J. Am. Chem. Soc. **1994,** *116,* 1125–1126

Direct Observation of Counterions Bound to a Charged Surfactant Monolayer by Sum-Frequency Vibrational Spectroscopy

David C. Duffy, Robert N. Ward,[†] and Paul B. Davies[*]

Department of Chemistry, University of Cambridge
Lensfield Road, Cambridge CB2 1EW, England

Colin D. Bain[*]

Physical Chemistry Laboratory
South Parks Road, Oxford OX1 3QZ, England

Received October 7, 1993

Aggregation of ionic surfactants is driven by the reduction in hydrophobic contacts between their alkyl chains and water, but is opposed by electrostatic repulsions between the charged headgroups of the surfactant. This repulsion is reduced by the adsorption of counterions at the surface of the aggregate in a region known as the electrical double layer.[1] An understanding of counterion adsorption is needed to rationalize phenomena associated with aggregation such as the "salting-in" of surfactants to form micelles,[2] sphere-to-rod transitions in micelles,[3] the viscoelasticity of micellar solutions,[4] and the electrophoretic mobility of surfactant aggregates.[5] In micellar catalysis, adsorbed counterions react with hydrophobic molecules that are solubilized within the micelle.[6] Electrostatic potentials at charged surfaces, which are heavily influenced by adsorption of ions, also play an important role in many biochemical processes, including ion conduction in membranes, fusion of phospholipid bilayers, and binding of charged drugs to membranes.[7]

In the Gouy–Chapman model, the distribution of counterions at the interface between a charged layer and the bulk solution is described as a continuous function with the greatest concentration of ions at the charged layer and with no distinction between "free" and "bound" ions.[8] Alternatively, the double layer can be viewed as an outer diffuse region, in which the ions are in random thermal motion, and an inner region where the mobility of the ions is severely restricted by a large electric field (the Stern model).[9] A number of techniques, such as NMR, ESR, and conductivity measurements, suggest that a large fraction of counterions, in the range 0.5–0.8, are "bound" to the aggregate with the remainder in the diffuse double layer (DDL).[10] However, the definition of "bound" ions varies from technique to technique, and the detailed structure of the interface is unclear. This communication provides the first study of bound counterions by vibrational spectroscopy. Infrared–visible sum-frequency spectroscopy (SFS) shows unequivocally that the asymmetric anion, SCN^-, adopts a preferential orientation in the Stern layer of a monolayer of the cationic surfactant, $C_{14}TA^+$ (tetradecyltrimethylammonium).

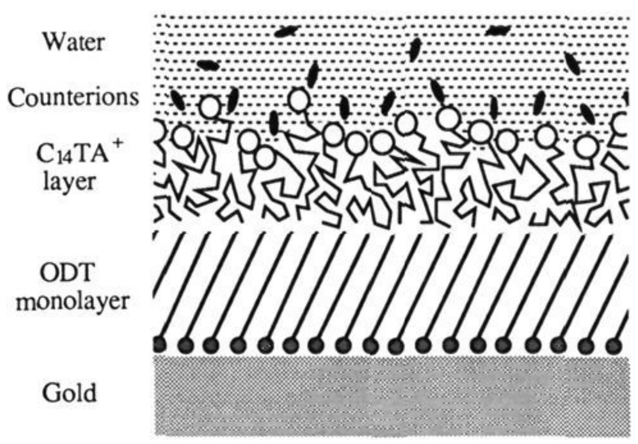

Figure 1. Schematic diagram of a monolayer of $C_{14}TA^+$ adsorbed to a self-assembled monolayer of ODT on gold. Open circles represent the positively charged surfactant headgroups; closed ellipses represent thiocyanate counterions. Note, however, that the exact location of the counterions is not known.

SFS is a nonlinear optical technique which has been well-documented elsewhere.[11-13] Briefly, a pulsed visible laser and a tunable pulsed infrared laser are superimposed at a surface, and the light emitted at the sum of their frequencies is detected. Emission at the sum frequency is resonantly enhanced by molecular vibrations; hence, when the infrared frequency is scanned, the emitted intensity provides a vibrational spectrum. A key feature of SFS is that light is only emitted from molecules in noncentrosymmetric environments. SFS is thus uniquely surface-sensitive and detects only those molecules that are adsorbed with a preferred orientation at an interface, even in the presence of the same molecules in solution. Since micellar solutions are generally isotropic,[14] and consequently sum-frequency inactive, we have studied counterions adsorbed to a *monolayer* of a surfactant.

