

Observations of Interfacial Population and Organization of Surfactants with Sum Frequency Generation and Surface Tension

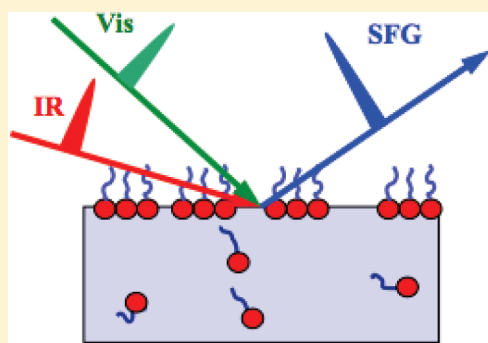
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S Supporting Information

ABSTRACT: The complementary interface-sensitive methods of sum frequency generation (SFG) and surface tension have been used to investigate surfactants at the air/water interface. SFG yields information on the density and orientation of surfactants at the interface, whereas surface tension yields information on the surface excess of surfactants, which, however, is not their interfacial density. The rapid rise in the SFG signal to its maximum value at 1 mM, which remained essentially constant thereafter, was attributed to the formation of large surfactant domains. Above 1 mM, the domains, all of which have the same density, dominated the SFG signal. As a consequence, the SFG signal remained essentially constant. The surface excess had an equally rapid rise to its maximum value at 1 mM, which remained constant until reaching a concentration of 3 mM, where it dropped to a zero value, indicating that a full surfactant monolayer had been formed. This coincides with the formation of bulk micelles, which is commonly referred to as the critical micelle concentration. The orientation of the surfactant carbonyl chromophore was obtained from polarization measurements of the SFG signal and showed a small change at and above a 1 mM concentration. The SFG results and the surface tension results, though inherently different, were found to be consistent with each other.



INTRODUCTION

An improved understanding of surfactant adsorption at the air/water interface is important in many areas of science and technology.^{1–4} Adsorption of surfactants to the air/water interface not only changes interfacial properties but also is a sensitive indicator of changes in the bulk solution. The sharp change in surface tension at a particular bulk surfactant concentration, called the critical micelle concentration, CMC, signals the formation of micelles in the bulk solution.³ Surface tension is a powerful method because of its sensitivity and the simplicity of experimental measurements. In the study reported here, both surface tension and a complementary method, namely, the interface selective nonlinear spectroscopy, vibrational sum frequency generation, have been used to investigate the adsorption of a surfactant to the air/water interface. The particular surfactant **S-10** (Scheme 1) used in this study was synthesized in order to achieve the following: moderate solubility, be surface-active, contain a strong SFG-active chromophore, that is, Raman- and IR-active, that is readily differentiated from interfacial water vibrations, and an orientation at the interface that can be obtained from SFG polarization measurements of a simple chromophore. The chromophore is carbonyl, $\text{C}=\text{O}$, and the symmetry axis is the carbon–oxygen bond axis.

From measurements of the surface tension as a function of the concentration of the surfactant in the bulk solution, one obtains, in conjunction with the Gibb's equation, the surface excess of the

surfactant. It is important to note that surface excess is not the population of surfactant at the interface but rather is the number of surfactant molecules, or moles, in the interface minus the number of surfactants in a bulk volume of the solution that contains the same number of solvent molecules at the interface. On the other hand, SFG yields the density of surfactant molecules at the interface.^{5–30} Because the intensity of the SFG signal is proportional to the square of the number of molecules, N^2 , in the area of the interface that is irradiated by the incident pulsed of light,^{32–35} we obtain the surfactant density by taking the square root of SFG signal. The combination of surface tension and SFG measurements has provided information on surfactant structure at the interface, the dependence of the surface excess on bulk surfactant concentration, the formation of micelles in the bulk solution, and the surface organization of surfactants into aggregates (surface micelles), which has received less attention than the bulk surfactant organization into aggregates (micelles).

