long hydrophobic perfluoroalkyl chain (C_4−C_{16}), which makes them chemically very stable[2,3] and strongly hydrophobic.[4] These unique properties led to the extensive use of PFASs in industrial and consumer products.[5,6] Consequently, thousands of tons of PFASs have been produced annually since the 1950s.[7] It was only in 2001 that the distribution of some of these PFASs in the environment all across the globe was discovered.[8] In particular, perfluorooctanesulfonic acid (PFOS) has been found to be one of the most prevalent PFASs in the environment, leading to health advisories for drinking water by the Environmental Protection Agency (EPA) and much continued study.[6,7,9] Because the elimination half-life of PFOS in humans is 5.4 years, the removal of even trace concentrations of this compound from the environment is important.[7,10]

Numerous studies have been conducted to determine the best strategies for PFOS sequestration or degradation, including sorptive removal,[11−13] flocculation,[14] and oxidative,[15] reductive,[16] thermal,[17] and microbial degradation.[18] One of the approaches for in situ sequestration of PFOS from groundwater is based on binding of PFOS to positively charged functional groups.[14] Polyquaternium polymers, which are polycationic polymers that are often added to water to remove organic and inorganic anions by coagulation,[19] are also suited for PFOS sequestration. Advantages of their use are their low cost, the ability to inject these polymers as solutions into the subsurface, the rapid reduction in aqueous phase PFOS, and the in situ application.[20] Because there are currently no efficient techniques available for in situ destruction of PFOS, polymer sequestrants are an attractive approach to stop expanding PFAS plumes, effectively immobilizing PFOS.

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Two polyquaternium polymers have been used to bind PFOS by electrostatic and nonpolar interactions.[20,21] Importantly, it was shown that these polyquaternium polymers bind to Ottawa sand and to soil from Tinker Air Force Base (Oklahoma City, Oklahoma), which immobilizes the PFOS–polymer aggregates and thereby results in effective containment. Although the sequestration of PFOS to Ottawa sand-bound polyquaternium polymers was studied to determine the quantity of PFOS that can be retained,[20] a quantitative understanding of PFOS binding to these polymers and to polymer–soil aggregates under environmental conditions has been lacking. Therefore, to understand model and design remediation strategies that use polyquaternium polymers as PFOS sequestrants, the binding interactions between PFOS and these polycations have been studied in this work.

Interactions of nonfluorinated surfactants and polymers have been studied since the early 1970's.[22−28] A few of these investigations implemented ion-selective electrodes (ISEs) as the chemical sensors to determine the fraction of freely dissolved surfactants coexisting with surfactants bound to polyelectrolytes.[25−27] Because ISEs measure selectively only the activity of freely dissolved ions and allow for in situ measurements even in turbid soil suspensions where many spectroscopic techniques fail, they are an excellent choice for such studies.[28,29] Moreover, in situ measurements using ISEs inherently avoid sample preparation that is typical of liquid chromatography and is often associated with artefacts due to surfactant adsorption to container and filter surfaces. Also, in situ ISE measurements are not affected by equilibrium shifts that result from changes in volumes and solvents in the course of ex situ analysis. In this context, various models have been proposed to quantify binding of surfactants to polyions, including models according to which the surfactants bind with a 1:1 stoichiometry to the individual charged repeat units of the polyions, as well as models involving cooperative binding.[22−24]

In this study, we found that a 1:1 binding model that does not invoke cooperativity accurately describes the binding interactions between PFOS and the individual repeat units of poly(dimethylamine-*co*-epichlorohydrin), **1**, and poly(diallyldimethylammonium), **2**, which each carry a positive charge (see Figure 1). These polyquaternium polymers are

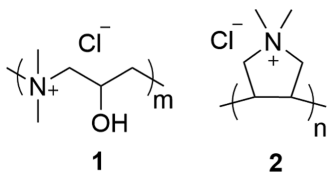

Figure 1. Repeat unit structures of poly(dimethylamine-*co*-epichlorohydrin) chloride, **1**, and poly(diallyldimethylammonium) chloride, **2**.

good candidates for sequestration of PFOS because they have a high charge density and a hydrophobic backbone and side chains. To measure free PFOS in the presence of these polymers using an ISE with a fluorous membrane, a fluorophilic imidazolium cation was synthesized for use as an anion-exchange site. Fluorous-phase ISEs have been shown before to have excellent selectivity for PFOS over other anions,[30] but anion-exchange sites used previously to prepare such ISEs were found to undergo oxidation, limiting the detection limits, and long-term stability of such sensors.[31] The newly prepared imidazolium anion-exchange site provides stable sensor responses, and the fluorous-phase membranes prepared therewith show very high selectivities for PFOS over both carbonate and bicarbonate, which allows for direct monitoring of PFOS binding. To simulate environmental conditions, binding of PFOS to the polyquaternium polymers was also measured in the presence of soil from Tinker Air Force Base, demonstrating the applicability of ISEs for such measurements. Because interactions of polyquaternium polymers and soil from Tinker Air Force Base have been reported previously,[21] equilibrium constants as determined in this work can be used to model the amount of polyquaternium polymers needed to sequester a desired amount of PFOS under environmentally relevant conditions.

