Observation of counterion binding in the inner Helmholtz layer at ionic surfactant-water interface

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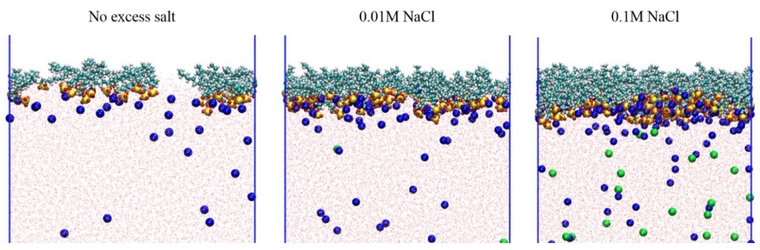
Introduction

- Ionic surfactants at air/water interfaces are crucial for industrial and biological processes, but their interfacial behavior, particularly the role of counterions, has lacked quantitative molecular-level understanding.

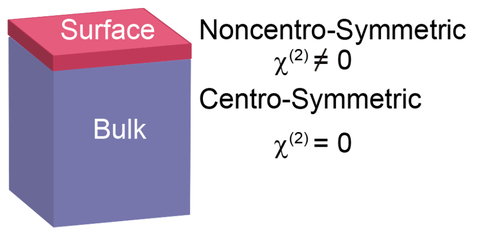


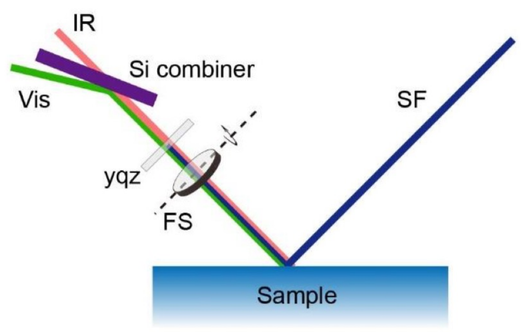
MD simulation: Counterion bonding

X-ray diffraction: Surface crystallization

Experiment Method

➢ **Phase-sensitive sum-frequency vibrational spectroscopy (PS-SFVS)**





Surface/interface specific

Experimental Result

➢ **Surface crystallization by PS-SFVS experiment**

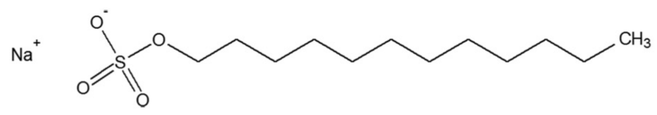
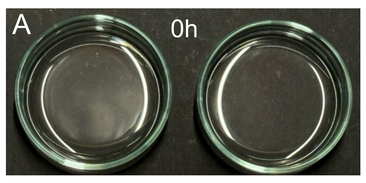
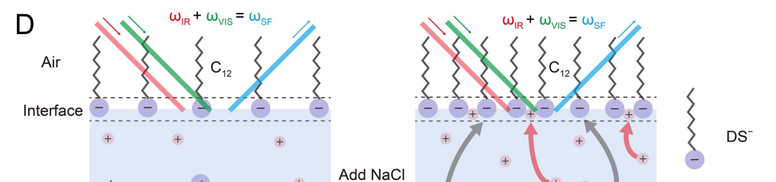
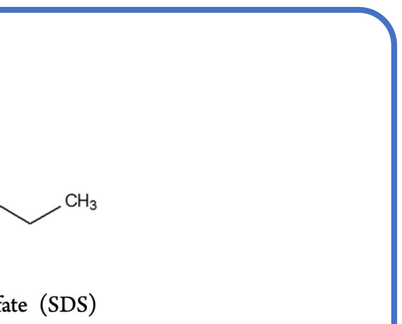


Figure 1. Chemical structure of the sodium dodecyl sulfate (SDS) molecule.

