

Adsorption of SDS and PEG on Calcium Fluoride Studied by Sum Frequency Generation Vibrational Spectroscopy

Michael T. L. Casford and Paul B. Davies*

Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom

Received: August 9, 2007; In Final Form: October 16, 2007

The adsorption of sodium dodecyl sulfate (SDS) from aqueous solution onto a calcium fluoride substrate (CaF_2), in the presence of polyethylene glycol (PEG) of different molecular weights, has been investigated using the interface specific nonlinear optical technique of sum frequency generation (SFG) vibrational spectroscopy. Spectra of adsorbed SDS (in the C–H stretching region) were recorded at the surface of a CaF_2 prism in contact with SDS solutions at concentrations up to the cmc (8 mM) of the pure surfactant and in contact with binary solutions containing SDS and PEG with molecular weights from 400 to 12 000. In contrast with SFG spectra from the same combinations of surfactant and polymer on a hydrophobic surface, there was no evidence of spectra arising from the actual polymer adsorbed on CaF_2 at any polymer molecular weight either in the absence or presence of surfactant. However, there was indirect evidence for the presence of adsorbed polymer from changes in the SDS SFG spectra in the presence of polymer compared with spectra when the polymer was absent. The SFG spectra of SDS at 0.8 mM were closely similar to each other at all polymer molecular weights and different from the spectra in the absence of the polymer. The spectral differences between the polymer present and polymer absent was much smaller when the solution concentration of surfactant was 8 mM.

Introduction

The interaction between polymers and surfactants in aqueous solution has attracted considerable attention and study over the past few decades.^{1–4} When the polymer is uncharged and the surfactant charged, the example of polyethylene glycol (PEG) and sodium dodecyl sulfate (SDS) has become a model system for studying polymer–surfactant interactions in solution.⁵ The strength of the interaction between polymer and surfactant is determined by ionic and polar forces and hydrophobic and hydrophilic interactions. In the case of SDS and PEG, the dominant interaction is the electrostatic interaction between the surfactant anionic head group and the polymer polar ether group with additional hydrophobic interactions between the ethylene oxide monomer units and the surfactant hydrocarbon tails. In binary solutions, SDS micellar structures form on the polymer chain,⁶ frequently referred to as the pearls on a string or necklace structure. Isothermal titration results show that a stepwise saturation of the polymer with surfactant occurs as the polymer chain length increases. This has been interpreted as an incremental increase in the number of micelle-like structures adsorbed on the chain.⁷

The adsorption of PEG and SDS onto solid surfaces from their binary solutions has been less widely investigated than their interaction in the bulk solution. Cosgrove and co-workers⁸ used photon correlation spectroscopy, nuclear magnetic resonance, neutron reflection, and small angle neutron scattering (SANS) to investigate the effect of SDS on the adsorption of PEG on polystyrene latex and colloidal silica/water interfaces. They concluded that at low SDS concentrations considerable desorption and thinning of the adsorbed polymer layer occurred. In contrast, at higher concentrations, the adsorbed PEG layer

thickened due to repulsion between the micelles adsorbed along the polymer strand. These results concur with those from neutron reflection studies of the adsorption of SDS and PEG at the air/water interface⁹ with the exception that Cooke et al. found actual desorption of the polymer at high SDS concentrations. In either case it suggests competition between polymer and surfactant, at least at low surfactant concentrations. Both Cosgrove et al. and Cooke et al. used polymers of a single molecular weight namely 200 kD and 25 kD, respectively. Furthermore, both studies focused on the polymer rather than the surfactant species adsorbed at the interface and in particular on its film thickness.

Over the past decade we have used the nonlinear optical technique of sum frequency generation (SFG) vibrational spectroscopy^{10–12} to study polymer/surfactant adsorption on hydrophobic solid surfaces.^{13–17} The SFG technique provides structural information on the adsorbates, mainly the surfactant, and hence complements the polymer thickness measurements from SANS, etc. For oppositely charged polymer and surfactant, the adsorption is strongly synergistic due to the Coulombic attraction between them.^{13–15} In the case of SDS/PEG, the interaction is weaker and their adsorption on hydrophobic surfaces at low surfactant concentrations, based on the SFG spectroscopic evidence, is competitive.¹⁶ For fixed concentrations of PEG 12 000 and concentrations of SDS up to the cmc, both the surfactant and polymer have their SFG active methyl and methylene groups orientated toward the surface. Using selective deuteration, i.e., of the surfactant it was demonstrated that (a) both surfactant and polymer are present at the lowest surfactant concentrations in the presence of fixed concentrations of the polymer and (b) that there is less ordered adsorption of the surfactant in the presence of the polymer. However, at higher surfactant concentrations, i.e., approaching the surfactant cmc, there is little difference in the surfactant spectral intensity and in the conformational order, with or without polymer present.

* Corresponding author. E-mail: pbd2@cam.ac.uk.