THEORY

Response Mechanism of PFOS–Selective Electrodes. ISEs are sensors that detect the concentration of target ions within a given sample solution by current-free measurements of the electrical potential, E, with respect to a reference electrode. The key component of the ISE is the ion-selective membrane, which is in direct contact with the sample. Any change in the measured potential (that is, E) is the direct result of a change in the phase boundary potential, $\Delta\Phi_{PB}$, at the interface of the sample and the ion-selective membrane. The latter is given as follows for a PFOS–selective electrode

$$\Delta\Phi_{PB} = \Phi^{o} - \frac{RT}{zF}\ln(a_{PFOS,sample}/a_{PFOS,mem}) \quad (1)$$

where R is the ideal gas constant, T is the temperature, F is Faraday's constant, Φ^{o} is a constant that depends on PFOS and the nature of the PFOS–selective membrane, z is the charge of PFOS, and $a_{PFOS,sample}$ and $a_{PFOS,mem}$ are the activities of PFOS within the sample and the membrane phase, respectively. Under conditions in which $a_{PFOS,mem}$ does not depend on $a_{PFOS,sample}$, eq 1 can be simplified to

$$\Delta\Phi_{PB} = \Delta\Phi^{o'} - \frac{RT}{zF}\ln a_{PFOS,sample} \quad (2)$$

which shows that the measured potential depends linearly on the logarithm of the activity of PFOS within the sample. The essence of making a good PFOS–selective electrode is, therefore, (i) to choose a membrane material that permits selective transfer of PFOS into the ISE membrane and (ii) to make $a_{PFOS,mem}$ independent of the sample. The latter is typically achieved by inclusion into the membrane matrix of strongly hydrophobic cations (commonly referred to as cationic sites).

For the work presented here, PFOS–selective membranes were doped with the fluorophilic salt **3**. Prior to their first use for measurements in samples of interest, the membranes were immersed into a potassium perfluorooctyl-1-sulfonate (KPFOS) solution, resulting in the transfer of PFOS into the fluorous sensing membrane in exchange for iodide transferring from the membrane into the aqueous phase. This process is referred to as conditioning and has to be performed with every new electrode. Conditioning loads the bulk of the PFOS–selective membrane with a constant concentration of PFOS that equals the concentration of fluorophilic cations. When the PFOS–selective electrode is subsequently immersed into samples that contain different concentrations of PFOS, this does not affect the composition of the membrane bulk, but it affects ion concentrations in the nanometer-thin charge

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separation layer at the interface of the sample and the PFOS−selective membrane (see Figure 2). The charge separation at this interface is the cause of the phase boundary potential, $\Delta\Phi_{PB}$. Interested readers are referred to tutorials and reviews on ISEs.[32,35,36]

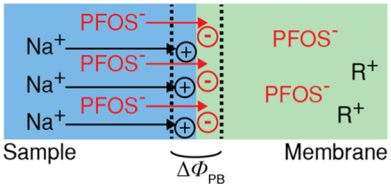

Figure 2. Illustration of the charge separation and phase boundary potential, $\Delta\Phi_{PB}$, at the interface of a PFOS−selective membrane and an aqueous sample solution. R^+ represents fluorophilic cationic sites confined to the sensing membrane.

Binding of PFOS to Polyquaternium Polymers and Sensor Response Model. Binding models that describe 1:1 binding of surfactants to the individual charged repeat units of polyions were reported previously.[24,25,27] Here, we present a new method to interpret potentiometric data for surfactant binding to the charged repeat unit of polyions by combining the 1:1 binding model with the ISE response model presented in the prior section. This allows for straightforward prediction and fitting of experimental potentiometric data in one step, avoiding more cumbersome initial calculations of bound and free concentrations of the surfactant ion, followed by fitting of binding isotherms, as previously suggested.[24,37] This streamlined approach is described in the following for PFOS as the species detected selectively by the ISEs.

Binding of PFOS to the charged units of the polyquaternium polymers in a 1:1 stoichiometry is described by the following reaction

$$[\mathrm{PFOS}]_{\mathrm{free}} + [\mathrm{R}]_{\mathrm{free}} \leftrightarrows [\mathrm{PFOS{\cdot}R}] \tag{3}$$

where $[\mathrm{PFOS}]_{\mathrm{free}}$ is the concentration of free PFOS within the sample solution, $[\mathrm{R}]_{\mathrm{free}}$ is the concentration of free charged polymer repeat units, and [PFOS·R] represents a section of the polymer with a bound PFOS molecule. This equilibrium is characterized by the binding constant, K

$$K = [\mathrm{PFOS{\cdot}R}]/([\mathrm{PFOS}]_{\mathrm{free}}[\mathrm{R}]_{\mathrm{free}}) \tag{4}$$

