

Charge Reversal Behavior at the CaF₂/H₂O/SDS Interface as Studied by Vibrational Sum Frequency Spectroscopy

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Received: November 26, 2002; In Final Form: February 24, 2003

We report in situ spectroscopic measurements of charge reversal behavior and surfactant bilayer formation at the salt/aqueous solution interface as the aqueous surfactant concentration is varied. The studies, which employ vibrational sum frequency spectroscopy to measure the vibrational response of sodium dodecyl sulfate and water at the CaF₂/H₂O interface, demonstrate the complex nature of the adsorption process which includes monomer adsorption, surfactant bilayer formation, surfactant restructuring, surface charge reversal, and water reorientation. These effects have been monitored directly for the first time by taking advantage of the spectroscopy and the nonlinear phase relationships between the CH and OH vibrational modes. The results provide important insight into the adsorption mechanism that is central to processes such as mineral ore flotation and separation, waste processing, and petroleum recovery.

Introduction

The adsorption of surfactants from an aqueous phase onto a salt or mineral surface plays a key role in a number of diverse fields including colloidal stabilization, lubrication, petroleum recovery, waterproofing, waste processing, and mineral ore flotation and separation.^{1–3} Common to these endeavors is the alteration of the interfacial properties due to the adhesion and aggregation of surfactant molecules at the solid surface. The attraction of aqueous surfactants to a solid phase is often driven by the electrostatic interaction between a charged surfactant headgroup and the intrinsic charge that many solids attain when immersed in an aqueous phase.^{4,5} The electrical potential in the interfacial region results in a driving force for the initiation of monomer adsorption and subsequent aggregation of the surfactant molecules through dispersion and van der Waals forces.⁶ These interactions can result in dramatic changes in the properties of the solid surface and the interfacial region as the surface charge is altered. In particular, the interfacial water structure brought about by intermolecular hydrogen bonding among water molecules can be disrupted quite dramatically.

In this paper, we report direct measurements of the adsorption of the anionic surfactant, sodium dodecyl sulfate (SDS), from an aqueous solution to the surface of the ionic, semisolid CaF₂ (fluorite). We make use of the nonlinear, surface specific spectroscopic technique vibrational sum frequency spectroscopy (VSFS) in order to simultaneously examine both the OH vibrational modes of hydrogen bonded interfacial water molecules and the CH vibrational modes arising from the surfactant tail. As the surfactant concentration is increased, the surfactant adsorption process progresses from monomer adsorption to bilayer formation at the surface. Accompanying this is a change in the surface charge that results in a reorientation of interfacial water molecules consistent with the reversal of the interfacial electric field through bilayer formation. This reorientation has

been detected by careful examination of the interferences that occur between OH vibrational modes from interfacial water molecules with CH vibrational modes arising from the tails of the SDS surfactant.

Experimental Method

Vibrational sum frequency spectroscopy (VSFS) is a surface specific nonlinear optical technique that makes use of two intense laser beams (one a fixed frequency visible beam and the other a tunable IR beam) that are coupled together, spatially and temporally, at an interface.⁷ The molecules within the interfacial region will interact with the intense electric fields by generating a response at the sum of the two incoming beam frequencies ($\omega_1 + \omega_2 = \omega_3$). Within the dipole approximation, this response is limited to molecules within a noncentrosymmetric environment, such as that found in an interface, and forbidden in a bulk centrosymmetric medium. As the IR frequency is tuned across a vibrational resonance of a molecule, the generated VSFS signal is enhanced and a vibrational spectrum of the interfacial molecules is obtained. On the molecular level, in order for a mode to be VSFS active, it must possess both a nonzero Raman and IR transition moment which will only occur for molecules lacking inversion symmetry. This fact, in conjunction with the noncentrosymmetric nature of the interface, leads to the surface specificity of this nonlinear process. Because of the coherent nature of VSF spectroscopy, each of the vibrational responses probed will have a distinct phase associated with it. Individual modes will interfere both constructively and destructively in the final detected response, and it is these interferences that can be used to attain orientational information about the individual species within the interfacial region.⁸ The laser system and experimental setup used in these studies has been described previously.^{9,10} Briefly, a 3.5 ns, 20 Hz Nd:YAG laser is used to produce the visible (532 nm) and tunable IR (2700–4000 cm⁻¹) beams used in the generation of the sum frequency spectra. We make use of a total internal reflection geometry by coupling both beams through a CaF₂ prism (ISP Optics) which is used as the solid substrate. A hollow cell is placed over the largest face of the

