☐ **Talk** ☒ **Poster**

Interfacial Miscibility and Structure of Binary Long-Chain PFAS and Cationic Hydrogenated Surfactant Mixtures

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Poly- and perfluoroalkyl substances (PFAS) are extremely persistent molecules ("forever chemicals") that pose a global threat due to their toxicity and widespread contamination in water resources. As a class of anionic surfactants, PFAS tend to accumulate at the air–water (A/W) interfaces, making foam fractionation an effective remediation strategy. Recent work has shown that the surface accumulation of PFAS can be enhanced by forming "ion-pair amphiphiles" or "catanionic surfactants" by mixing PFAS with other cationic surfactants.[1–3] However, the fundamental understanding of the synergism between anionic fluorinated and cationic hydrogenated surfactants remains limited.

Previous studies show that mixed monolayers of long-chain anionic hydrocarbons and perfluorocarbons typically phase-separate at the A/W interface due to chain incompatibility.[4–5] The headgroup interactions are also important, especially in mixed oppositely charged hydrocarbons and perfluorocarbons, and these interactions are poorly understood. Here, we investigate a simplified model system consisting of insoluble, long-chain fluorinated fatty acid and oppositely-charged, hydrogenated fatty amines using synchrotron-based liquid surface scattering techniques. The mixture forms Langmuir monolayers over a range of compositions. Grazing-incidence X-ray Diffraction (GIXD) revealed that the 1:1 mixed monolayer exhibits a stable binary phase with hexagonal packing, with the composition of the binary phase reaffirmed by X-ray reflectivity (XR). The average area per molecule (APM) measured by GIXD lies between the APMs of individual components, consistent with the APM from Langmuir isotherms. Across different stoichiometric ratios, the binary phase persists with systematic changes in the average APM, despite weak overall repulsive interactions.

This strong miscibility arises from balanced intermolecular forces between the headgroups and tails that dictate surface structure and interfacial phase behavior of the co-assembled films. These insights into molecular-level interactions and synergistic assembly provide a deeper understanding of mixed PFAS/surfactant systems and offer guidance for the rational design of improved PFAS remediation strategies using cationic surfactants.

References

[1] Pennell, K. D. et. al. Accumulation of PFOA and PFOS at the Air–Water Interface. *Environ. Sci. Technol. Lett.* **6**, 487–491 (2019).

[2] Li, Y.-F. et al. Perfluorooctanoic acid (PFOA) removal by flotation with cationic surfactants. *Chemosphere* **266**, 128949 (2021).

[3] Buckley, T. et al. Using foam fractionation to estimate PFAS air-water interface adsorption behaviour at ng/L and μg/L concentrations. *Water Res.* **239**, 120028 (2023).

[4] Paige, M. F. et. al. Molecular-Level Structure and Packing in Phase-Separated Arachidic Acid-Perfluorotetradecanoic Acid Monolayer Films. *Langmuir* **34** (36), 10673– 10683 (2018).

[5] Paige, M.F. et. al. Mixing in Langmuir Monolayers: Perfluorotetradecanoic Acid and a Gemini Surfactant without a Linker. *Langmuir* **39** (46), 16503-16512 (2023).