To relate K to experimental data, the terms $[\mathrm{PFOS}]_{\mathrm{free}}$ and $[\mathrm{R}]_{\mathrm{free}}$ must be replaced with known parameters or experimental observables, i.e., the total PFOS concentration, $[\mathrm{PFOS}]_{\mathrm{total}}$, and the total concentration of free charged polymer repeat units, $[\mathrm{R}]_{\mathrm{total}}$. As shown in the Supporting Information, solving the combination of eqs 3 and 4 gives $[\mathrm{PFOS}]_{\mathrm{free}}$ as follows

$$[\mathrm{PFOS}]_{\mathrm{free}} = (-1 + K[\mathrm{PFOS}]_{\mathrm{total}} - K[\mathrm{R}]_{\mathrm{total}} + \sqrt{4K[\mathrm{PFOS}]_{\mathrm{total}} + (1 - K[\mathrm{PFOS}]_{\mathrm{total}} + K[\mathrm{R}]_{\mathrm{total}})^2})/(2K) \tag{5}$$

Equation 5 describes $[\mathrm{PFOS}]_{\mathrm{free}}$ in a system where $[\mathrm{PFOS}]_{\mathrm{total}}$ and $[\mathrm{R}]_{\mathrm{total}}$ can be experimentally controlled, leaving only the binding constant, K, as a variable.

As it follows from eq 2, the response of an ISE for PFOS in its working range is given as[32]

$$E = E^{\circ} + \frac{RT}{zF}\ln a_{\mathrm{PFOS}} \tag{6}$$

where E° is the standard potential of the electrochemical cell (including contributions from the reference electrode and the liquid junction between the reference electrode and the sample).[38,39] For the experiments described below, the ionic strength is dominated by the 10 mM $NaHCO_3$ used to simulate groundwater, allowing us to simplify eq 6 by assuming a constant activity coefficient for PFOS, which can, therefore, be combined with E° into a new constant $E^{\circ\prime}$

$$E = E^{\circ\prime} + \frac{RT}{zF}\ln[\mathrm{PFOS}]_{\mathrm{free}} \tag{7}$$

Finally, insertion of the right-hand side of eq 5 for $[\mathrm{PFOS}]_{\mathrm{free}}$ into eq 7 gives

$$E = E^{\circ\prime} + \frac{RT}{zF}\ln((-1 + K[\mathrm{PFOS}]_{\mathrm{total}} - K[\mathrm{R}]_{\mathrm{total}} + \sqrt{4K[\mathrm{PFOS}]_{\mathrm{total}} + (1 - K[\mathrm{PFOS}]_{\mathrm{total}} + K[\mathrm{R}]_{\mathrm{total}})^2})/2K) \tag{8}$$

Equation 8 shows that for a given $[\mathrm{R}]_{\mathrm{total}}$, the stronger PFOS binds to the polymer, the lower the PFOS concentration that is detected, and because of the negative charge of PFOS ($z = -1$), the higher E becomes. For a fixed total concentration of PFOS, eq 5 predicts that the concentration of $[\mathrm{PFOS}]_{\mathrm{free}}$ decreases continuously as the concentration of $[\mathrm{R}]_{\mathrm{total}}$ increases, and eq 8 shows that E increases (see Figure S5).

However, the fluorous ISEs used for this work have a lower limit of detection (i.e., the lowest concentration that can be detected) that is determined by very small fluxes of KPFOS from the inner filling solution across the sensing membrane into the sample solution, locally contaminating samples at their interface to the sensing membrane of the ISE with PFOS.[40] This prevents E from increasing without end, as it is predicted by eq 8,[29] and it results in a lower limit of detection for PFOS that is determined by the KPFOS flux and therefore unaffected by (i) the concentration and/or pH of the bicarbonate buffer used and (ii) the amount of HCl used to adjust the pH. To account for this quantitatively, it is also important to recognize that the ISE's limit of detection is lowered (i.e., improved) when polyquaternium polymer is added to the aqueous sample. This can be explained by binding of this polyquaternium polymer to the PFOS that is leaching continuously at very low concentrations out of the sensing membrane into the sample (referred to here as $[\mathrm{PFOS}]_{\mathrm{limit}}$). To account for this in the fitting model, an additional term, $[\mathrm{PFOS}]_{\mathrm{limit}}$, is added to eq 8, giving

$$E = E^{\circ\prime} + \frac{RT}{zF}\ln([\mathrm{PFOS}]_{\mathrm{limit}} + (-1 + K[\mathrm{PFOS}]_{\mathrm{total}} - K[\mathrm{R}]_{\mathrm{total}} + \sqrt{4K[\mathrm{PFOS}]_{\mathrm{total}} + (1 - K[\mathrm{PFOS}]_{\mathrm{total}} + K[\mathrm{R}]_{\mathrm{total}})^2})/2K) \tag{9}$$

ISE response curves as predicted using eq 9 are presented in Figure 3.