EXPERIMENTAL SECTION

The experimental SFG setup used in our measurements of the sum frequency spectra is described in earlier work.^{29–31} Briefly,

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Scheme 1. Chemical Structure of the Surfactant *N*-(4'-Methoxy-10-benzoyldecyl)-*N,N,N*-trimethylammonium Bromide (S-10)

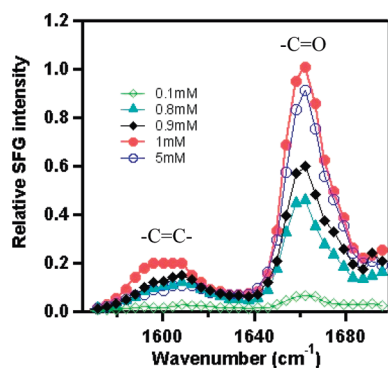
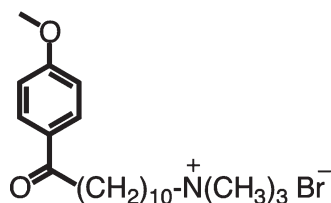


Figure 1. SSP polarized SFG spectra of S-10 surfactant at different concentrations at the air/water interface.

SFG spectra were measured by mixing a spectrally narrowed 800 nm pulse from a home-built pulse shaper with a bandwidth of 10 cm^{-1} and time duration of 2.5 ps, with a femtosecond IR pulse from an OPA. The output energy at 800 nm after pulse shaping was $30\text{ }\mu\text{J}$ per pulse, and a typical energy of the IR pulse was $8\text{ }\mu\text{J}$. The sum frequency generated, after temporal and spatial overlap of these two pulses at the sample surface, was detected using a monochromator and a charged coupled device, CCD camera. The SFG intensities were normalized to a GaAs reference. The two polarization combinations measured in each experiment were SSP and PPP, where the first letter denotes the polarization of the sum frequency, the second one that of the visible light, and the last one that of the IR light. These polarizations are connected with the laboratory coordinates by nonlinear Fresnel coefficients and appropriate projections and are correlated with molecular hyperpolarizability at interfaces.^{32–35} In order to determine the orientational structure, we used the intensity ratio method in our data analysis.^{32–35}

The chemical structure of the S-10 surfactant is depicted in Scheme 1. Details of the synthesis of the S-10 surfactant are described in the Supporting Information.³⁶

RESULTS AND DISCUSSION

SFG Spectrum of S-10 Surfactant. Figure 1 shows the SSP SFG spectra at different concentrations of the surfactant. As can be seen in Figure 1, there are two prominent peaks located at 1622 and 1668 cm^{-1} , which are assigned to the $-\text{C}=\text{O}$ stretch mode and the $-\text{C}=\text{C}-$ stretch mode in the benzene ring of the surfactant.^{37,38} An important feature in Figure 1 is the sharp increase in the amplitude of the SFG signal originating from the carbonyl chromophore for a very small change in the bulk

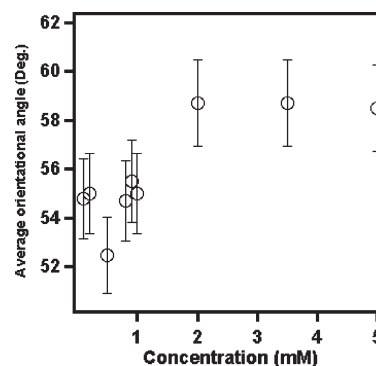


Figure 2. Average orientational angles of the $-\text{C}=\text{O}$ chromophore of the S-10 surfactant as a function of concentration.

concentration, that is, a change of 0.1 mM in going from 0.9 to 1 mM .

