

## Structure of a Monolayer of Hexadecyltrimethylammonium *p*-Tosylate at the Air–Water Interface

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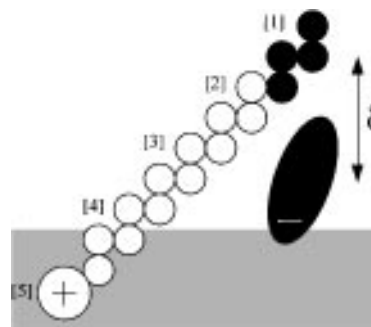
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Received August 13, 1997

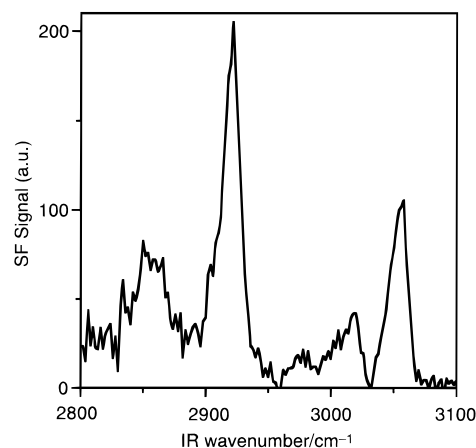
Single-chain cationic surfactants form small spherical micelles in dilute solutions. Addition of aromatic counterions can transform these micelles into long, threadlike aggregates with dramatic effects on the optical properties and rheology of the solution.<sup>1</sup> Here we show that aromatic anions also cause major and unexpected changes to the structure of monolayers at the air–water interface. We have used neutron reflection (NR)<sup>2</sup> and sum-frequency spectroscopy (SFS)<sup>3</sup> to study monolayers of hexadecyltrimethylammonium *p*-tosylate (CTA<sup>+</sup>Ts<sup>-</sup>).<sup>4</sup> NR allows us to determine the number density of each species in the monolayer and the location of the counterions with respect to the surfactant. SFS is sensitive to the orientation of the counterions and to changes in the structure of the surfactant monolayer caused by the *p*-tosylate ions.

We first present the results obtained by neutron reflection.<sup>5</sup> Selective deuteration of the CTA<sup>+</sup> and Ts<sup>-</sup> ions allows the area per molecule of each ion at the interface to be determined independently.<sup>6</sup> At the surface of a solution containing 1 mM CTA<sup>+</sup>Br<sup>-</sup> + 3 mM Na<sup>+</sup>Ts<sup>-</sup>, the areas (*A*) per CTA<sup>+</sup> ion and per Ts<sup>-</sup> ion were 52 and 65 Å<sup>2</sup>, respectively. Thus 80% of the counterions are bound to the monolayer.<sup>7</sup> The remaining 20% of the Ts<sup>-</sup> counterions are presumed to reside in the diffuse part of the electrical double layer. A control experiment on 1 mM CTA<sup>+</sup>Br<sup>-</sup> + 3 mM Na<sup>+</sup>Br<sup>-</sup> yielded *A* = 42 Å<sup>2</sup> per CTA<sup>+</sup> ion.<sup>8</sup> Counterions usually decrease the area per molecule for charged surfactants by screening the repulsive electrostatic interactions between the headgroups.<sup>9</sup> *p*-Tosylate has the opposite effect on the packing density.

Determining the location of the counterions requires a more sophisticated labeling scheme (Figure 1).<sup>10</sup> Five variants of CTA<sup>+</sup>Br<sup>-</sup> were synthesized in which successive blocks of four



**Figure 1.** Labeling scheme used to determine the position of the tosylate ions in the surfactant monolayer by NR. The surfactant is subdivided into five blocks: four blocks containing four carbons each and the headgroup. One block is deuterated (black) and the remainder (white) are contrast matched to water. The tosylate ion (black) is fully deuterated. The relative location of the tosylate ion and the surfactant chain reflect the experimental results in Table 1. The figure is schematic and should not be taken to imply that the chains are all-trans or uniformly tilted.