As Figure 3 shows, the ISE's response at low polyquaternium polymer concentrations is unaffected by the inclusion of $[\mathrm{PFOS}]_{\mathrm{limit}}$. However, at high polyquaternium polymer concentrations (i.e., low concentrations of PFOS in the bulk of the aqueous sample), E does not continue to increase continuously, as predicted by eq 8 and shown in Figure S5. The plateau at high polymer concentrations is the result of the limit of detection of the PFOS ISE. Equation 9 was used to fit all experimental data discussed in the following.

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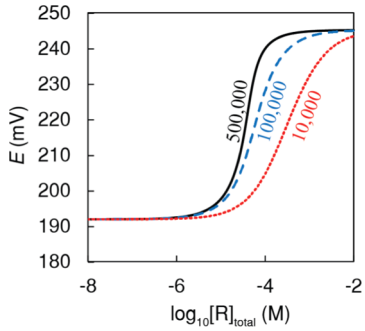

Figure 3. Predicted measured potential, E, versus the logarithm of the total polyquaternium polymer concentration. Black, blue, and red traces are predicted for $[PFOS]_{total}$ = 41.6 μM, $E^{o\prime}$ = −63.8 mV, $[PFOS]_{limit}$ = 6 μM, and the values of 10^4, 10^5, and 5×10^5 M^{-1}, of the binding constants, K, as indicated in the figure. Note that the numerical values for the former three parameters were obtained from fits of data shown in Figure 4.

RESULTS AND DISCUSSION

Equilibrium Constants for Binding of PFOS to Polyquaternium Polymers in Absence of Soil. Data collected during additions of KPFOS to 10 mM sodium bicarbonate solutions were used to experimentally determine the standard potential, $E^{o\prime}$ (Figure 4).

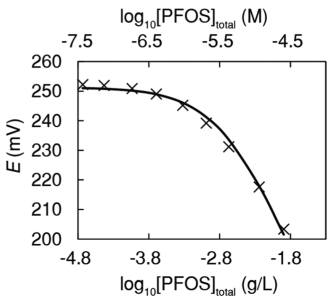

Figure 4. E values measured during the addition of KPFOS to a 10 mM $NaHCO_3$ solution (×) and a fit (solid line) based on the Nikolskii−Eisenman equation[41] (see Supporting Information for more details).

The highest concentration of PFOS used for sensor calibrations was limited by the concentration of the PFOS solution used for these additions, which was kept below the solubility limit of PFOS (1.3 mM).[9] Polyquaternium polymer was then added to the sample solution, which caused E to increase as $[PFOS]_{free}$ decreased. Figure 5 shows data characteristic of the addition of poly(dimethylamine-*co*-epichlorohydrin) and poly(diallyldimethylammonium) to PFOS-containing solutions. The experimental data exhibit the same trend as predicted by eq 9 and Figure 3, where E rises with increasing polyquaternium polymer concentrations. For clarity, data for two fits of polyquaternium polymer additions to a solution of constant $[PFOS]_{total}$ are presented (for a more comprehensive set of data, see Figures S6 and S7).

Data for addition of either poly(diallyldimethylammonium) or poly(dimethylamine-*co*-epichlorohydrin) into solutions of constant $[PFOS]_{total}$ were collected with three separate ISEs. Equilibrium constants for binding of PFOS to poly(diallyldimethylammonium) chloride and poly(dimethylamine-*co*-epichlorohydrin) were calculated to be 2.7 ± 0.6 × 10^5 and 6.4 ± 0.7 × 10^5 M^{-1}, respectively (95% confidence intervals). A similar equilibrium constant for binding of the longer but nonfluorinated molecule 1-decylsulfonate to poly(L-lysine)[24] at neutral pH was reported to be 2 × 10^5 M^{-1}. Equilibrium constants for PFOS binding to solid surfaces such as powdered multiwalled carbon nanotubes[42] and alumina[43] measured using liquid chromatography−mass spectrometry (LC−MS) techniques have been reported as 2.9 × 10^6 and 3.1 × 10^7 M^{-1}, respectively. In addition, these techniques report adsorption capacities of 5.2 × 10^{-3} g PFOS/g multiwalled carbon nanotubes and 2.2 × 10^{-5} g PFOS/g alumina, respectively. For comparison, the binding of one PFOS molecule to each polymer repeat unit results in 3.08 g PFOS/g poly(diallyldimethylammonium) and 3.63 g PFOS/g poly(dimethylamine-*co*-epichlorohydrin). In view of environmental remediation, the applicability of polyquaternium polymers as solutions and the high mass efficiency in the use of polyquaternium polymers as compared to other adsorbents may be advantageous.

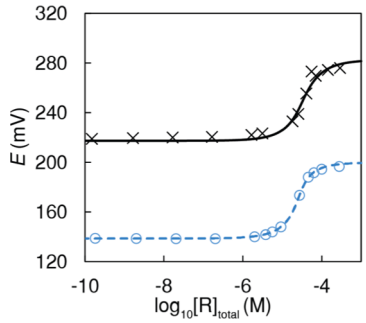

Figure 5. E values measured during the addition of poly(diallyldimethylammonium) (black ×) or poly(dimethylamine-*co*-epichlorohydrin) (blue circles) to a 25.4 μM KPFOS solutions (10 mM $NaHCO_3$, pH = 7). The black and dashed blue lines represent fits of the experimental data fitted based on eq 9.