Subsequently, Casford et al.¹⁷ investigated how the adsorption from binary solutions of SDS and PEG varied with polymer molecular weight. It was found that inhibition of surfactant adsorption at the lower SDS concentrations occurred for polymer molecular weights of 600 and above, although actual SFG detection of adsorbed polymer at the lowest polymer molecular weights was not possible. Only for PEG 400 was surfactant adsorption unaffected by the presence of the polymer.

These results were obtained for adsorption on a model hydrophobic surface. Since the polymer contains hydrophilic as well as hydrophobic functionalities, it is conceivable that a change in orientational and conformational order might occur for adsorption on hydrophilic substrates. A study of the adsorption of SDS from solution onto CaF₂ using SFG spectroscopy has previously been reported by Becraft et al.^{18,19} They showed that on this positively charged substrate, surfactant adsorption proceeded from monolayer adsorption to bilayer formation and charge reversal as the surfactant concentration increased from 0.04 mM (1/200 cmc) to 3 mM (~1/2 cmc). The SFG spectra of PEG at the CaF₂/air and CaF₂/water interfaces have also been recorded for spin-coated films of PEG 400 by Dreeson et al.²⁰ and Chen et al.²¹ Dreeson et al. observed that PEG did not adsorb to the substrate from solution and that the structure of a spin-coated film of PEG underwent major changes when exposed to water. This article reports a study of adsorption on CaF₂ from binary solutions of SDS and PEG of different molecular weights.

Experimental Details

The liquid samples were contained in a stainless steel flow cell with an integral calcium fluoride prism. SFG spectra were recorded on a nanosecond spectrometer, details of which can be found elsewhere,²² in both ppp and ssp polarization combinations (sum frequency, visible, infrared) in a counter propagating total internal reflection (TIR) beam geometry. The input beams of the IR and visible lasers were set as close to the critical angle of CaF₂ (71°) as possible in order to enhance the signal from the prism surface. Separation of the SFG output from reflected 532 nm radiation was achieved through a 532 nm holographic notch filter and a combination of edge and band-pass filters. Usually 60 shots per point were co-added on a digital storage oscilloscope (Le Croy) at 2.1 Giga samples per second, and the spectra were scanned at intervals of 2 cm⁻¹ between 2800 cm⁻¹ and 3100 cm⁻¹. Individual spectra were co-added for 6 h, normalized by that of pure water (or D₂O), and analyzed using a Levenberg–Marquardt least-squares fitting routine.²³ Up to six repeat spectra were recorded for each selected concentration.

All glassware, o-rings, and stainless steel components were cleaned following standard procedures and rinsed 20 times with 18.2 MΩ cm⁻¹ Milli-Q water. SDS from Aldrich was doubly recrystallized from ethanol prior to use. Perdeuterated SDS (CDN Isotopes) was used as received. Most of the spectra were recorded using poly(ethylene glycol) (Aldrich) with number average molecular weights (M_n) of 400, 600, 900, 1500, and 12 000 ($M_w/M_n = 1.1$). These samples were used as received. Lower polydispersity ($M_w/M_n = 1.00$ – 1.05) samples of the nearest equivalent values were used to confirm the results, obtained from Polypur and Polymer Laboratories plc, and also used as received.

SDS solutions were prepared immediately prior to use at above the cmc concentration and diluted with freshly prepared stock solutions of either Millipore water or PEG (500 ppm) in Millipore water as required. For recording the SFG spectra, solutions were introduced into the cell from a 100 mL reservoir

via cleaned Teflon tubing and circulated in a closed system using a peristaltic pump for 30 min prior to acquisition of the spectra. The pump was stopped immediately prior to spectral acquisition. At the conclusion of each acquisition, the cell was drained *in situ* and then refilled with the next solution which was circulated for 30 min as before.

Results

The SFG spectra of SDS adsorbed on CaF₂ from aqueous solutions of different surfactant concentrations in the absence of polymer are shown in Figure 1 for both ppp and ssp polarizations. The surfactant concentrations were chosen to permit these spectra to be directly compared with those measured on the hydrophobic gold substrate, reported earlier.¹⁷ This comparison is made for the ppp polarization combination in Figure 2. In the 1cmc spectra at the CaF₂/aqueous interface in ppp polarization shown in Figure 1 there are three clearly resolved peaks at 2870, 2930, and 2955 cm⁻¹, which are readily assigned to the three well documented methyl resonances, r^+ , r^+_{FR} , and r^- , respectively. There is also a broad feature underlying the ppp spectrum between 2900 and 2950 cm⁻¹ which may be assigned to the methylene Fermi resonance mode d^+_{FR} . For the ssp polarization combination the two r^+ resonances are clearly present, and the slight asymmetry of the r^+ resonance suggests the presence of a weak d^+ contribution around 2850 cm⁻¹. Generally, then the spectrum in the C–H region accords with the ssp spectrum reported by Becraft, Moore, and Richmond,¹⁸ albeit at lower pHs in their study. However, from the spectral fits in Figure 1, it is apparent that the d^+ resonances are not obviously intense features of the spectrum of SDS alone on CaF₂.