Orientation of the Surfactant $-\text{C}=\text{O}$ Chromophore. The calculation of the orientations of the $-\text{C}=\text{O}$ group at the interface assumes a narrow orientational distribution. The symmetry of the $-\text{C}=\text{O}$ group is $C_{\infty v}$. Thus, there are three nonzero hyperpolarizability elements, which are $\beta_{zzz}^{(2)}$, $\beta_{xxz}^{(2)} = \beta_{yyz}^{(2)} = r * \beta_{zzz}^{(2)}$, where z is parallel to the $-\text{C}=\text{O}$ bond and x and y are perpendicular to the $-\text{C}=\text{O}$ bond, and $r = \beta_{xxz}^{(2)}/\beta_{zzz}^{(2)}$. On the basis of the standard calculation method of an orientational angle and the assumption that molecular orientation has delta function distribution,^{21,29,35,39} the orientational angles of the $-\text{C}=\text{O}$ stretch mode of the surfactant at different concentrations are shown in Figure 2. A significant feature is the change in the $-\text{C}=\text{O}$ orientation that, though small, $\sim 4^\circ$, clearly shows a sharp increase above a 1 mM bulk surfactant concentration.

Surface Tension, Surface Excess, and SFG Field E_{SFG} . Surface tension measurements (Figure 3A) in conjunction with calculation of the Gibbs adsorption of an ionic surfactant (eq 1) were used to obtain the surface excess of the surfactants (Figure 3B). The relationship is given by the Gibbs adsorption equation.^{1,3}

$$\Gamma = -\frac{1}{\zeta RT} \frac{\partial \gamma}{\partial \ln c} \quad (1)$$

In eq 1, Γ is the surface excess concentration of solutes, c is the molar concentration of solutes, and γ is the surface tension of solutes. For a nonionic surfactant, ζ is equal to 1, whereas for a 1:1 strong electrolyte surfactant, $\zeta = 2$.³ The surface excess at a bulk concentration C is obtained by taking the derivative of the surface tension at C . The concentration dependence of the sum frequency field, E_{SFG} , which is the square root of the SFG intensity, is shown in Figure 3B together with the surface excess for purposes of comparison.

To summarize the results shown in the various figures, it is seen that there is a marked change at a bulk surfactant concentration of $\sim 1\text{ mM}$ in the carbonyl SFG spectrum, the strength of the SFG signal, the carbonyl orientation, and the surface excess. There is also a marked change in the surface tension and the related surface excess at a bulk surfactant concentration of $\sim 3\text{ mM}$. In addition, the SFG results show that the properties being measured remain essentially constant above 1 mM . This latter result indicates that there is either no change or SFG does not detect any marked change in the surfactant density above

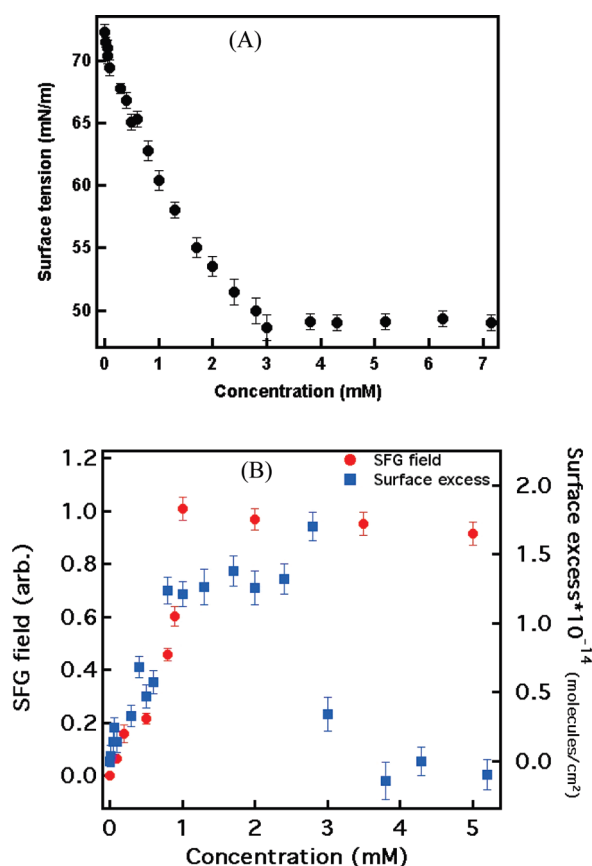


Figure 3. (A) Surface tension plotted as a function of S-10 concentration. (B) Surface excess and SFG field amplitudes of the $\text{C}=\text{O}$ chromophore.