Effect of Soil on Systems Containing Polyquaternium and PFOS. To more closely simulate environmental conditions that are relevant to PFOS sequestration from an environmentally relevant sample, soil from Tinker Air Force Base was first equilibrated for 1 week with polyquaternium polymers in an aqueous solution that contained 10 mM $NaHCO_3$ (adjusted to pH = 7). Then, the blend of soil and polymer was added (by stepwise addition from an aqueous mixture) to buffered solutions that contained PFOS. For the interpretation of such an experiment, in addition to PFOS binding to the polymer (eq 3), three additional equilibria were initially considered to either directly or indirectly affect the concentration of freely dissolved PFOS (i.e., PFOS bound neither to soil nor polymer)

$$[PFOS]_{free} + [soil] \leftrightarrows [soil{\cdot}PFOS] \quad (10)$$

$$[R]_{free} + [soil] \leftrightarrows [soil{\cdot}R] \quad (11)$$

$$[soil{\cdot}R] + [PFOS]_{free} \leftrightarrows [soil{\cdot}R{\cdot}PFOS] \quad (12)$$

Although PFOS is known to bind certain types of soil,[44] we found that in the absence of polyquaternium polymers, PFOS does not bind to soil from Tinker Air Force Base when buffered soil mixtures were added into solutions with $[PFOS]_{total}$ = 0.35 mM, resulting in soil concentrations as high as 14.7 g soil/L (Table S1). Measured E values during the addition of soil remained constant within ±1 mV, indicating that even at the high concentration of $[PFOS]_{total}$, which

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should promote binding, $[PFOS]_{free}$ did not change. Would PFOS binding to soil have been observed, the equilibrium described by eq 10 could have been studied in detail using the presented technique. However, for this work, there was no need to consider this additional equilibrium reaction. Therefore, equilibrium constants for binding of PFOS to polyquaternium polymers in the absence of soil (eq 3) were determined quantitatively as discussed in the previous section considering only the equilibria described by eqs 11 and 12. Binding of polyquaternium polymers to soil (eq 11) from Tinker Air Force Base has been studied in detail in a previous study for the same conditions used here.[20] This binding leads to a reduction of the concentration of the polymer in solution. However, soil-bound polymer still binds PFOS (eq 12), although with an affinity expected to be different from that of the dissolved polymer.

Experimental data for PFOS binding to polymer−soil mixtures as a function of the polymer concentration are shown in Figures 6, S8, and S9, along with sensor responses predicted using the binding constants determined for soil-free conditions.

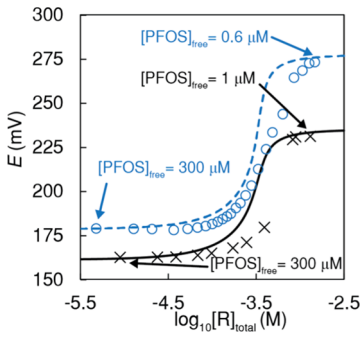

Figure 6. Evidence for polymer binding to soil: experimental E values collected during the addition of a poly(diallyldimethylammonium)/soil mixture (black ×) or a poly(dimethylamine-*co*-epichlorohydrin)/soil mixture (blue circles) to a 300 μM KPFOS solution (10 mM $NaHCO_3$, pH = 7). The solid black and dashed blue lines are predictions for PFOS binding to the polymer if soil was absent (K = 2.7×10^5 and 6.4×10^5 M^{-1}, respectively).

For each polyquaternium polymer, the concentration of polymer required to bind a given amount of PFOS increased as a result of the presence of soil. In addition, in the plots of $\log_{10}[PFOS]_{free}$ versus $\log_{10}[R]_{total}$, the onset of binding at $[R]_{total} \approx 10^{-3.5}$ M is characterized by a smaller slope (more pronounced for poly(dimethylamine-*co*-epichlorohydrin)), indicating reduced binding constants of PFOS to the polycationic polymer (see Figure 3). Moreover, the onset of the binding region moved to higher polymer concentrations (i.e., $\log_{10}[R]_{total}$), resulting in a shift of the entire response to the right (see Figure S10 for further illustration).