**Figure 2.** SF spectrum acquired from the surface of a solution containing 1 mM CD<sub>3</sub>(CD<sub>2</sub>)<sub>15</sub>N<sup>+</sup>(CD<sub>3</sub>)<sub>3</sub> Br<sup>-</sup> and 3 mM Na<sup>+</sup>*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>-SO<sub>3</sub><sup>-</sup>. The infrared field was p-polarized, and the visible and sum-frequency fields were s-polarized. The peak signal level corresponded to about four photons per laser pulse.

carbons in the chain or the headgroup were deuterated. Reflection of neutrons from each block-deuterated surfactant was measured in the presence of deuterated Ts<sup>-</sup>. The deuterated block and the tosylate ions each generate a sheet of scattering sites. The remaining protonated parts of the surfactant do not scatter neutrons coherently.<sup>11</sup> The neutrons reflected from these two sheets interfere with each other. The separation,  $\delta$ , between the two scattering sheets determines whether the interference is constructive or destructive and can be determined from the NR profiles. The values of  $\delta$  in Table 1 show that the center of the *p*-tosylate ion distribution<sup>12</sup> is equidistant from the headgroup of the surfactant and the methyl terminus of the hydrocarbon chain and coplanar with the third deuterated block in the surfactant.

In SFS, the vibrational spectra of the surfactant and counterion can also be distinguished by selective deuteration. Figure 2 shows a SF spectrum in the C–H stretching region of a monolayer of deuterated CTA<sup>+</sup> + Ts<sup>-</sup> on D<sub>2</sub>O.<sup>13</sup> The strongest

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(5) The experiments were performed on the beam line SURF at the ISIS spallation neutron source. A polychromatic neutron beam was deflected onto the surface of contrast-matched water at a grazing angle of  $\theta = 1.5^\circ$ . The intensity of the specularly reflected beam,  $R(Q_z)$ , was measured as a function of the momentum transfer,  $Q_z = 4\pi/\lambda \sin \theta$ , normal to the surface. NR profiles were modeled within the kinematic approximation. For further experimental details, see: Lu, J. R.; Thomas, R. K. *Surfactant Adsorption and Surface Solubilization* (Sharma, R., Ed.). *ACS Symp. Ser.* **1995**, *615*, 342.

(6) Full details of the experimental procedures and data analysis will be presented elsewhere.

(7) This value represents the saturation level: increasing the concentration of Na<sup>+</sup>Ts<sup>-</sup> to 10 mM did not increase further the bound fraction or change the area per surfactant molecule. All solutions were above the cmc.

(8) The area per molecule in the absence of added electrolyte is  $44 \pm 2$  Å<sup>2</sup>.

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(11) The scattering lengths of CD<sub>2</sub> and CH<sub>2</sub> groups are  $20.0 \times 10^{-5}$  and  $-0.8 \times 10^{-5}$  Å, respectively. Addition of a small amount of fully deuterated CTA<sup>+</sup>Br<sup>-</sup> cancels out the residual scattering density from the protonated parts of the chain.

(12) The center of scattering of the *p*-tosylate ion is almost exactly at the center of the aromatic ring.

**Table 1.** Separations ( $\delta$ ) between Deuterated Blocks (Figure 1) and *p*-Tosylate Ions Determined by Neutron Reflection

deuterated block	[1]	[2]	[3]	[4]	[5]
$\delta \pm 1$ (Å)	7	6	0	3	6

peak ( $2922\text{ cm}^{-1}$ ) is assigned to the symmetric methyl stretching mode of the tosylate ion and the principal aromatic peak ( $3057\text{ cm}^{-1}$ ) to a superposition of two C–H stretching modes:  $\nu_2$  and  $\nu_{20b}$ .<sup>14</sup> SFS is a coherent optical technique and therefore carries information in the phase of the emitted light as well as the intensity. The phase of the peaks shows that the *p*-tosylate ions are oriented with their methyl groups pointing away from the aqueous subphase.<sup>15,16</sup> The relative intensities of peaks taken with different polarizations of the laser beams suggest a mean angle between the long axis of the anion and the surface normal,  $\theta = 30\text{--}40^\circ$ .<sup>6,17</sup> This mean value implies a relatively narrow distribution of angles about the surface normal: for example, we would obtain  $\theta = 60^\circ$  if the tilts were randomly distributed in the upper half plane.