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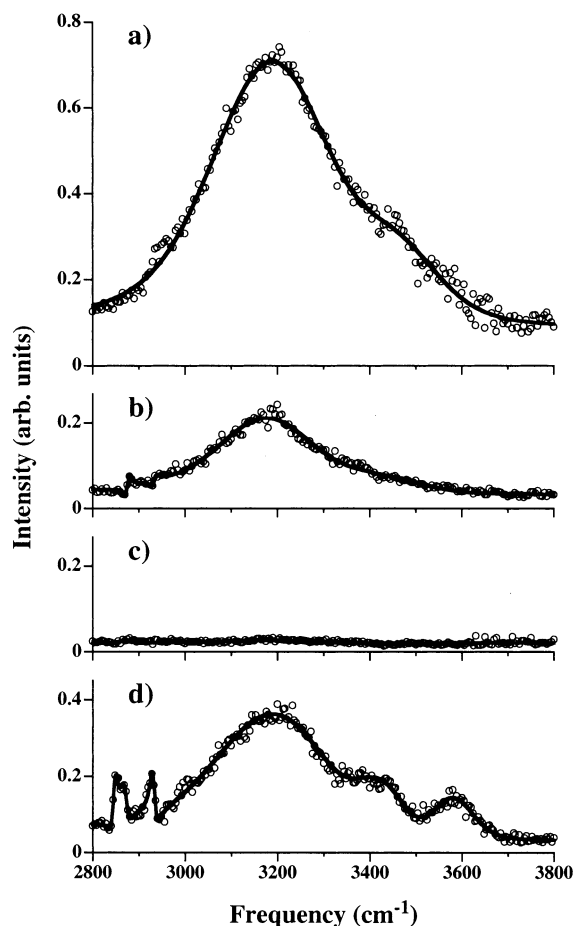


Figure 1. Vibrational sum frequency spectra of the $\text{CaF}_2/\text{H}_2\text{O}/\text{SDS}$ interface spanning the entire OH and CH stretching regions: (a) neat $\text{CaF}_2/\text{H}_2\text{O}$, (b) 6.1×10^{-5} M SDS, (c) 2.0×10^{-4} M SDS, and (d) 3.0×10^{-3} M SDS.

prism (50×50 mm), sealed with an O-ring, and filled (~ 50 mL) with the solution of interest. All solutions were prepared with $18 \text{ M}\Omega$ Nanopure water using ACS reagent grade chemicals. Additions of SDS solutions were made via micropipet with constant stirring provided by a mechanical stirring paddle. Signal intensity at the peak frequency of the water response was monitored during the additions to ensure equilibrium was attained. All spectra were normalized to fluctuations in the monitored IR power.

Results and Discussion

The vibrational sum frequency spectra of H_2O molecules in the interfacial region between the ionic solid CaF_2 (fluorite) and a bulk aqueous phase has been studied previously.⁹ The $\text{CaF}_2/\text{H}_2\text{O}$ interface is a rather interesting system exhibiting strong pH dependent behavior as a result of the preferential dissolution of surface F^- ions. This surface dissolution results in a strongly positively charged fluorite surface which orients water molecules within the interfacial region. As the aqueous phase is adjusted toward more neutral pH conditions, the surface charge diminishes and reverses sign at the point of zero charge (PZC) of the $\text{CaF}_2/\text{H}_2\text{O}$ interface. In addition, in the basic pH range, the fluorite surface exhibits ion exchange between the surface ions and aqueous phase hydroxide species and/or dissociated water molecules leading to formation of surface CaOH oscillators.