This contrasts with the spectra of SDS recorded in ppp polarization on the hydrophobic gold substrate where both the d resonances are prominent at all concentrations. Two further differences with the ppp spectra on the hydrophobic gold substrate are noteworthy. First, on CaF₂ there are no observable features below SDS solution concentrations of 1/10th the surfactant cmc (0.8 mM). This is partly due to the absence of a strong nonresonant background, i.e., from the gold substrate, which is known to enhance the signal intensity. This effect is absent for the CaF₂ substrate. Furthermore, surfactant adsorption due to electrostatic attraction between the surfactant head group and the charged substrate is expected to be a minimum at the pH used in this study. Second, the ppp spectra in Figure 1 also show, albeit only weakly, the lower edge of the SFG water spectrum commencing around 2980 cm⁻¹ as reported in detail by Becraft et al.^{18,19} This feature is included in the modeled spectra reported here. A further consequence of the absence of a nonresonant background in the CaF₂ spectral recordings is the loss of polar orientation information; the spectra are always peaks regardless of polar orientation.

Spectra Using Solutions of 0.83 mM SDS and Different MW PEG. Figure 3 shows the spectra, recorded in both polarizations, of the adsorbate formed on CaF₂ from solutions containing SDS at a constant concentration of 0.8 mM, approximately 1/10th cmc of pure SDS, and PEGs of molecular weights 400, 600, 900, 1500, and 12 000 at a constant concentration of 500 ppm. No spectra which could be attributed to the adsorbed polymer itself were detected either in the absence or presence of surfactant. This was confirmed in the latter case by recording spectra from solutions containing polymer and perdeuterated SDS (spectra not shown). The adsorbate spectra obtained using the binary solutions should be compared with those at the same SDS concentration in the absence of polymer

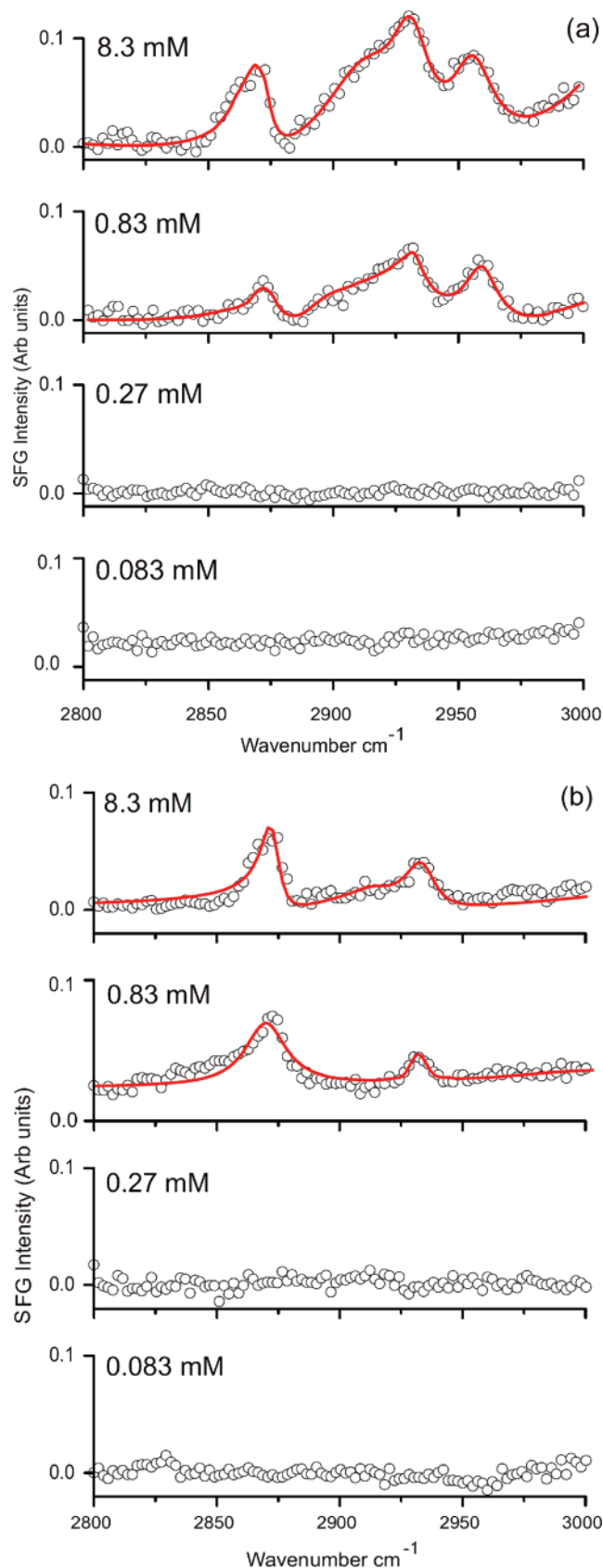


Figure 1. Sum frequency generation vibrational spectra of SDS adsorbed at the CaF_2 surface in contact with different surfactant solution concentrations. (a) Spectra in ppp beam polarization combination, and (b) in ssp polarization combination. In both a and b, the concentration of SDS increases from the bottom most to the top most spectra as: 0.083 mM, 0.27 mM, 0.83 mM, and 8.3 mM. Open circles in these and later figures are experimental data points, and solid lines are model fits to the spectra as described in the text.

