

PFAS SURFACTANT BINDING TO FUNCTIONAL POLYMERS FOR ENVIRONMENTAL SEPARATIONS**P. Alexandridis^{1,*}, S. Kancharla¹, A. Choudhary²; D. Dong², D. Bedrov², M. Tsianou¹**¹ Department of Chemical and Biological Engineering, University at Buffalo, The State University of New York (SUNY), Buffalo, NY 14260-4200, U.S.A.² Department of Materials Science and Engineering, University of Utah, 122 South Central Campus Drive, Room 304, Salt Lake City, UT 84112, U.S.A.* *palexand@buffalo.edu***ABSTRACT**

Surface active per- and polyfluoroalkyl substances (PFAS) find niche applications because of their high chemical and thermal stability, their incompatibility with both water and hydrocarbons, and their unique ability to render surfaces non-stick. However, several widely used PFAS surfactants have been found extremely resistant to degradation, accumulate in the environment, and have long half-lives in humans, consequently causing great concern. In the context of developing materials and processes for sequestering PFAS surfactants from aqueous media, we research how such surfactants associate with (bind to) other molecules or surfaces. To this end, we utilize complementary experiments and modeling, and present here examples on how the structure of micelles formed in water by the notorious PFAS surfactant perfluorooctanoate (PFOA) responds to the presence of various additives (salt, urea, ethanol) and polymers (homopolymer poly(ethylene oxide) (PEO), PEO-based amphiphilic block copolymers, and polymer networks) across a wide range of compositions. A detailed description emerges on how PFAS distribute around polymer segments, which is used to rationalize the macroscopic properties of the mixtures.

KEYWORDS: PFAS, fluorocarbon, surfactant, self-assembly, micelle, adsorption, remediation**1. INTRODUCTION**

Per- and polyfluoro alkyl substances (PFAS) are synthetic compounds composed of a fully or partially fluorinated carbon chain. PFAS include fluorinated polymers, surfactants, ethers, esters, alcohols and thiols. A major PFAS subgroup are fluorinated surfactants that comprise fluorinated hydrophobic chains and hydrophilic headgroups. The high electronegativity, low polarizability and small size of fluorine give rise to strong C–F bond, weak –CF₂– intermolecular forces and strong hydrophobic interactions which, in turn, result in outstanding properties of PFAS surfactants, including incompatibility with both water and hydrocarbons, high wetting ability, strong surface activity, and high chemical and thermal stability. These properties render PFAS surfactants useful in many applications, including nonstick cookware, food packaging paper, stain repellent and waterproof clothing, paints, cosmetics, and firefighting foams. [1,2]

The widespread use of PFAS surfactants in industrial processes (mainly fluoropolymer manufacturing), consumer products, and fire-fighting foams has resulted in their release into the environment and accumulation in water including drinking, waste, marine, surface and groundwater. Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) are the most extensively produced and frequently detected PFAS in the environment. The presence of PFAS in the aqueous environment poses serious concerns because these compounds are not receptive to conventional water treatment methods, thus their removal is quite difficult. PFAS surfactants can enter the human body through water and food that got contaminated from contact with PFAS-

treated packaging or cookware, and can cause adverse health effects such as thyroid dysfunction, immune response suppression, kidney disease, altered cholesterol levels or metabolic diseases, reproductive toxicity, neurodevelopmental problems, and various cancers. [1]

Consequently, “legacy” PFAS such as PFOA, PFOS, and their related compounds have been banned in many countries, including the United States and European Union. In response to these restrictions, manufacturers have introduced shorter-chain PFAS such as perfluoro-2-propoxypropanoic acid (GenX) for commercial applications. However, in October 2021 an assessment by the US Environmental Protection Agency concluded that GenX is more toxic than the PFOA surfactant it was intended to replace, and set a safe daily dose of GenX 3 ng/kg of body weight, while that of PFOA and PFOS is 20 ng/kg of body weight. [1]

These findings necessitate the removal of PFAS present in the aquatic environment. Adsorption is effective for sequestering PFAS from water due to cost efficiency, high efficacy, simplicity of design, and ease of operation. The uptake of PFAS on various adsorbents is attributed to multiple interactions such as electrostatic interactions, hydrogen bonding, hydrophobic effects, van der Waals forces and π - π bonding. [2] Hence, for the design of effective adsorbent materials for PFAS surfactant removal, a fundamental understanding is important of PFAS surfactant interactions and molecular organization in water and with other species present in the aqueous solution, and on surfaces that are in contact with water. The sequestration of PFAS from aqueous solution is a pressing and challenging environmental pollution problem which necessitates colloid and surface science to offer solutions for the benefit of a sustainable future. [1]