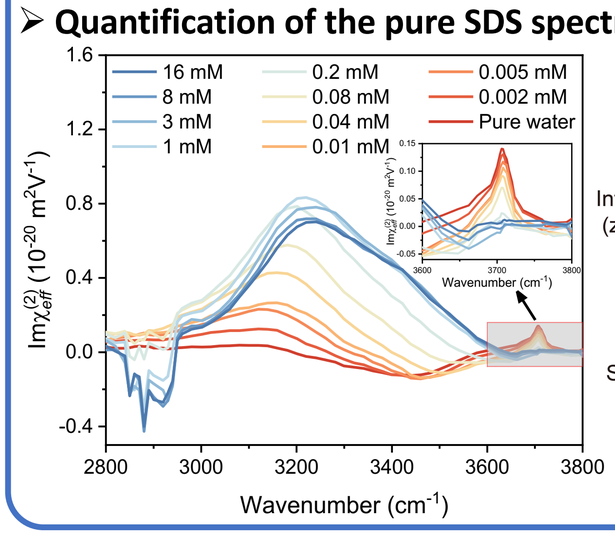


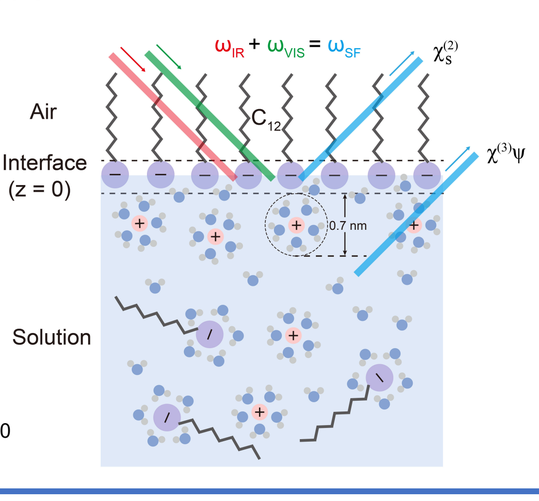


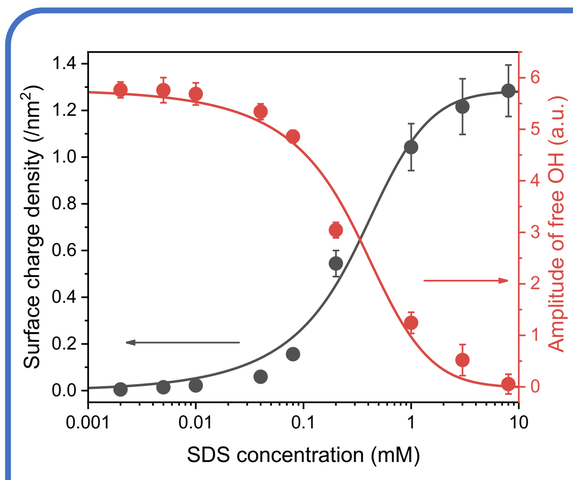


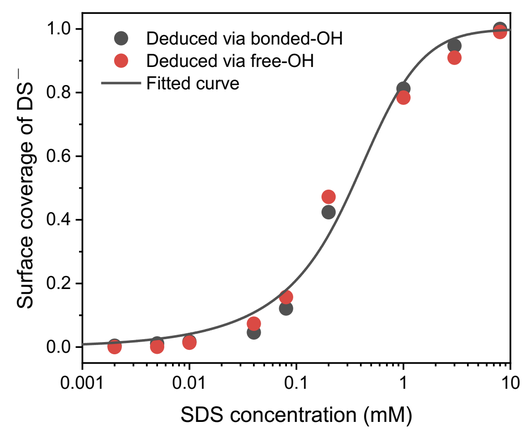
- 0.6 mM SDS (left) vs 0.6 mM SDS + 500mM NaCl (right)

➢ **Quantification of the pure SDS spectra**









$$\chi_{S,eff}^{(2)}(\omega) = \chi_S^{(2)}(\omega) + \chi^{(3)}(\omega) \cdot \int_{0^+}^{\infty} \hat{z}\, E_0(z) e^{i\Delta k_z z} dz$$

$$Im\chi_{S,eff}^{(2)}(\omega) = Im\chi_S^{(2)}(\omega) + Im\chi^{(3)}(\omega) \cdot \int_{0^+}^{\infty} \hat{z}\, E_0(z) cos(\Delta k_z z) dz$$

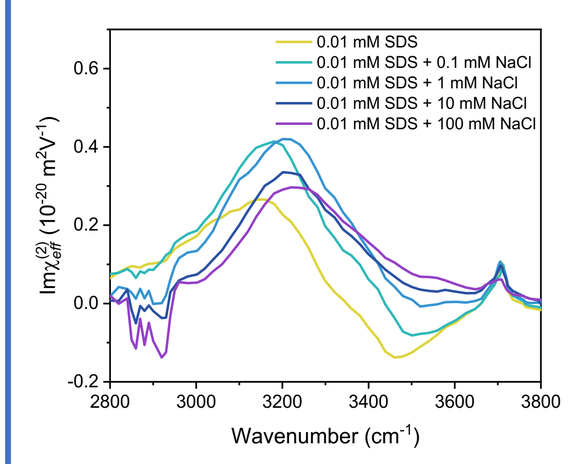
$$+ Re\chi^{(3)}(\omega) \cdot \int_{0^+}^{\infty} \hat{z}\, E_0(z) sin(\Delta k_z z) dz$$