1 mM. This is to be contrasted with the significant change in the surface tension in going from a bulk concentration of 1 mM to 3 mM. It is seen clearly in Figure 3A that surfactant molecules continue to be adsorbed up to 3 mM. To reconcile these apparently opposing results, it is proposed that large surface aggregate domains are formed on reaching a 1 mM concentration.^{40,41} It is because the intensity of the SFG signal scales with the square of the number of surfactant molecules per unit area that the much higher density of surfactants in the domains relative to the density of free surfactant molecules results in the domains dominating the SFG signal. The surfactants in the domains have the same density as in the full surfactant monolayer. At a concentration of 1 mM, the size of the domains is sufficiently large that the incident light subtends an interfacial area that is smaller than the size of the domains. Therefore, further increase in the domain size as the full monolayer coverage is reached does not change the SFG, as is shown in Figure 3B. On the other hand, the addition of free surfactants beyond 1 mM, to the interface, reduces the high surface free energy by displacing water molecules in the remaining surfactant-free part of the air/water interface located between the domains. This adsorption is manifested in the continuing decrease in surface tension as the bulk surfactant concentration increases from 1 to 3 mM. At 3 mM and beyond, the surface tension remains constant, indicating that a full monolayer has been formed. A sharp drop in the surface excess to a value of zero is observed to occur at 3 mM, as expected from the Gibbs

equation, eq 1, because the surface tension has ceased to change as the bulk concentration is increased; that is, a full monolayer has been formed. The observation that the Gibbs excess remains at zero above 3 mM, and that no additional surfactants adsorb to the interface above 3 mM, as shown by the constant surface tension and SFG signal, requires the concentration of free surfactant in the bulk solution to remain constant. If this was not the case, the surface excess would continue to change and not go to zero, but rather would become negative. The process that occurs at 3 mM is the formation of micelles; that is, the critical micelle concentration has been reached. Our results show that, when more surfactant molecules are added to the bulk solution above 3 mM, they are taken up by the micelles in the solution.

The formation of domains that we have described is consistent with a surface pressure versus area per molecule phase diagram of long-chain surfactants that is interpreted in terms of surface phases, that is, the gas, the gas–liquid expanded-coexistence region, the liquid expanded, and the liquid condensed regions.^{1,3,40} In this latter model, the presence of surfactant domains and free surfactants that finally condense to the liquid expanded phase, which is compressed further to the liquid condensed phase, is consistent with our explanation. Although the surfactant used in our study may be too soluble to form well-defined surface phases, the general ideas, for example, the domains being present in the gas-expanded liquid coexistence region, are of value for purposes of comparison.

CONCLUSIONS

Measurements of the vibrational SFG signal and surface tension as a function of bulk concentration yielded new insights into the organization of the surfactant, *N*-(4'-methoxy-10-benzoyldecyl)-*N,N,N*-trimethylammonium bromide, at the air/water interface. They yield different information. The amplitude of the SFG electric field scales as the population of surfactant molecules in the irradiated area of the interface, that is, surfactant density, whereas surface tension yields the surface excess of surfactants, which, however, is not the density of surfactants at the interface, but rather the relative density at the interface with respect to its bulk density. It was found that both the surface excess and the SFG field had the same rapid rise up to 1 mM, with both reaching their maximum values. The SFG field above 1 mM was a plateau. It was proposed that large domains are formed at 1 mM, resulting in the incident light pulses sampling the same domain interfacial density and thus yielding a constant SFG signal. The continued adsorption of surfactant molecules did not alter the domain density but did reduce the surface tension as surfactant molecules displaced the high surface energy water molecules located between the surfactant domains. At 3 mM and above, the surface tension became constant and the surface excess has a value of zero, indicating that a full monolayer and that the critical concentration to form bulk micelles has been reached. This is in agreement with the SFG results, finding that both no additional surfactant molecules are adsorbed and a full monolayer has been formed.

ASSOCIATED CONTENT

S Supporting Information. Details of the synthesis of the S-10 surfactant. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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