The studies described in this paper were conducted at near-neutral pH conditions (pH 5.1). This pH is below the PZC of

the $\text{CaF}_2/\text{H}_2\text{O}$ interface;^{11–13} therefore, the surface charge remains positive and facilitates the alignment of water molecules in the interfacial region.⁹ The spectrum of the neat $\text{CaF}_2/\text{H}_2\text{O}$ interface at pH 5.1 is shown in Figure 1a. The two main features evident in the spectrum are a large peak response at $\sim 3210 \text{ cm}^{-1}$ and a smaller “shoulder” located at $\sim 3440 \text{ cm}^{-1}$. Prior studies of water at several different solid interfaces^{14–16} have assigned these two peaks to hydrogen bonded water molecules with differing levels of coordination. The $\sim 3210 \text{ cm}^{-1}$ peak response arises from the collective vibrational motion of tetrahedrally coordinated water molecules. Generally, water molecules in this type of highly coordinated, symmetrical hydrogen bonding environment have sum frequency responses shifted and broadened by several hundred wavenumbers from their gas phase values (typically seen at $\sim 3700 \text{ cm}^{-1}$).¹⁷ Water molecules that experience intermolecular hydrogen bonding environments that are less coordinated tend to have sum frequency peak responses centered in the $3400\text{--}3500 \text{ cm}^{-1}$ range. These molecules experience a more disordered hydrogen bonding environment (because of either asymmetric or bifurcated hydrogen bonds) which shifts their peak responses by only a few hundred wavenumbers from their gas-phase values.

Small additions of the negatively charged surfactant SDS to the neat $\text{CaF}_2/\text{H}_2\text{O}$ interface (pH 5.1) results in a decrease in the VSF intensity across the entire OH stretching region of water as shown in Figure 1b. We attribute this decrease in signal to the adsorption of the SDS surfactant through the electrostatic attraction of the negatively charged headgroup to the positively charged CaF_2 surface.² The adsorption results in a lower net charge at the surface and consequently a decreased electric field penetrating into the solution phase. With the decrease in the near surface field, the tendency of water dipoles to align with the field is decreased. This reduces the depth of penetration of the electric field into the aqueous phase and consequently the number of water molecules being aligned.¹⁸ In addition to the decrease in the response from the OH oscillators, Figure 1b displays the onset of multiple sharp transitions in the small deconstructive peaks in the spectral region from 2850 to 2950 cm^{-1} . These peaks are attributed to interferences between the sum frequency response from the CH oscillators in the surfactant tail and OH oscillators.^{19,20} These interferences are a result of the coherent nature of the VSF spectroscopy and will be discussed later in this paper.

At a bulk SDS concentration of 2×10^{-4} M, the signal level from interfacial water molecules is reduced to nearly zero as shown in Figure 1c. At this concentration, the effective charge from the CaF_2 surface has been largely compensated by the negatively charged sulfate headgroup. Although barely perceptible in this figure, the interferences from the CH resonances are present in the spectra as seen in Figure 1b. The reduction in the response from the interfacial water molecules in going from the neat $\text{CaF}_2/\text{H}_2\text{O}$ interface to the $\text{CaF}_2/\text{H}_2\text{O}/\text{SDS}$ interface indicates that the adsorbed SDS molecules significantly disrupt the water structure at the solid/aqueous interface. However, the rather small response from the CH oscillators suggests that the SDS tails are very disordered, leading to only a low intensity peak from the pendant CH_3 groups at the terminal end of the molecules.²¹

The “effective” PZC of the $\text{CaF}_2/\text{H}_2\text{O}/\text{SDS}$ interface (the point at which the positively charged CaF_2 surface has been neutralized by adsorption of the negatively charged surfactant) occurs at just above 2×10^{-4} M SDS, as discussed above. By increasing the bulk concentration above 2×10^{-4} M, the sum frequency response from interfacial water returns in both the