To fit the experimental data, we used previously reported[20,21] information about binding of polyquaterniums polymers to the same Tinker Air Force Base soil samples as used in this study. Specifically, it was known from the work that 97.9 and 98.5% of poly(diallyldimethylammonium) chloride and poly(dimethylamine-*co*-epichlorohydrin), respectively, are bound to this type of soil at the same concentrations we used in this study. With the vast majority of each polymer bound to soil, and considering the equilibrium constants for PFOS binding to the polycationic polymers determined for soil-free conditions, it follows that the concentration of charged repeat units free in solution is not large enough to bind a significant amount of PFOS (<2% of the total PFOS bound) for the concentration range of $\log_{10}[R]_{total}$ shown in Figure 6. Therefore, it can be concluded that PFOS binds predominantly to soil-bound polymer, resulting in soil/polymer/PFOS aggregates. Experimental data were fitted to eq 9 using the concentration of charged repeat units bound to soil, i.e., 97.9 or 98.5% of the total concentration of poly(diallyldimethylammonium) chloride and poly(dimethylamine-*co*-epichlorohydrin), respectively. Data and fits characteristic of this binding are presented in Figure 7

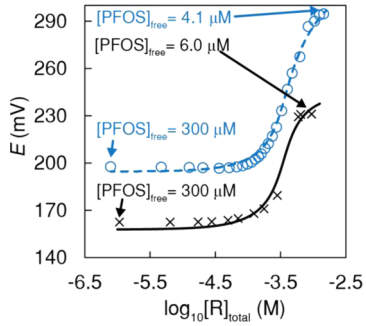

Figure 7. E values measured during the addition of soil-bound poly(diallyldimethylammonium) (black ×) or poly(dimethylamine-*co*-epichlorohydrin) (blue circles) to a 300 μM KPFOS solutions (10 mM $NaHCO_3$, pH = 7). The black and dashed blue lines represent fits of the experimental data fitted based on eq 9.

(for full sets of data, see Figures S11 and S12). Equilibrium constants for binding of PFOS to soil-bound poly(diallyldimethylammonium) chloride and poly(dimethylamine-*co*-epichlorohydrin) were determined to be $9.3 \pm 0.6 \times 10^4$ and $7.3 \pm 1.2 \times 10^4$ M^{-1}, respectively (95% confidence intervals). For comparison, binding constants, measured by LC−MS, of PFOS to sand-bound poly(diallyldimethylammonium) chloride and poly(dimethylamine-*co*-epichlorohydrin) were reported to be an order of magnitude weaker, with $K = 3.1 \times 10^3$ and 1.6×10^3, respectively[20] (the affinity of the polyquaternium polymer to sand was stronger than its affinity for soil from Tinker Air Force Base).

In the presence of soil, binding constants decreased 3-fold and 9-fold for poly(diallyldimethylammonium) chloride and poly(dimethylamine-*co*-epichlorohydrin), respectively, as compared to the corresponding soil-free systems. Although these binding constants are noticeably reduced, the PFOS that is bound to polymer is retained on soil particles, is no longer mobile, and can be employed to contain groundwater contaminant plumes. Importantly, the thus determined binding constants can be used to model quantitatively real-life sequestration of PFOS.

Prediction of the Effect of Polyquaternium Polymer Concentrations on the Efficiency of PFOS Sequestration. The equilibrium constants determined for PFOS binding to poly(diallyldimethylammonium) chloride and poly(dimethylamine-*co*-epichlorohydrin) in soil-containing samples can also be used to determine the concentrations of polyquaternium polymers needed to bind a targeted fraction of PFOS. To illustrate this graphically, a three-dimensional plot is presented in Figure 8.

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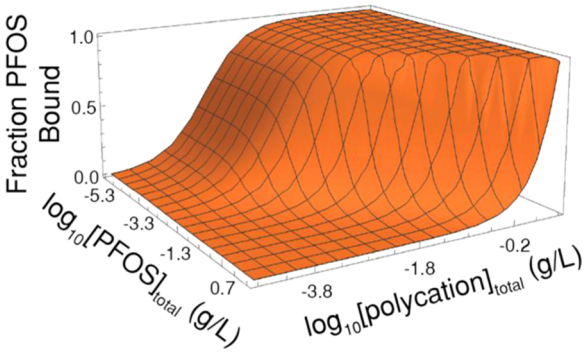

Figure 8. Three-dimensional plot showing the fraction of sequestered PFOS as a function of the total soil-bound polymer and total PFOS concentrations (calculated for $K = 9.3 \times 10^4$ M^{-1}), where $\log_{10}[\text{polycation}]_{total}$ is the concentration of poly(diallyldimethylammonium) in g/L.

As Figure 8 illustrates, the fraction of PFOS bound to the polycationic polymer in a given system strongly depends both on $[\text{PFOS}]_{total}$ and the total polymer concentration. As the concentration of PFOS increases, an increasing amount of polyquaternium polymer must be added to ensure near complete binding of PFOS to soil (Table S2). As the desired fraction of bound PFOS increases, there is diminishing returns for any additional polymer added to the system. The bound fraction of PFOS, as illustrated in Figure 8, is important because it illustrates the effectiveness of PFOS removal from the environment. However, the concentration of PFOS that remains freely dissolved in solution is also important, as it provides the final outcome on whether the purified water has been successfully decontaminated. For example, an increase from 99 to 99.9% of PFOS removed from solution represents only a small change in fraction bound, but it corresponds to a very large change in free PFOS concentration that is difficult to visualize with an illustration as Figure 8. Therefore, the data of Figure 8 are replotted in Figure 9 to show the concentration of PFOS that goes unbound based on the concentrations of $[\text{PFOS}]_{total}$ and $[\text{R}]_{total}$ (see Figure S13 for poly(dimethylamine-*co*-epichlorohydrin) data). Here, a logarithmic *y*-axis allows for intuitive visualization of the concentration of PFOS that is not bound to the polymer−soil blend, which is the portion of PFOS that will not be sequestered from the aqueous phase.