2. RESULTS & DISCUSSION

PFAS surfactants in aqueous solutions self-assemble and form micelles above the critical micellization concentration (CMC). CMC values vary depending on the PFAS surfactant’s hydrophobic chain length, hydrophilic headgroup, counterion, and presence of any additives in the aqueous solution. Short-chain PFAS surfactants are more hydrophilic compared to long-chain ones and they form micelles at much higher CMCs (Figure 1). [1]

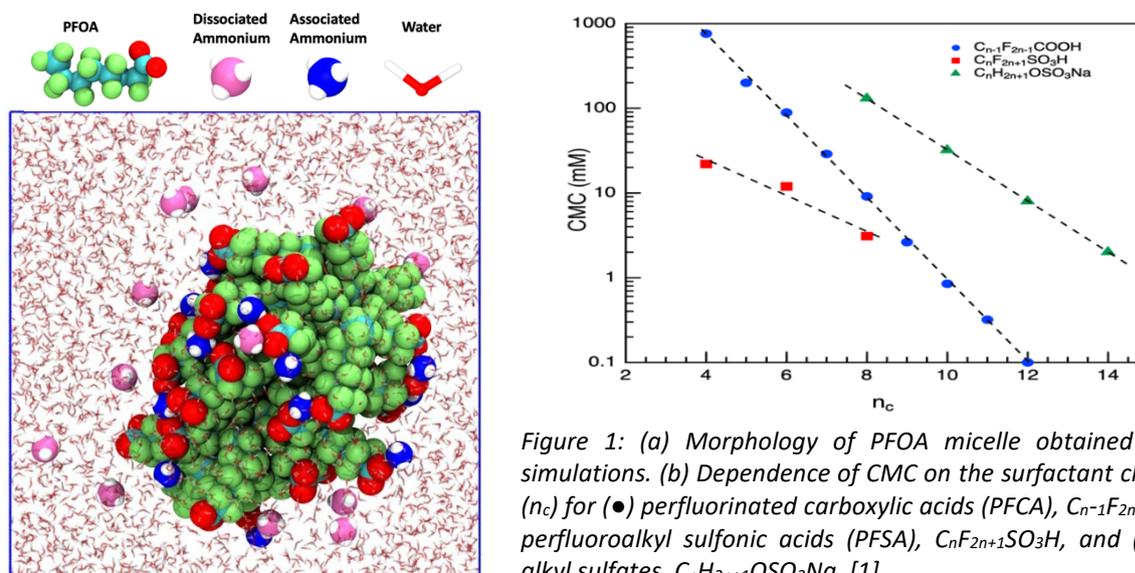


Figure 1: (a) Morphology of PFOA micelle obtained from MD simulations. (b) Dependence of CMC on the surfactant chain length (n_c) for (●) perfluorinated carboxylic acids (PFCA), $C_{n-1}F_{2n-1}COOH$, (■) perfluoroalkyl sulfonic acids (PFSA), $C_nF_{2n+1}SO_3H$, and (Δ) sodium alkyl sulfates, $C_nH_{2n+1}OSO_3Na$. [1]

Information on the CMC of emerging PFAS surfactants is not available in the literature. A very recent study on GenX interaction and self-assembly reported the CMC of GenX in water to be 150 mM. [3] Comparing the C6 fluorinated surfactants GenX and perfluorohexanoic acid (PFHxA), the branched fluoroether chain of GenX is found 30% less hydrophobic than a linear fluorocarbon chain with the same number of carbon atoms. Counterions play an important role in screening repulsion between

ionic surfactant headgroups and, hence, affect the CMC. [1] In the presence of added electrolyte in water, the CMC of PFAS surfactants decreases. [4] The effect of salt on the CMC is stronger for longer-chain PFAS surfactants compared to shorter ones. The CMC of sodium perfluorooctanoate (NaPFO) decreased by 80%, and the CMC of NaPFHx decreased by 50% upon addition of 0.25 M NaCl. [4] The presence in water of organic compounds can affect the self-assembly of fluorinated surfactants. [5] When 10% ethanol is added to water, the CMC of PFOA decreased to half its value in plain water, indicating a co-surfactant effect, however, at 20% ethanol only a minor additional reduction in the CMC is observed. [6]