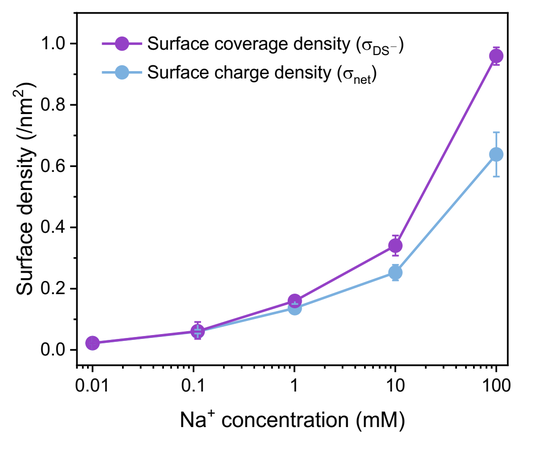
$$\nabla^2\phi = \frac{eC}{\epsilon_0\epsilon_r} \frac{2\,sinh\left(\frac{e\phi}{k_BT}\right)}{1 + 2v\,sinh^2\left(\frac{e\phi}{2k_BT}\right)}$$

$$\phi_0 = -\frac{2k_BT}{e} sinh^{-1}\left\{\sqrt{\frac{1}{2v}\left[exp\left(\frac{ve^2\sigma^2}{4C\varepsilon_0\varepsilon_r k_BT}\right) - 1\right]}\right\} \qquad \nu = 2a^3C$$

- a is the effective size of the counter ions and C is the bulk ionic strength.

➢ **Surface excess of counterion**





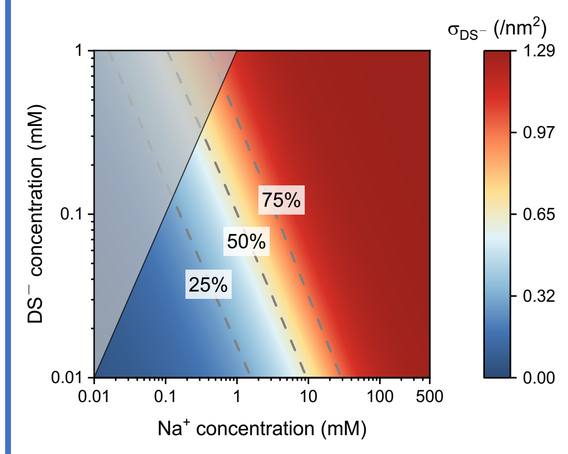
- This result indicates that the dehydrated Na+ ions can adsorb at the same Helmholtz plane as DS−, contributing to the total surface charge density.

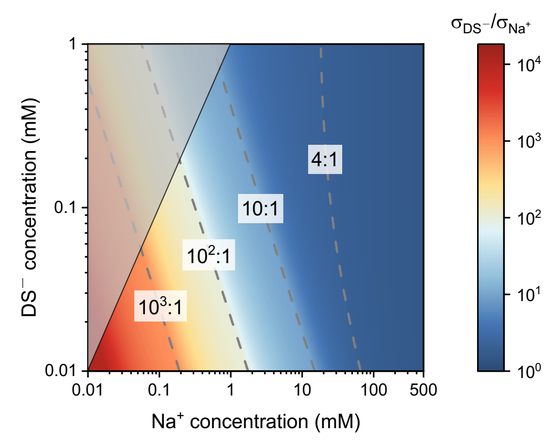
➢ **Modified Langmuir adsorption model**

$$K_S \cdot exp\left(\frac{e\phi_0}{k_BT}\right) exp\left(\frac{1}{2}g'\theta_S\right) \cdot C_{SDS} = \frac{\theta_S}{1-\theta_S}$$

$$K_{Na} \cdot exp\left(-\frac{e\phi_0}{k_BT}\right) \cdot C_{Na^+} = \frac{\theta_{Na}}{1-\theta_{Na}}$$

where $\theta_S = \frac{\Gamma_{DS^-}}{\Gamma_\infty}$ and $\theta_{Na} = \frac{\Gamma_{Na+}}{\Gamma_{DS^-}}$ are the surface fractional coverage of DS^- and Na^+





Conclusion

- First experimental evidence for Na^+ accumulation within the inner Helmholtz plane;
- Extract a set of thermodynamic parameters that characterize the interfacial adsorption equilibria;
- Reveal central role of counterion adsorption process in facilitating surface crystallization.

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