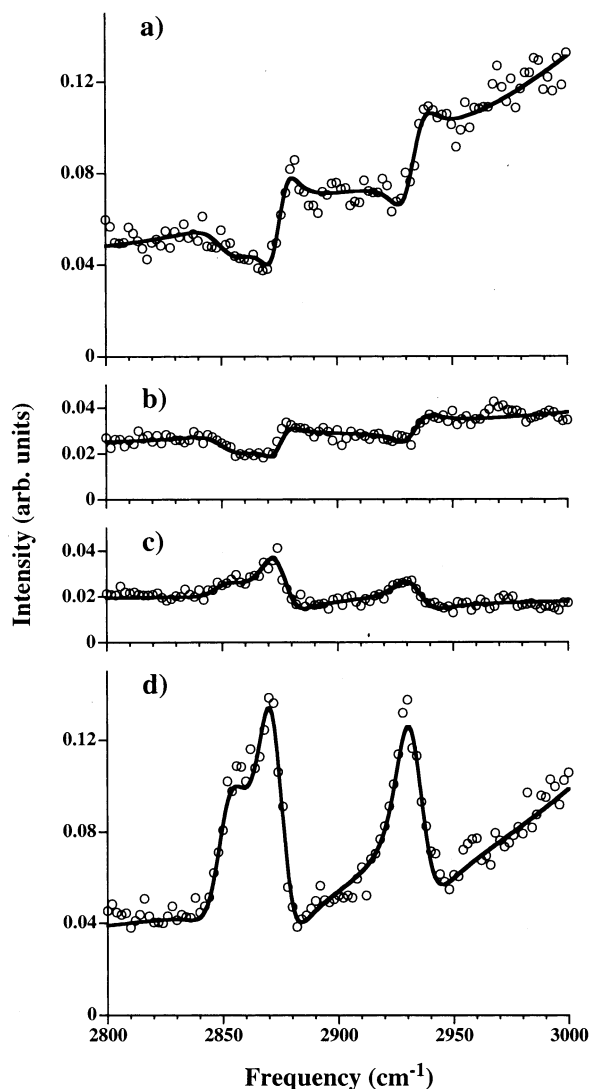


Figure 2. Charge reversal behavior at the $\text{CaF}_2/\text{H}_2\text{O}/\text{SDS}$ interface as evidenced by the interferences between the surfactant CH modes and water OH modes. Surfactant concentrations are (a) 4.1×10^{-5} , (b) 2.0×10^{-4} , (c) 3.5×10^{-4} , (d) 9.2×10^{-4} M SDS.

3210 and 3440 cm^{-1} peaks. Figure 1d shows the $\text{CaF}_2/\text{H}_2\text{O}/\text{SDS}$ interface at a bulk SDS concentration of 3×10^{-3} M. The spectrum shows several new features; in addition to intensity from the tetrahedrally coordinated water molecules (3210 cm^{-1}) and more disordered water molecules (3440 cm^{-1}), there are several sharp peaks evident in the $2800\text{--}3000 \text{ cm}^{-1}$ region and a broad peak centered at $\sim 3570 \text{ cm}^{-1}$. We assign the sharp feature centered at 2850 cm^{-1} to the symmetric stretch of CH_2 groups ($\text{CH}_2(\text{ss})$) in the surfactant backbone and the two peaks at 2873 and 2933 cm^{-1} to the CH_3 symmetric stretch split by a Fermi resonance with an overtone of a CH_3 bending mode. These assignments are in agreement with several previous VSFS studies of surfactants at a variety of interfaces.^{16,22–24} We assign the broad peak centered at $\sim 3570 \text{ cm}^{-1}$ to water molecules solvating the negatively charged sulfate headgroup of the SDS. This is in agreement with previous sum frequency studies at the $\text{CCl}_4/\text{H}_2\text{O}$ interface^{25,26} where these peaks from weakly hydrogen bonded water molecules were assigned to either water in the primary or secondary solvation shell of a charged headgroup. The behavior of the $\text{CaF}_2/\text{H}_2\text{O}/\text{SDS}$ interface above 2×10^{-4} M is consistent with the formation of a bilayer of SDS molecules on the surface of the CaF_2 as the surfactant molecules associate through van der Waals interactions between