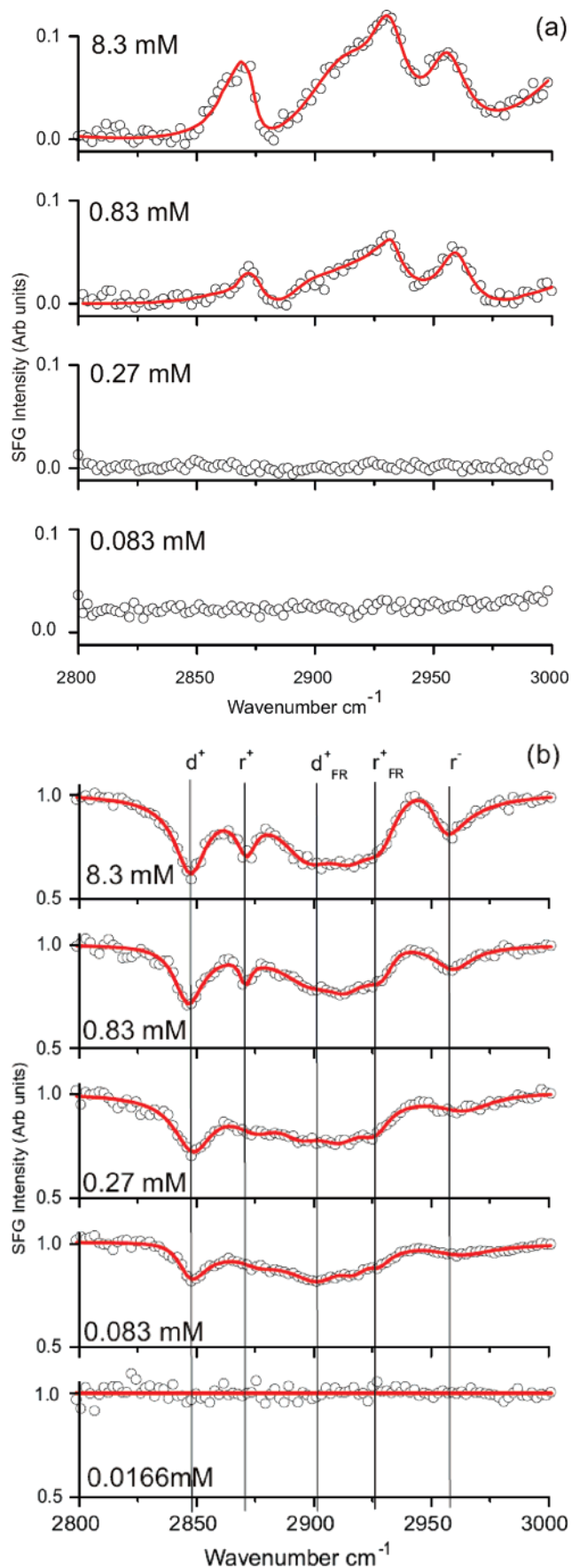


Figure 2. Comparison of SFG spectra, recorded in ppp polarization, of the adsorbate from SDS solutions in contact with (a) CaF_2 , data taken from Figure 1a, and (b) on hydrophobic gold. The SDS solution concentration for the recording of the bottom most spectrum in b is 0.0166 mM; all other concentrations are as described in Figure 1.