The size and structure of PFAS surfactant micelles formed in aqueous solutions depend strongly on the surfactant hydrophobic chain length and can change in the presence of additives. Direct structural information on PFAS surfactant micelle size and structure is limited. NaPFO at 110 mM forms ellipsoidal micelles with an association number of about 25 and 17.0 Å radius. NaPFHx forms smaller micelles with association number = 15 and radius = 13.0 Å. [4] The size of PFAS surfactant micelles increases with the surfactant chain length. Structural information on micelles formed by emerging PFAS surfactants is not yet available. The first report on GenX micelle structure and composition was just published, revealing rather small but still well-defined micelles having association number 6 – 8 and 10 Å radius (Figure 2). [3] GenX micelles are ellipsoidal in shape with the fluorocarbon chains accessible to the aqueous solvent. Atomistic molecular dynamics (MD) simulations have shown that GenX molecules prefer to align along the micelle surface, the GenX anionic headgroup interacts strongly with water, the CF₃ groups of the GenX tail and side branch are exposed to water, whereas the ether oxygen is sterically hindered from water by fluorinated groups and the headgroup. GenX micelles have association number 5 times lower that of PFOA micelles and are almost half in size. [3] Added salt in aqueous solution increases the micelle association number and size. The effect of salt on micelle size was observed to be stronger for the rather long-chain NaPFO compared to the shorter chain NaPFHx. [4]

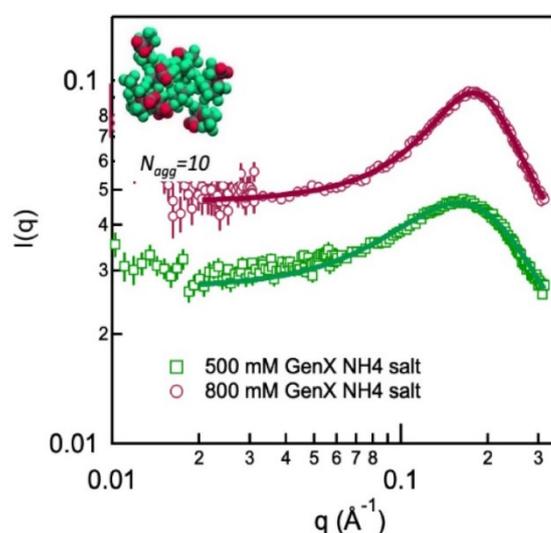


Figure 2: SANS intensity profiles of GenX in D₂O. Solid lines represent fits using core-shell ellipsoid form factor and Hayter RMSA structure factor. A snapshot of a GenX micelle from MD simulations is shown in the inset. [3]

Solvents used to regenerate PFAS adsorbent materials, such as ethanol, can dissolve PFOA micelles at high concentrations. Complementary high-resolution small-angle neutron scattering (SANS) measurements and (MD simulations have shown ethanol at lower concentrations (less than 13 wt%) to localize at the PFOA micelle surface and interior, acting as a co-surfactant. A transition to a co-solvent behavior was observed at higher ethanol concentrations, where ethanol molecules penetrate the PFOA micelles, render them looser, and eventually break them into small clusters. [6]

PFAS surfactants can bind to macromolecules in aqueous solution. [7] Our recent study on PFOA - poly(ethylene oxide) (PEO) mixtures in aqueous solution has shown that PFOA binds to PEO at a critical association concentration (CAC) which is lower than its CMC in water. MD simulations showed that PFOA+PEO mixed micelles are ellipsoid and, using this shape, analysis of SANS data determined that micelles comprise 33 PFOA molecules (at 110 mM PFOA) bound to one PEO molecule (molecular weight = 10000). The PFOA+PEO mixed micelles have 10% higher association number and are 40% more elongated compared to polymer-free PFOA micelles at the same PFOA concentration (110 mM). In polymer-free PFOA micelles, a significant portion of F atoms are exposed to water. According to both MD and SANS results, PEO chains adjust their conformations to effectively partition on the PFOA micelle surface shielding the fluorocarbon from contact with water. PEO does not penetrate the PFOA micelle interior. The binding of PFAS to a polymer that is not fluorinated has practical implications, as the use of fluorinated polymers to adsorb PFAS has raised concerns due to the potential release into the environment of additional PFAS compounds associated with said polymers. PEO, on the other hand, is rather innocuous and low-cost.

Polymer hydrophobicity is an effective design parameter that can be varied in order to achieve PFAS binding that is stronger and/or commences at lower surfactant concentration. Here there is a trade-off because, when hydrophobicity increases a lot, then the polymers become insoluble in water, and are of little use in sequestering PFAS from water. The solution to this trade-off is block copolymers, where one block is water-soluble while the other is hydrophobic. Block copolymers of hydrophilic PEO and hydrophobic poly(propylene oxide) (PPO), commercially available as Pluronic or Poloxamers, can self-assemble in aqueous solutions into micelles, with a PPO-rich core and highly hydrated PEO shell. [7] PFOA can interact with Pluronic molecules in aqueous solution to form mixed micelles which include polymer in the micelle core that is formed primarily by surfactant chains. The hydrophobic driving force for locating PPO in the mixed micelle interior is consistent with the much lower CAC values with PEO-PPO-PEO block copolymer, compared to CAC values in aqueous PEO homopolymer solution. [7]