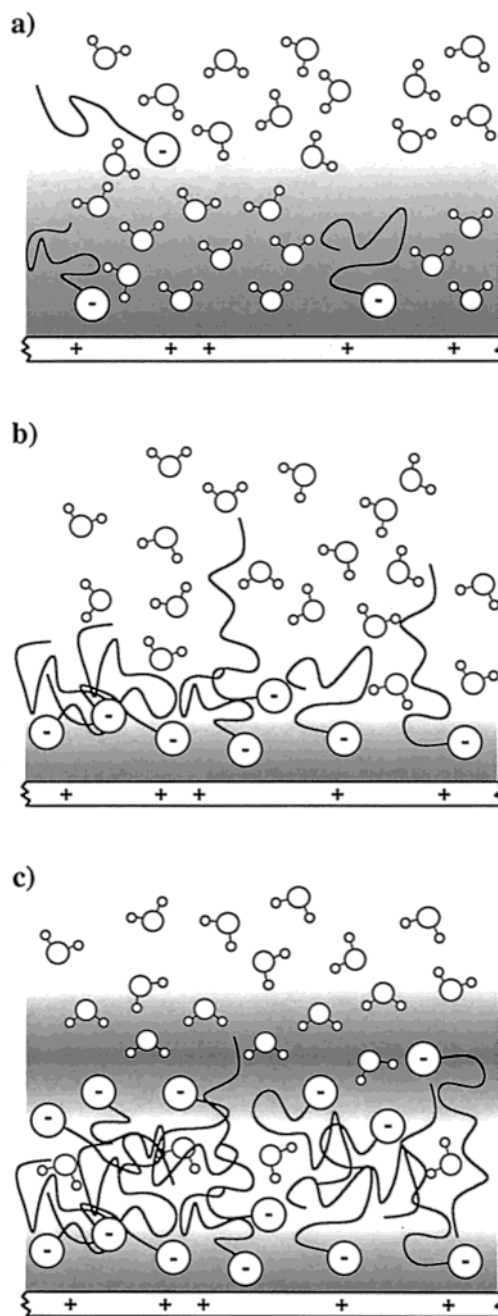


Figure 3. Diagram of the three distinct adsorption regions of SDS on CaF_2 . (a) Monomer adsorption of anionic SDS to the positively charged CaF_2 surface, (b) the PZC of the $\text{CaF}_2/\text{H}_2\text{O}/\text{SDS}$ interface and randomization of interfacial water molecule structure, and (c) bilayer formation and charge reversal at the $\text{CaF}_2/\text{H}_2\text{O}/\text{SDS}$ interface and the return of interfacial water structure above this layer.

the disordered surfactant tails.²⁷ This classic example of bilayer formation orients the charged sulfate headgroups toward the aqueous phase with the surfactant tails interdigitated below.²⁸ With the reintroduction of an electrostatic orienting force from the charged headgroups, the water molecules in the interfacial region above the bilayer will again orient their dipoles in alignment with the field.¹⁸ Evidence of this alignment is shown by the return of the sum frequency signal from the interfacial water molecules, much like that seen at the neat $\text{CaF}_2/\text{H}_2\text{O}$ interface. It is possible that the behavior of this system results from a continuation of monomer adsorption. However, there is a strong driving force for the formation of a bilayer in order to minimize the charge repulsion of the SDS headgroups, to

maximize van der Waals interactions between the surfactant tails, and to orient the SDS headgroups toward the aqueous phase where interactions with the water molecules would help to reduce the total energy of the system. Further evidence for bilayer formation from D₂O studies of the same interface will be detailed in an upcoming publication.²⁹