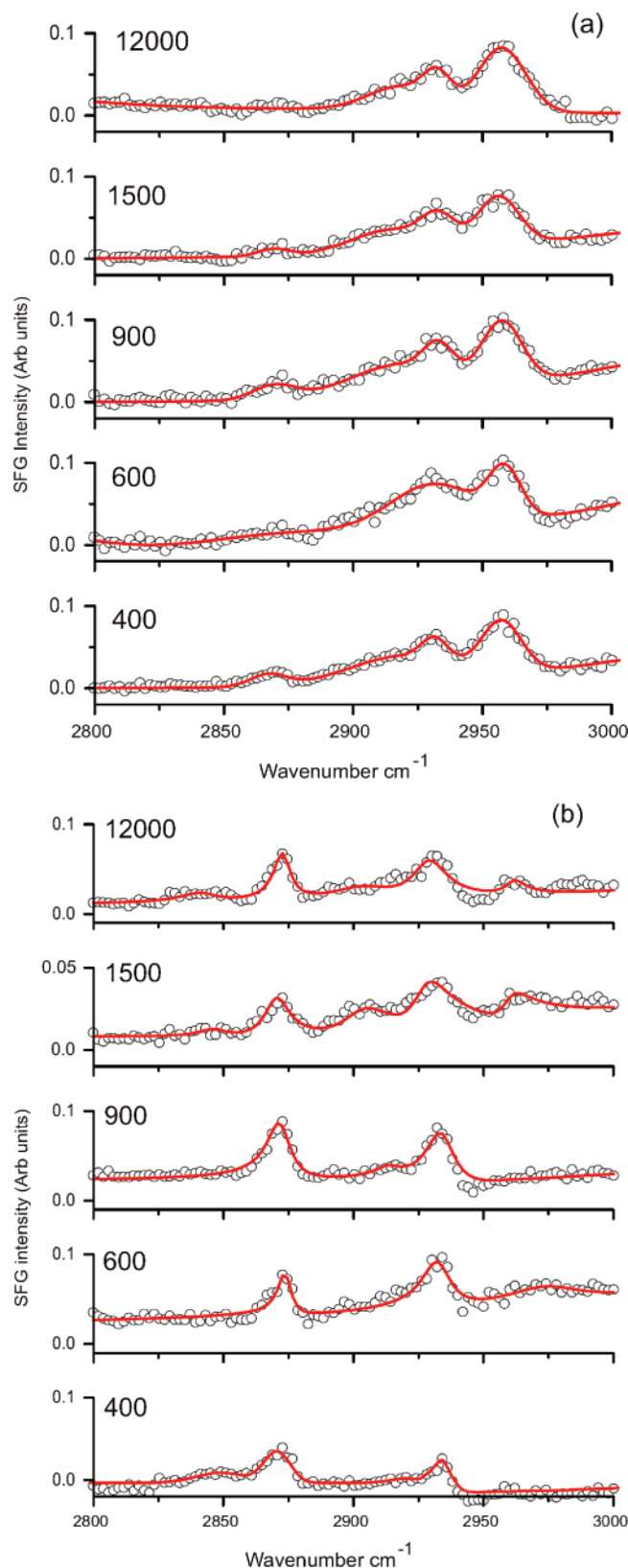


Figure 3. SFG spectra of SDS recorded on CaF_2 in contact with aqueous solutions containing surfactant at 0.83 mM concentration and different molecular weight PEG. (a) ppp polarization; (b) ssp polarization. Polymer molecular weight used from the bottom most to the top most spectra in both a and b: 400, 600, 900, 1500, 12 000.

shown in Figures 1, parts a and b (second panels from the top). The spectra of the adsorbates using solutions containing polymers with different molecular weights are similar to each other and noticeably different from the spectra using the pure

0.8 mM SDS solution. Specifically, in the ppp polarization combination the r^+ resonance at 2870 cm^{-1} is barely detectable and the r^+_{FR} and r^- resonances at 2930 and 2955 cm^{-1} , respectively, have a reversed intensity ratio (Figure 3a). Similar intensity differences can be seen in the ssp spectra when comparing Figure 3b with 1b. All the spectra are weaker than the corresponding spectra with 8 mM SDS (Figure 4) which are described below.

Spectra from Solutions of 8.3 mM SDS and Different MW PEG. The spectra corresponding to those shown in Figure 3 but at a constant SDS concentration of 8 mM, approximately the cmc of SDS in pure water, are shown in Figure 4. Generally, in both polarization combinations, the spectra of SDS adsorbed from a pure solution at the cmc concentration (top most spectra in Figure 1) are more intense than any of the spectra from mixed solutions. Although the spectra recorded using solutions of different polymer molecular weight at first sight look similar to each other and to the pure SDS spectra, on closer examination there are some differences between them (and which are not apparent in the spectra at 0.8 mM shown in Figure 3). First, the overall intensity of the resonances from the mixed solutions decreases slightly with increasing polymer molecular weight up to PEG 1500 and then increases again. For the SDS/PEG 12 000 combination (topmost spectra in Figure 4) the intensity of the resonances has almost regained that of the pure SDS spectrum. Second, in the ssp spectra a small resonance appears at about 2850 cm^{-1} which is much more distinctive than in the spectrum recorded for pure SDS adsorption, described earlier. This corresponds closely to the position expected for a d^+ methylene symmetric stretch resonance. This assignment is supported by the observation of a broad resonance at around 2915 cm^{-1} in the ppp spectra which is a well-known d^+ Fermi resonance feature. This same feature is weakly present in the ssp spectrum taken using binary mixtures with PEG 12 000.