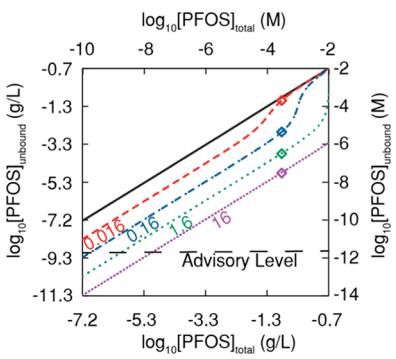

Figure 9. Plot showing the concentration of unbound PFOS versus the total amount of PFOS in a system. The dashed black line shows the EPA health advisory PFOS level ($\log_{10}[1.86\ \text{pM}] = -11.7$).[9] The solid line in black stands for a system without polymer. All other lines are labeled with the concentration (in g/L) of the soil-bound poly(diallyldimethylammonium) polymer. Colored diamonds refer to data from Figures 7 to S11.

The concentrations of unbound PFOS from Figure 9 can be directly compared to the recommended EPA health advisory level of 70 parts per trillion, which corresponds to 1 ng/L or 1.86 pM. The input concentration of polyquaternium polymer bound to soil can be adjusted to achieve the maximum allowable free concentration of PFOS ($\log_{10}[1.86\ \text{pM}] = -11.7$). At a contaminant concentration in groundwater that is typical in view of EPA data (≈0.1 nM),[9] a charged repeat unit concentration of 1 mM lowers the free PFOS concentration to <0.1 nM (Figure 9), which is below the health advisory level. This 1 mM concentration of charged repeat units corresponds to a concentration of 0.16 g/L of poly(diallyldimethylammonium) polymer (which in the absence of soil is miscible with water at any concentration but will bind to soil, as discussed above). Concentrations above this range could be used to provide a permeable absorptive barrier that has a sufficiently high effective capacity to keep the PFOS concentration low over extended periods of time.

■ CONCLUSIONS

In summary, the equilibrium constants for PFOS binding to the polyquaternium polymers poly(diallyldimethylammonium) chloride and poly(dimethylamine-*co*-epichlorohydrin) were determined in absence and presence of soil using fluorous-phase ISEs. These sensors were fabricated using a semi-fluorinated imidazolium cation as an anion-exchanger specifically developed for this purpose. Binding constants can be determined directly by fitting emf data obtained when adding polyquaternium polymers to solutions of PFOS, which streamlines the data interpretation reported in prior work. Even though the affinity of the polyquaternium polymers for PFOS was decreased by the presence of soil, PFOS was still bound with affinities of $9.3 \pm 0.6 \times 10^4$ and $7.3 \pm 1.2 \times 10^4$ M^{-1} for poly(diallyldimethylammonium) chloride and poly(dimethylamine-*co*-epichlorohydrin), respectively. These quantitative data can be used to predict the concentrations of polyquaternium polymers required to reduce the concentration of unbound PFOS. Specifically, PFOS concentrations can be reduced below the EPA health advisory level of 0.1 nM using poly(diallyldimethylammonium) chloride concentrations as low as 0.16 g/L.

■ EXPERIMENTAL SECTION

Materials. Potassium perfluorooctyl-1-sulfonate (KPFOS) and imidazole were purchased from Alfa Aesar, KCl, $NaHCO_3$, 1*H*,1*H*,2*H*,2*H*-perfluoro-7-methyloctyl iodide, perfluoroperhydrophenanthrene, and 1 M HCl from Sigma Aldrich, and poly(diallyldimethylammonium) chloride and poly(dimethylamine-*co*-epichlorohydrin) from Accepta (Manchester, U.K.). All materials were used as received. Polypropylene volumetric flasks and beakers (purchased from BRAND, Wertheim, Germany) were used to reduce PFOS adsorption to container surfaces.[31]

Preparation of PFOS−Selective Membranes. PFOS−selective membranes were prepared to contain 1.0 mM of the anion-exchanger salt 1,3-di(1*H*,1*H*,2*H*,2*H*-perfluoro-7-methyloctyl)imidazolium iodide (**3**; to provide permselectivity)[32] and 10 mM of the fluorophilic electrolyte 1,3-di(1*H*,1*H*,2*H*,2*H*-perfluoro-7-methyloctyl)imidazolium tetrakis[3,5-bis(perfluorooctyl)phenyl]borate (**4**; to reduce

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membrane resistance)[33,34] in perfluoroperhydrophenanthrene as the inert fluorous membrane matrix (see Figure 10). The syntheses of **3** and **4** and the preparation of the fluorous-phase PFOS−selective electrodes are described in the Supporting Information.