A thin film of water containing the surfactant and SCN^- was trapped between a planar hydrophobic surface and a prism. The hydrophobic surface was provided by a self-assembled monolayer of octadecanethiol on gold.[15] The surfactant, $C_{14}TA^+$,[16] physisorbs to the hydrophobic surface forming a monolayer in which the hydrocarbon tails of the surfactant are oriented toward the hydrophobic surface.[17] The positively charged quaternary ammonium groups are therefore exposed at the surfactant–water interface (Figure 1).

Figure 2 shows the SF spectrum of $C_{14}TA^+SCN^-$,[18] from 1950 to 2150 cm^{-1}, as a function of concentration. The visible, IR, and SF beams were all p-polarized. The constant background SF signal arises from the surface of the gold, and the peak at 2050 cm^{-1} is assigned to the CN stretching mode of thiocyanate ions.[19] The selection rules of SFS dictate that the peak must be associated with ions that have adopted a preferred orientation within the double layer. The CN peak was also observed for a monolayer derived from 3×10^{-3} mol dm^{-3} tetradecyltrimethylammonium bromide ($C_{14}TAB$)[18] in a solution of 2.5×10^{-4} mol dm^{-3}

[†] Present address: Unilever Research, Port Sunlight Laboratory, Quarry Road East, Bebington, Wirral, Merseyside L63 3JW, England.

(1) Adamson, A. W. *Physical Chemistry of Surfaces*, 5th ed.; Wiley: New York, 1990. Rosen, M. J. *Surfaces and Interfacial Phenomena*, 2nd ed.; Wiley: New York, 1989.

(2) Underwood, A. L.; Anacker, E. W. *J. Colloid Interface Sci.* **1987**, *117*, 242–250.

(3) Lindblom, G.; Lindman, B. *J. Colloid Interface Sci.* **1973**, *42*, 400–409.

(4) Hoffmann, H.; Ebert, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 902–991.

(5) Stigter, D. *Recl. Trav. Chim. Pays-Bas* **1954**, *73*, 593–610.

(6) Bunton, C. A.; Nome, F.; Quina, F. H.; Romsted, L. S. *Acc. Chem. Res.* **1991**, *24*, 357–364.

(7) Leading references may be found in the following: McLaughlin, S. *Annu. Rev. Biophys. Biophys. Chem.* **1989**, *18*, 113–136.

(8) Chapman, D. L. *Philos. Mag.* **1913**, *25*, 475–481.

(9) Stigter, D. *J. Phys. Chem.* **1964**, *68*, 3603–3611.

(10) Lindman, B.; Wennerström, H. *Top. Curr. Chem.* **1980**, *87*, 1–83.

(11) Shen, Y. R. *Nature* **1989**, *337*, 519–525. Eisenthal, K. B. *Annu. Rev. Phys. Chem.* **1992**, *43*, 627–661.

(12) Ong, T. H.; Davies, P. B.; Bain, C. D. *Langmuir* **1993**, *9*, 1836–1845.

(13) Ong, T. H. Ph.D. Thesis, Cambridge, 1993.

(14) Even in anisotropic solutions, the surfactant aggregates are locally centrosymmetric.

(15) Bain, C. D.; Whitesides, G. M. *Angew. Chem.* **1989**, *101*, 522–528. Nuzzo, L. H.; Dubois, D. L. *Annu. Rev. Phys. Chem.* **1992**, *43*, 437–463.

(16) Alkytrimethylammonium surfactants are widely used as textile softeners and emulsifying agents. $C_{14}TA^+$ forms spherical micelles in solution at concentrations above 3.6×10^{-3} mol dm^{-3} (Lianos, P.; Zana, R. *J. Colloid Interface Sci.* **1981**, *84*, 100–107). Adsorption at the hydrophobic surface occurs at much lower concentrations.