Discussion

The adsorption of SDS in the presence of PEG of different molecular weights has now been investigated by SFG on two chemically different substrates, namely the charged CaF_2 hydrophilic substrate used here and the uncharged hydrophobic substrate of perdeuterated octadecane thiol (d-ODT) on gold examined earlier.¹⁷ Considering first the ppp polarization spectra of the adsorbate from pure SDS solutions in the absence of polymer, Figure 2, the spectra on hydrophobic gold are generally more intense than on CaF_2 at all the concentrations examined due in part to the enhancement provided by the nonresonant effect of the gold. Furthermore, it is interesting to note that no spectra are observed, in either polarization, at the CaF_2 substrate at the lower SDS concentrations of 1/30th and 1/100th of the cmc (Figure 1).

The marked difference in the spectral features on the two substrates, both in their absolute intensities spectrum versus spectrum and in the relative intensities of the resonances within a spectrum, suggests different adsorbate configurations. It is known that on hydrophobic gold the surfactant is adsorbed with its methyl end group pointing at the substrate and with its hydrocarbon chains, close packed but with sufficient conformational disorder to produce quite intense d resonances (Figure 2b), extending into the solution. In contrast, on CaF_2 the surfactant is adsorbed electrostatically via its anionic head group, although the adsorption observed here is likely to be weaker than when lower pHs are employed. This may explain the absence of any spectra at concentrations below about 1/10 cmc. Becraft et al.¹⁸ reported weak SDS spectra between about 1/40th

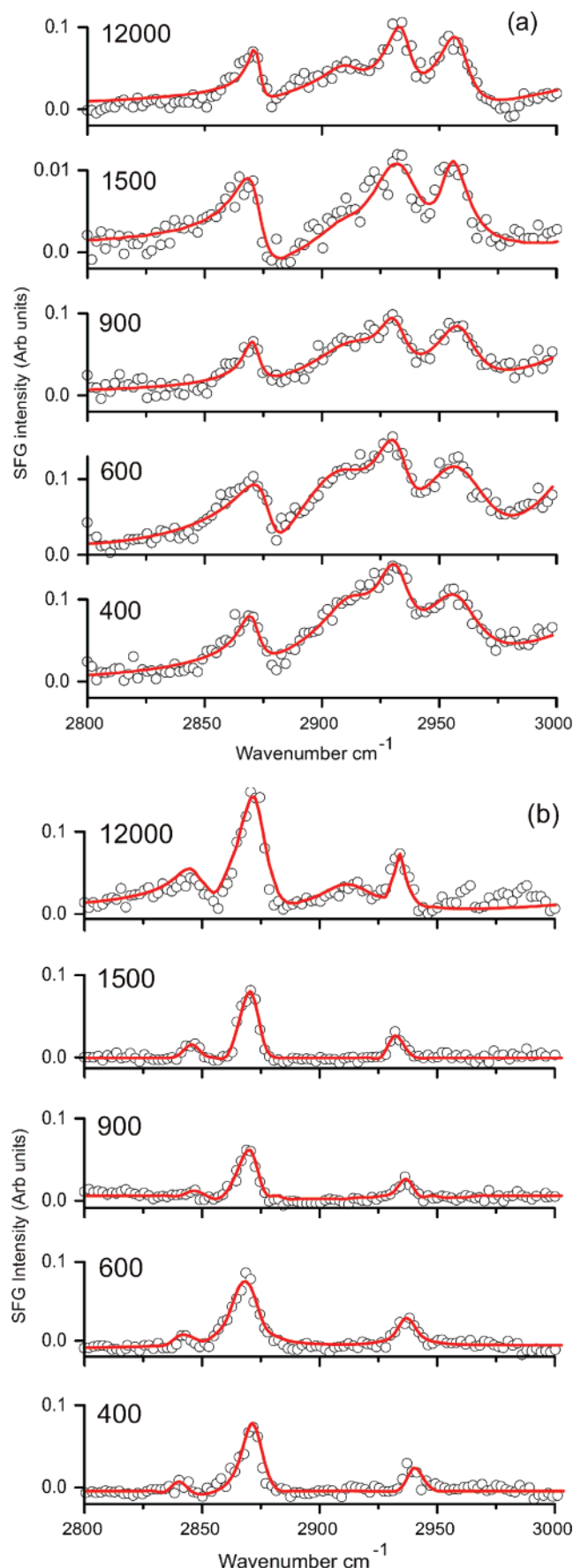


Figure 4. SFG spectra of SDS recorded under the same conditions as Figure 3 except with a surfactant concentration of 8.3 mM.

and 1/20th cmc. The adsorption in their case is presumably enhanced by the greater electrostatic charge on the substrate at

the lower pH selected for their study. This dependence on pH is emphasized by the distinct O–H shoulder on their SDS spectra in the C–H stretching region when a pH of 5.1 was used. Conversely at a pH of 7, i.e., that used here, Becraft and Richmond²⁴ find negligible O–H SFG intensity. It follows that under these conditions there would be a lower degree of SDS adsorption with no corresponding enhancement in the C–H region.