Finally, we address the conformation of the surfactant chains. Figure 3 compares SF spectra of  $1\text{ mM CTA}^+\text{Br}^-$  in the presence of either  $3\text{ mM deuterated Na}^+\text{Ts}^-$  or  $3\text{ mM Na}^+\text{Br}^-$ . Since the intensity of the sum-frequency signal depends on the inverse square of the area per molecule, we have normalized the spectra by  $A^{-2}$  to reveal more clearly the changes in the conformation of the molecules. The broad peak at  $2850\text{ cm}^{-1}$  arises from the symmetric  $\text{CH}_2$  stretch and is a qualitative measure of conformational defects in the chain (an all-trans hydrocarbon chain is sum-frequency inactive). The intensity of this mode is the same for  $\text{Br}^-$  and  $\text{Ts}^-$  counterions. The sharp peak at  $2878\text{ cm}^{-1}$  arises from the symmetric stretch of the terminal methyl group of the surfactant chain. The intensity of this peak can be related quantitatively to the orientation of the methyl group. If we take a simple model in which the outer parts of the hydrocarbon chains are uniformly tilted,<sup>18</sup> the tilt of the chains increases from  $58^\circ$  in  $\text{CTA}^+\text{Br}^-$  to  $67^\circ$  in  $\text{CTA}^+\text{Ts}^-$ . These angles are within experimental error of the values expected for a uniformly tilted monolayer with the density of a liquid hydrocarbon near its freezing point ( $56$  and  $63^\circ$  for areas per molecule of  $42$  and  $52\text{ Å}^2$ , respectively).<sup>19</sup>

(13) A pulsed visible laser ( $\lambda = 532\text{ nm}$ ,  $3.5\text{ ns}$ ) and a tunable, pulsed infrared laser ( $\lambda = 3.2\text{--}3.6\text{ }\mu\text{m}$ ,  $\sim 1\text{ ns}$ ) were overlapped at the air–water interface, and the blue light emitted at the sum of the two input frequencies was detected with a charge-coupled detector. Spectra were normalized to a reference spectrum acquired simultaneously from GaAs. For further experimental details, see: Bell, G. R.; Bain, C. D.; Ward, R. N. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 515.

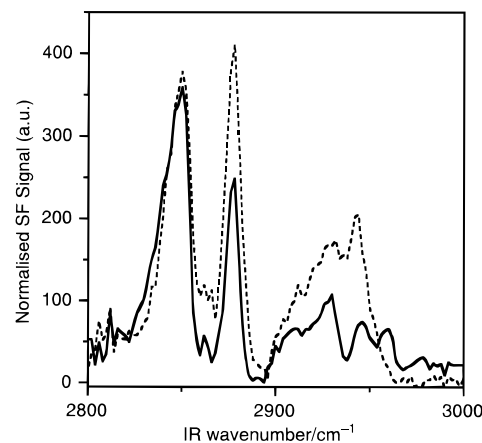
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(15) The phase of the emitted light, relative to that of a reference monolayer of known structure, is deduced from the interference between the molecular signal and the weak background signal from the  $\text{D}_2\text{O}$ .

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**Figure 3.** SF spectra acquired from the surface of a solution containing  $1\text{ mM CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3\text{Br}^-$  and  $3\text{ mM Na}^+ p\text{-CD}_3\text{C}_6\text{D}_4\text{SO}_3^-$  (solid line) or  $3\text{ mM Na}^+\text{Br}^-$  (dashed line). The infrared field was p-polarized, and the visible and sum-frequency fields were s-polarized. The spectra are normalized by the values of  $A^{-2}$  determined by NR.

By combining all the information from neutron reflection and sum-frequency spectroscopy, we obtain the following description of the surfactant monolayer in the presence of *p*-tosylate ions. Eighty percent of the counterions are bound to the monolayer, with a mean location coplanar with the sixth methylene unit of the hydrocarbon chain, counting from the headgroup. The ions are oriented close to the surface normal with the aromatic ring pointing away from the water. The sulfonate groups lie, on average, about  $3\text{ Å}$  above the plane of the trimethylammonium cations. Previous neutron studies have shown that water penetrates this far into the hydrocarbon region,<sup>20</sup> so the sulfonate ions almost certainly retain their solvation shells. To generate space for the tosylate ions within the monolayer, the area per surfactant molecule increases by one-quarter. Similar orientations for the tosylate ion and the hydrocarbon chains in the monolayer are favored on packing grounds. It is therefore likely that the hydrocarbon chains rise steeply away from the water surface before turning over to lie flatter in the region above the tosylate ions. Such a conformation would maintain a liquid-like density in the monolayer and agree with the orientation of the terminal methyl group inferred from the sum-frequency spectra. Since the same fundamental molecular interactions control aggregation at surfaces and in solution, the threadlike micelles formed by  $\text{CTA}^+\text{Ts}^-$  in solution are likely to share many of the structural features of these monolayers on a molecular scale.

**Acknowledgment.** This work was supported by the EPSRC and by Unilever Research Port Sunlight Laboratory. D.C.D. thanks Emmanuel College, Cambridge, for a Research Fellowship.

JA972842C

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