(17) Ward, R. N.; Davies, P. B.; Bain, C. D. *J. Phys. Chem.* **1993**, *97*, 7141–7143. Ward, R. N. Ph.D. Thesis, Cambridge, 1993.

(18) $C_{14}TAB$ was obtained from Aldrich (98%) and recrystallized three times in acetone. $C_{14}TA^+SCN^-$ was prepared by exchanging $C_{14}TAB$ three times with excess NaSCN.

(19) Jones, L. H. *J. Chem. Phys.* **1956**, *25*, 1069–1072: the frequency of the CN stretch in solid K^+SCN^- is 2053 cm^{-1}.

0002-7863/94/1516-1125$04.50/0

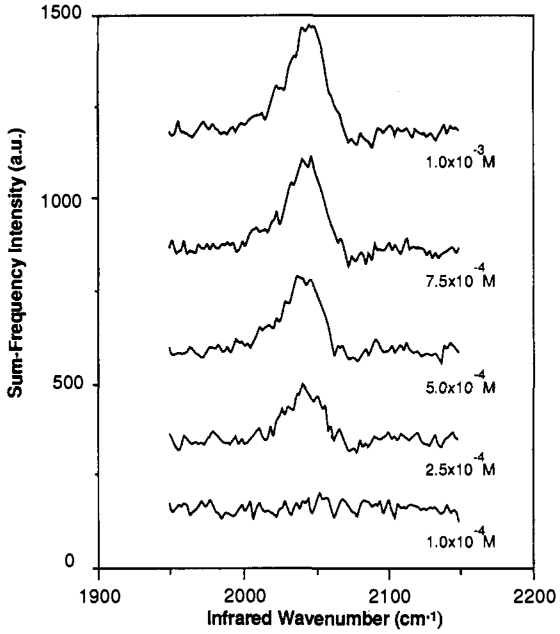

Figure 2. Sum-frequency spectra in the CN stretching region of aqueous solutions of $C_{14}TA^+SCN^-$ in contact with a hydrophobic monolayer of octadecanethiol on gold. The critical micelle concentration of $C_{14}TA^+SCN^-$ is approximately 8×10^{-4} M (determined from surface tension measurements at 20 °C). The spectra have been offset for clarity, and the zero of intensity refers to the concentration of 5×10^{-4} M.

NaSCN: if either the surfactant or the SCN^- was excluded, no peak was observed. The SCN^- is bound to the monolayer in preference to the bromide, as expected from the relative positions of the two ions in the lyotropic series.[1,2] Solutions of NaSCN containing an anionic surfactant (sodium dodecyl sulfate) or nonionic surfactant (dodecanol), which also form adsorbed monolayers with their hydrocarbon chains oriented toward the hydrophobic surface, showed no peak in the CN stretching region even at thiocyanate concentrations of 1 mol dm^{-3}. Whatever interaction is giving rise to the CN peak in Figure 2 is therefore specific to the cationic surfactant.[20]

In the Stern model, the ions we detect could lie either in the Stern layer or in the diffuse double layer. If the electric field in the DDL is sufficiently large to produce a substantial net orientation in the thiocyanate ions, we would also expect a highly dipolar neutral, such as acetonitrile (CH_3CN, μ = 3.39 D), to be oriented. We were, however, unable to detect the CN mode of CH_3CN by SFS from a 1% solution of CH_3CN in $C_{14}TAB$ at its cmc. We infer that the SCN^- ions detected by SFS lie in the Stern layer. This observation was unexpected given that Eisenthal has detected polarized water molecules in the double layer of a charged monolayer by second harmonic generation.[21] The difference in sensitivity of the two experiments may simply reflect the fact that the concentration of water (55 mol dm^{-3}) is much higher than that of either thiocyanate or acetonitrile (<1 mol dm^{-3}). The large difference between the CN stretching frequency of the SCN^- ion detected by SFS (2050 cm^{-1}) and the vibrational frequency of the ion in aqueous solution (2067 cm^{-1})[19] provides further evidence that the thiocyanate ions we detect do not reside in the DDL.