The presence of predominantly methyl resonances in the spectra on CaF₂ implies that only the methyl end groups of the surfactant chain are conformationally ordered enough to contribute to the spectrum. The marginally detectable d⁺ resonance suggests that the hydrocarbon tail is completely disordered and certainly more so than on hydrophobic gold. The general picture then, in the absence of the polymer, is compatible with the earlier SFG studies at lower pHs¹⁸ and with the general conclusion reached by Martin and Rochester²⁵ that SDS adsorption on CaF₂ is primarily driven by electrostatic interaction between the sulfate anion (head group) and Ca²⁺ sites on the substrate. However, it is not possible to say from the present study how much of the surfactant adsorption, if any, involves regions of surfactant bilayers.

The lower sensitivity of the experiment on CaF₂ precluded detecting spectra from the polymer itself, in contrast with the successful detection of polymer SFG spectra (for the higher molecular weight polymers) on the hydrophobic surface¹⁷. Nevertheless there is strong indirect evidence for the presence of the polymer at the interface from the surfactant spectra obtained here. Comparison of the spectra in the presence of the polymer at 1/10th cmc shown in Figure 3 with those in the absence of the polymer shown in Figure 1 reveal several differences particularly for the ppp polarization where the r⁺ resonance is barely detectable, except for the lowest molecular weight polymer, while the relative intensities of the r⁺_{FR} and r[−] resonances are reversed from their relative values in the absence of the polymer. The r⁺ resonance is clearly present in the ssp spectra but generally with lower intensity than the r[−] resonance in contrast with the ratio of intensities without polymer.

The spectra of SDS in the presence of the polymer at the surfactant cmc concentration (Figure 4) bear a closer resemblance to the spectra in the absence of the polymer (Figure 1) than at the lower surfactant concentration. Specifically the three methyl resonances in the ppp polarization spectrum and the two methyl resonances in the ssp spectrum have similar relative intensities to their intensities in the corresponding spectra without the polymer. This trend seems to be independent of polymer molecular weight within the run to run precision of the spectra although there was a marginal tendency for weaker spectra when polymers of weight 900 to 1500 were used. The appearance of more intense d resonances in the spectra when the polymer was present suggests that the polymer is increasing the conformational ordering of the hydrocarbon chain of the surfactant. This it may do by synergistic hydrocarbon chain–chain interaction as has been concluded by Martin and Rochester²⁵ in their study of adsorption of SDS and the nonionic polymer TX-100 on CaF₂.

The general conclusion to be drawn from the present work is that there is evidence from changes in the SFG spectra of the surfactant for the presence of the polymer at the interface both at 0.8 mM and at 8 mM concentrations of SDS. At the higher concentration the appearance of distinct methylene d resonances suggests that as the SDS solution concentration increases, changes in the configuration of the SDS at the interface are

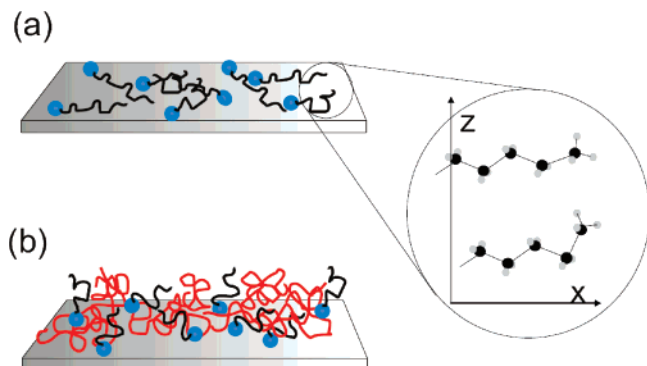


Figure 5. Schematic representation of the SDS orientation (a) in the absence of polymer and (b) with polymer present. The enhanced view of the SDS structure in part (a) shows the widely varying methyl tilt angle of the proposed surfactant orientation.

occurring in comparison with the lower surfactant concentration when polymer is present. Furthermore, the difference with the spectra recorded at the cmc without the polymer present and where no obvious d resonances were observed suggests that this configuration is different from that when the polymer is present. The changes in the spectra observed here suggest that at low surfactant concentrations both polymer and surfactant are adsorbed at the interface with little conformational order in the surfactant tail. At the higher surfactant concentrations, more surfactant is bound to the polymer, possibly causing a greater proportion of the polymer strand to leave the surface. Consequently the “compressed” chains of the surfactant would then be drawn further from the substrate facilitating closer packing, hence the appearance of more intense d resonances. The nature of the adsorbed polymer–surfactant system then changes from one where polymer and surfactant are both adsorbed on the substrate at low surfactant concentrations with relatively little interaction between them to a situation where at higher surfactant concentration there is a stronger polymer surfactant interaction which in turn increases the conformational order of the surfactant tails. The proposed orientation of the surfactant upon adsorption in the absence (a) and presence (b) of polymer is presented in Figure 5.