Further evidence of the charge reversal at the CaF₂/H₂O/SDS due to bilayer formation comes from careful investigation of the VSF spectra in the CH stretching region from 2800 to 3000 cm⁻¹. Figure 2a–d shows the VSF spectra of the CaF₂/H₂O/SDS interface at SDS concentrations below (Figure 2a,b) and above the PZC (Figure 2c,d). In all four figures, the OH stretching response from interfacial water molecules appears as the “tail” from 3000 cm⁻¹ which slowly decreases to background level in the 2800–2850 cm⁻¹ region. As a result of the coherent nature of the sum frequency process, the CH stretching modes will interfere, either constructively or destructively, with the “tails” of the OH resonances depending on the relative orientation of the oscillating groups.^{19,20} At the SDS concentrations shown in Figure 2a,b, the interfacial water molecules should be oriented, on average, with their oxygen atoms nearest the positively charged CaF₂ surface and their hydrogens pointing out toward the aqueous phase. This is confirmed in Figure 2a, where the CH oscillators interfere destructively with these H₂O oscillators resulting in dips in the spectrum at 2850, 2873, and 2933 cm⁻¹. At higher concentrations of adsorbed SDS (2 × 10⁻⁴ M, Figure 2b), the OH oscillator response is considerably decreased due to randomization of the interfacial water molecules; however, the destructive interferences can still be detected in the spectrum. Charge reversal occurs between 2 × 10⁻⁴ and 3.5 × 10⁻⁴ M SDS. This is evident in Figure 2c, where constructive interference of the OH oscillators with the CH oscillators is now apparent in the spectrum. The orientation of the water molecules has flipped by 180° (H atoms closest to the CaF₂ surface) which results in the phase relationships between the CH and OH oscillators moving from destructive to constructive interference. Higher bulk concentrations of SDS result in the enhancement of both the OH and CH oscillator responses (Figure 2d) as the surface charge (now negative) steadily increases as a result of the continued adsorption of SDS molecules to the bilayer. This behavior continues up to SDS concentrations of ~7 × 10⁻³ M, where the VSF response of all features reach their maximum value. An illustration of the three distinct surface environments (monomer adsorption, surface charge compensation, and bilayer formation) is shown in Figure 3. A more detailed analysis of the results and fits to the data will appear in a later comprehensive publication.²⁹

Conclusion

We have shown direct evidence of the charge reversal behavior and bilayer formation upon the adsorption of the anionic surfactant sodium dodecyl sulfate (SDS) onto the semisubtle ionic solid CaF₂ and the dramatic effect of this adsorption on the orientation and structure of interfacial water molecules. This complex solid/liquid system can be broken down into three distinct regions: (1) At low surfactant concentrations (below 2 × 10⁻⁴ M), the anionic surfactant molecules adsorb as monomers to the oppositely charged CaF₂ surface. This adsorption serves to disrupt the well ordered tetrahedrally bound water molecule network within the interfacial region by steadily neutralizing the electric field emanating from the positively charged surface. The SDS monomers adsorb with their disordered tails protruding into the aqueous phase. (2) At SDS concentrations between 2 × 10⁻⁴ and 3.5 × 10⁻⁴

M the surface charge on the CaF₂ solid reverses (the point of zero charge, PZC) with a commensurate flip in the orientation of the interfacial water molecules. (3) At SDS concentrations above 3.5 × 10⁻⁴ M, a bilayer is formed on the CaF₂ surface with the negatively charged sulfate headgroups penetrating into the aqueous phase. Water molecules are aligned by the electric field originating from the negatively charged “surface” of the SDS bilayer through the electric field/dipolar interactions. The interfacial water molecules are now oriented, on average, 180° from their original neat solid/liquid positions. This orientational information is obtained by careful analysis of the interferences between resonant vibrational modes of the CH and OH oscillators contributing to the VSF spectra. These studies are part of a larger investigation into the adsorption behavior of surfactant molecules onto ionic solids and the affect of this adsorption on the interfacial water structure.

Acknowledgment. The authors gratefully acknowledge the financial support of the Department of Energy, Basic Energy Sciences DE-FG06-96ER45273 and the Petroleum Research Fund of the American Chemical Society. One author (F.M.) acknowledges the sabbatical support provided by Whitman College.

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