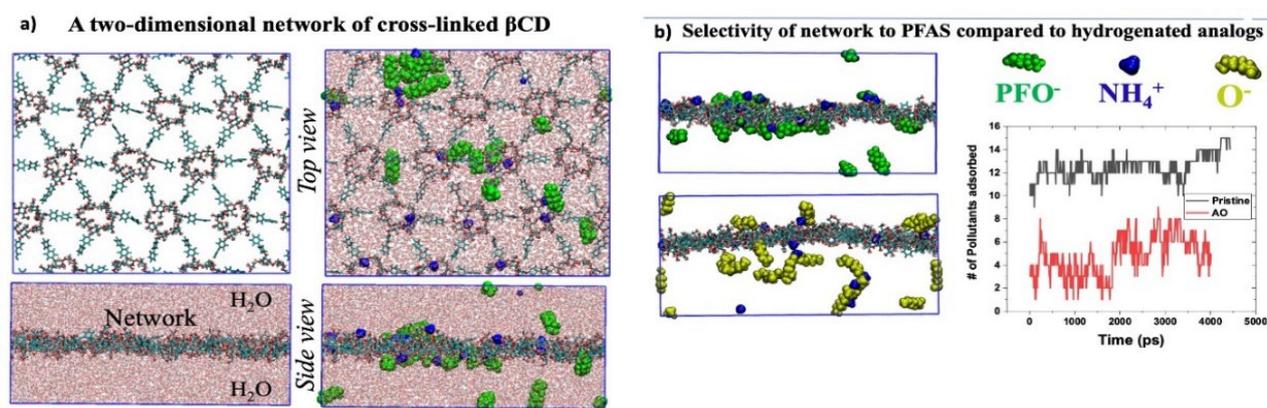


Figure 3: (a) Snapshots from MD simulations of a model CD-based network crosslinked with fluorinated linkers. (b) Snapshots illustrating the selectivity of the network to adsorption of PFOA compared to its hydrogenated analogs. A number of fluorinated and hydrogenated surfactants are shown adsorbed onto the networks. [8]

The ability of atomistic MD simulations to explore interactions and mechanisms of binding of PFAS surfactants to polymer networks has been demonstrated in our recent work. [8] Specifically, we have shown that experimentally realized networks comprised of cyclodextrins (CD) cross-linked by fluorinated linkers (Figure 3a) can facilitate the dissociation of PFAS from their counterions (e.g., NH_4^+). The former preferentially interact with fluorinated cross-linkers, while the latter form hydrogen bonds strongly with CDs. The analysis of molecular scale interactions reveals that the mechanism of adsorption of PFOA pollutants on CD-based network is governed by two primary

factors. First, the adsorption of ammonium counterion on CD segments of the network gives rise to strong ionic interactions between the PFOA headgroup and the network. While the network is not ionic by design, the strong interaction of polar segments (i.e., CDs) with cations effectively renders this network similar to those where cationic groups are incorporated to the network polymer chains. Second, the presence of fluorinated linkers creates fluorophilic pockets for the fluorocarbon part of PFOA to adsorb. The combination of these interactions is important to simultaneously achieve effective adsorption and selectivity of the network towards PFOA (Figure 3a). The polymer network can be designed to preferentially adsorb PFAS. The network with fluorinated linkers provides three-fold higher adsorption efficiency for the APFO pollutant compared to its hydrogenated counterpart ammonium octanoate (Figure 3b), confirming the preferential interaction towards fluorinated surfactants. [8]

3. CONCLUSIONS

Aqueous solution properties of PFAS, together with an improved understanding on how to modulate PFAS surfactant self-assembly in water with additives, can inform the fate and transport of PFAS in the environment and PFAS sequestration from aqueous media. Fundamental knowledge on PFAS surfactant–polymer interactions supports the design of new materials to selectively capture and remove such surfactants from aqueous media. Self-assembly into micelles is a key feature of surfactants in aqueous solution, and reveals how PFAS surfactants interact with themselves and with solvent (water) and other molecules present in solution. A close connection exists between self-assembly in solution and that on surfaces. The capability established in our study to predict from first principles micelle formation and structure confirms that such multiple and often competing interactions have been properly accounted for. Micelles are relevant to environment and health in that PFAS surfactants, while typically found in very low bulk solution concentrations, they tend to concentrate a lot (partition) in the vicinity of surfaces in the context of separations (activated carbon, ion exchange resins) and in the context of biointerfaces (proteins, lipid membranes).

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