Conclusions

SFG spectroscopy has been used to study the adsorption of SDS from aqueous solution on CaF_2 at neutral pH in the presence of the nonionic polymer PEG, using PEGs of different molecular weights. Although it was not possible to detect an SFG signal from the polymer itself, for which there are several possible explanations such as spectrometer sensitivity and unfavorable polymer conformations, its presence at the solid/aqueous solution interface was inferred from changes in the SDS spectra themselves. Spectra of the adsorbed SDS were different in the presence of polymer from those with polymer absent from solution. No substantial differences in the SDS spectra were

observed when polymers of different molecular weights from 400 to 12 000 were used. However, some small changes in spectral intensities generally, and in the relative intensities of the resonances, were noted. The spectral results are compatible with a model in which both polymer and surfactant are adsorbed on CaF_2 from binary solutions and in which the polymer induces greater conformational order of the surfactant hydrocarbon chains at (notionally) the cmc of the surfactant than at lower surfactant concentrations.

Acknowledgment. We are grateful to Professor David Neivandt of the University of Maine and Dr. Simon Johnson of Unilever for helpful discussions. MTLC thanks the Engineering and Physical Sciences Research Council for a studentship and Unilever R&D Port Sunlight and the Isaac Newton Trust for supplementary financial support.

References and Notes

- (1) Goddard, E. D. *Colloids Surf.* **1986**, *19*, 255.
- (2) Goddard, E. D.; Ananthapadamanabhan, K. P. *Interactions of Surfactants with Polymers and Proteins*; Ananthapadamanabhan, K. P., Ed.; CRC Press: Boca Raton, FL, 1993.
- (3) Kwak, J. C. T. *Surfactant Science Series Volume 77: Polymer Surfactant Systems*; Marcel Dekker: New York, 1998.
- (4) Jönsson, B.; Lindman, B.; Holmberg, K.; Kronenberg, B. *Surfactants and Polymers in Aqueous Solution*; John Wiley and Sons: New York, 1999.
- (5) Dai, S.; Tam, K. C. *J. Phys. Chem. B* **2001**, *105*, 10759.
- (6) Shirahama, K. *Colloid Polym. Sci.* **1974**, *252*, 978.
- (7) Bernazzani, L.; Borsacchi, S.; Catalano, D.; Gianni, P.; Mollica, V.; Vitelli, M.; Asaro, F.; Feruglio, L. *J. Phys. Chem. B* **2004**, *108*, 8960.
- (8) Cosgrove, T.; Mears, S. J.; Obey, T.; Thompson, L.; Wesley, R. D. *Colloid Surf. A: Physicochem. Eng. Asp.* **1999**, *149*, 329.
- (9) Cooke, D. J.; Dong, C. C.; Lu, J. R.; Thomas, R. K.; Simister, E. A.; Penfold, J. *J. Phys. Chem. B* **1998**, *102*, 4912.
- (10) Shen, Y. R. *The Principles of Non Linear Optics*; Wiley: New York, 1984.
- (11) Shen, Y. R. *Nature* **1989**, *337*, 519.
- (12) Gracias, D. H.; Chen, Z.; Shen, Y. R.; Somorjai, G. A. *Acc. Chem. Res.* **1999**, *320*, 930.
- (13) Duffy, D. C.; Davies, P. B.; Creeth, A. M. *Langmuir* **1995**, *11*, 2931.
- (14) Windsor, R.; Neivandt, D. J.; Davies, P. B. *Langmuir* **2001**, *17*, 7306.
- (15) Windsor, R.; Neivandt, D. J.; Davies, P. B. *Langmuir* **2002**, *18*, 2199.
- (16) Casford, M. T. L.; Davies, P. B.; Neivandt, D. J. *Langmuir* **2003**, *19*, 7386.
- (17) Casford, M. T. L.; Davies, P. B.; Neivandt, D. J. *Langmuir* **2006**, *22*, 3105.
- (18) Becraft, K. A.; Moore, F. G.; Richmond, G. L. *J. Phys. Chem. B* **2003**, *107*, 3675.
- (19) Becraft, K. A.; Moore, F. G.; Richmond, G. L. *Phys. Chem. Chem. Phys.* **2004**, *6*, 1880.
- (20) Dreeson, I.; Humbert, C.; Hollander, P.; Mani, A. A.; Ataka, K.; Thiry, P. A.; Peremans, A. *Chem. Phys. Lett.* **2001**, *333*, 327.
- (21) Chen, C.-Y.; Evan, M. A.; Wang, J.; Chen, Z. *Macromolecules* **2002**, *35*, 9130.
- (22) Lambert, A. G.; Neivandt, D. J.; Briggs, A. M.; Usadi, E. W.; Davies, P. B. *J. Phys. Chem. B* **2002**, *106*, 10693.
- (23) Lambert, A. G., Ph.D. Thesis, University of Cambridge, 2001.
- (24) Becraft, K. A.; Richmond, G. L. *Langmuir* **2001**, *17*, 7721.
- (25) Martin, M. L. G.; Rochester, C. H. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 873.