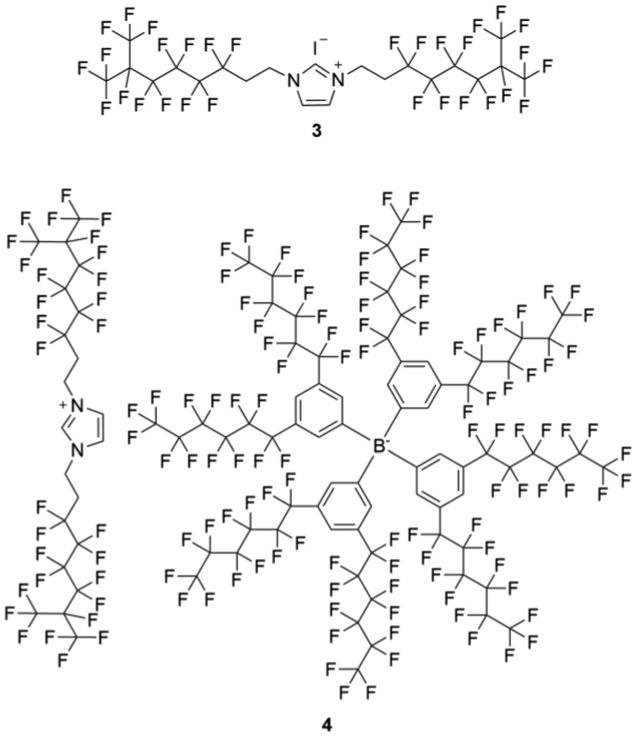

Figure 10. Chemical structures of the fluorophilic salts used for the development of PFOS−selective electrodes used in this work. Compound **3** imparts permselectivity and compound **4** reduces electrical resistance.

Polyquaternium Polymer Additions to Solutions of Constant Total PFOS Concentrations. After equilibration of the ISEs with pH-buffered PFOS solutions (as described in the Supporting Information), the electrodes were rinsed and placed in a solution containing only 10.0 mM $NaHCO_3$ (pH = 7.0, adjusted with 1.0 M HCl). Potentials were monitored until they were stable (≈20 min). Then, the concentration of PFOS was increased stepwise to 25.4 μM by small additions (Δlog[PFOS] ≈ 0.3) of a concentrated KPFOS solution (0.735 mM), while monitoring the potential after each addition. Once the concentration of 25.4 μM KPFOS was reached, poly(diallyldimethylammonium) chloride or poly(dimethylamine-*co*-epichlorohydrin) was added stepwise, increasing the concentration of the polymer in increments of log[polymer] ≈ 0.3. The measured electrical potential was allowed to stabilize after each addition (≈5 min).

Potential readings as a function of the PFOS concentration were fitted with the Nernst equation. These fits were used to determine the standard cell potential and the limit of detection of the sensor, which was likely determined by a transmembrane flux of KPFOS from the inner filling solution of the electrode through the membrane into the sample. These values were then used as constants when fitting data measured during the addition of polyquaternium polymer. A detailed description of the fitting process is included in the Results and Discussion.

Soil Preparation. Soil was obtained from Tinker Air Force Base, a Department of Defense Facility located in the South Central United States (Oklahoma City, OK). Located within the Central Red-bed Plains of the Central Lowland Physiographic Province, Tinker Air Force Base soil is colored red by ferric anhydride. Soil oven-dried overnight at 100 °C was sieved to a 40−50 mesh size range (i.e., 0.420−0.297 mm) to ensure media homogeneity. Pre-existing PFAS contamination of the soil was evaluated by mixing 5 g of soil with 20 mL of methanol for 72 h in a centrifuge tube. After centrifugation for 15 min, the methanol supernatant was decanted and analyzed with high-performance liquid chromatography−mass spectrometry for PFAS content, but none was detected.

Polyquaternium Polymer−Soil Additions to Solutions of Constant Total PFOS Concentrations. Solutions of a polyquaternium polymer and Tinker Air Force Base soil were prepared by mixing 100 mL of 10 mM $NaHCO_3$ (pH = 7), 25 g of Tinker soil, and 2.277 g/L of poly(diallyldimethylammonium) chloride or 2.274 g/L of poly(dimethylamine-*co*-epichlorohydrin). Polyquaternium/soil mixtures were stirred for 1 week prior to use to ensure equilibrium binding. In addition, mixtures not containing a polyquaterniums polymer were prepared. The volume displaced by the addition on 25 g of Tinker Air Force Base soil to 100 mL of water was measured to be 9.8 mL. This displaced volume was corrected for when adding well-mixed polyquaternium/soil mixtures to PFOS-containing solutions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b03275.

Syntheses of compounds **1** and **2**; and details pertaining to the ion-selective membrane preparation; potentiometric measurements; Nikolskii−Eisenmann equation; calculation of the free concentration of PFOS in a system containing polyquaternium polymers; average concentration of charged repeat units within a polyquaternium polymer chain; and properties of $NaHCO_3$ as buffer (PDF)

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Notes

The authors declare no competing financial interest.

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