Sum-frequency emission carries information on orientation not only in its intensity but also in its phase. Peaks are observed in Figure 2 because there is constructive interference between the light emitted by the SCN^- ions and the background signal from the gold. If the polar orientation of the thiocyanate ions were inverted, the phase of the light emitted by the ions would change by 180°.[17] Consequently, destructive interference with the background gold signal would lead to a dip, rather than a peak, in the spectrum. To determine the polar orientation of the SCN^- ions, we have compared the SF spectrum in Figure 2 with the spectrum of SCN^- adsorbed to a gold electrode (Figure 3). It is believed that the peak at 2128 cm^{-1} in Figure 3b corresponds to the SCN^- bound to the electrode through the sulfur atom.[13,22] Since the CN resonance has the same phase for SCN^- bound to gold and to the surfactant monolayer, the polar orientation of the ion is almost certainly the same. Thus the thiocyanate counterions in the Stern layer have a net orientation in which the sulfur atoms are directed toward the monolayer. A specific interaction between the quaternary ammonium headgroup of the surfactant and the sulfur of the SCN^- is the likely cause of this orientation. The observed orientation is consistent with simple electrostatics: *ab initio* calculations[23] suggest that the sulfur atom carries a greater negative charge than the nitrogen atom. Hard and soft acid and base theory[24] would also predict this orientation since both sulfur and tetramethylammonium ions are classed as "soft". Ion solvation also has to be considered in order to explain the preferential binding of SCN^- over ions such as Br^-. There is some evidence that anions may partially shed their hydration shell in the Stern layer,[10] so the preferred orientation of the SCN^- may also be related to differences in the binding strength of the hydration shell at the two ends of the ion.

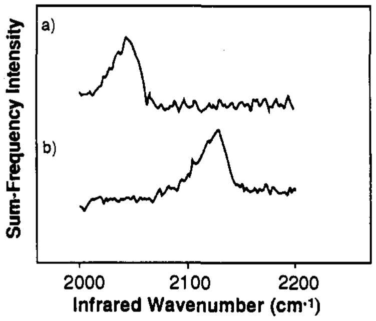

Figure 3. Sum-frequency spectra in the CN stretching region of (a) 7.5 $\times 10^{-4}$ M $C_{14}TA^+SCN^-$ in contact with ODT on gold and (b) SCN^- adsorbed on a gold electrode at a potential of +0.4 V vs saturated calomel electrode (SCE).

In conclusion, sum-frequency spectroscopy has provided the first vibrational spectrum of a counterion in the headgroup region of a surfactant monolayer. The appearance of a resonance assigned to the CN stretch of the thiocyanate counterion indicates that this ion has a preferred orientation at the interface, although the fraction of counterions adopting this orientation can not be determined directly.[25] It is likely that the bound counterions reside within a few angstroms of the charged layer, corroborating the view of this region as consisting of an outer diffuse region with an inner Stern layer. The phase of the light emitted from the CN groups indicates that the counterions are bound through the sulfur atom.

Acknowledgment. We thank the SERC and Unilever Research (Port Sunlight Laboratory) for equipment grants and CASE studentships for D.C.D. and R.N.W. We also gratefully acknowledge the support of the Royal Society.

---

(20) Binding of inorganic ions to the polar head group of non-ionic surfactants has been proposed (Ray, A.; Némethy, G. *J. Am. Chem. Soc.* **1971**, *93*, 6787–6793). We have not yet studied these systems.

(21) Zhao, X.; Ong, S.; Eisenthal, K. B. *Chem. Phys. Lett.* **1993**, *202*, 513–520.

(22) Ong, T. H.; Davies, P. B.; Bain, C. D. *J. Phys. Chem.* **1993**, *97*, 12047–12050.

(23) Parrini, F.; Morales, R. G. E. *J. Mol. Struct. (Theochem)* **1993**, *282*, 59–63.

(24) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533–3539.

(25) There are two obstacles to accurate quantitation. First, the hyperpolarizability of SCN^- is not known accurately and will, like the infrared transition dipole moment, be sensitive to environment. Second, SFS only measures net orientation. One could add an arbitrary number of randomly oriented SCN^- ions to the interface without changing the SF spectrum.