Effect of Chain Length on the Structure of Monolayers of Alkyltrimethylammonium Bromides (C$_n$TABs) at the Air−Water Interface

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Sum-frequency (SF) spectroscopy and ellipsometry have been used to study monolayers of the cationic surfactants C$_n$TAB (CH$_3$(CH$_2$)$_{n-1}$N$^+$(CH$_3$)$_3$Br$^-$) (n = 12, 14, 16, and 18) at the air-water interface at a constant surface area of 44 Å^2/molecule. The SF spectra of all four surfactants are very similar and yield a mean chain tilt of 58° near the methyl terminus. The ellipsometric data suggest that the density of the chain region in the monolayers is close to that of a liquid hydrocarbon, which is consistent with the chain tilt derived from the sum-frequency spectra. These results are in quantitative agreement with detailed structural profiles of C$_{12}$TAB and C$_{16}$TAB determined by Thomas and co-workers by neutron reflection.

Introduction

Surfactants are widely employed to modify the properties of the surface of water. The performance of a surfactant depends on its molecular structure and on the conditions under which it is employed, such as the concentration of the surfactant and the temperature, acidity, and ionic strength of the aqueous phase. The behavior of a surfactant is often quantified in terms of easily measurable quantities such as the effectiveness and efficiency of adsorption[1] and the surface tension γ at the critical micelle concentration (cmc). For a limited number of surfactants, precise measurements of thermodynamic quantities, such as the excess enthalpy and entropy of adsorption, have been made.[2] In specific applications, other empirical quantities, such as foam height, have been widely reported. From such measurements, general correlations can be drawn between the performance of surfactants and structural features of the surfactant molecules, such as the length and nature (linear, branched, fluorinated, etc.) of the hydrophobic chain and the size, charge, and polarity of hydrophilic headgroup.[3] While invaluable to the formulations chemist, such empirical correlations are of limited value in developing a fundamental understanding of the behavior of surfactants at interfaces. The structure of the surfactant monolayer is one of the primary determinants of the interfacial properties.[4] Consequently, a knowledge of the relationship between molecular structure and interfacial structure is a prerequisite for a more general understanding of the performance of surfactants.

Until recently, virtually no attempt had been made to understand the microscopic structure of a surfactant monolayer in terms of the molecular constitution of the surfactant. This inactivity arose not from the myopia of surface chemists but from a lack of suitable techniques for studying the molecular structure of surfactant monolayers. The development of X-ray and neutron reflectivity in the 1980's allowed, for the first time, direct structural measurements on surfactant monolayers. In a detailed study, Thomas and co-workers sought to isolate one

structural feature of the surfactant, the chain length.[5] They used neutron reflection (NR) to determine the structure of monolayers of alkyltrimethylammonium bromides (CH$_3$(CH$_2$)$_{n-1}$N$^+$(CH$_3$)$_3$Br$^-$, C$_n$TAB, n = 12, 14, 16, and 18) at a constant area per molecule of 44 ± 2 Å^2.[5,6,7] The initial conclusion of this study was as remarkable as it was unexpected: the thickness of the monolayer appeared to be independent of chain length. This result implied that the density of the monolayer and the tilt of the chains from the chain normal increased with increasing chain length.[5] In this article, we report measurements on this same system with two other surface-sensitive techniques, sum-frequency spectroscopy, and ellipsometry. The data we present suggest that the structures of all four monolayers are very similar and that neither the mean chain tilt nor the density varies significantly with chain length. The thicknesses measured by NR are, however, convoluted with a large contribution from the roughness of the interface which masks subtle changes in the structure of the monolayer. Detailed density profiles of two chain lengths, C$_{12}$ and C$_{16}$, obtained by Thomas et al. by isotopic labeling are in remarkably good agreement with the data presented here.[5,6]

Experimental Details

The SF spectrometer[8] and the experimental procedures for acquiring[9] and analyzing[10] SF spectra have been described in detail elsewhere. Briefly, the pump lasers beams were a frequency-doubled Nd:YAG laser (Spectron Lasers, 532 nm, 3.5 ns, 10 mJ/pulse, 2 mm diameter) and a tunable infrared laser (2800−3000 cm^{-1}, 1 ns, 1 mJ/pulse, 0.5 mm diameter) generated by stimulated Raman scattering the output of a tunable dye laser in high-pressure hydrogen. The SF light (∼460 nm) was detected with a back-thinned CCD (Princeton Instruments). The SF spectra were referenced to a spectrum acquired simultaneously from GaAs. The angles of incidence were θ_{vis} = 55° and θ_{IR} = 50° and a counterpropagating geometry was employed. The infrared laser was p-polarized, the visible laser s-polarized, and the sum-frequency beam s-polarized. This combination of polarizations is most sensitive to structural changes in the monolayer.[9] Surfactant solutions were prepared in D$_2$O (Aldrich) at a concentration just above the critical micelle concentration (cmc) for each surfactant (see Table 1).

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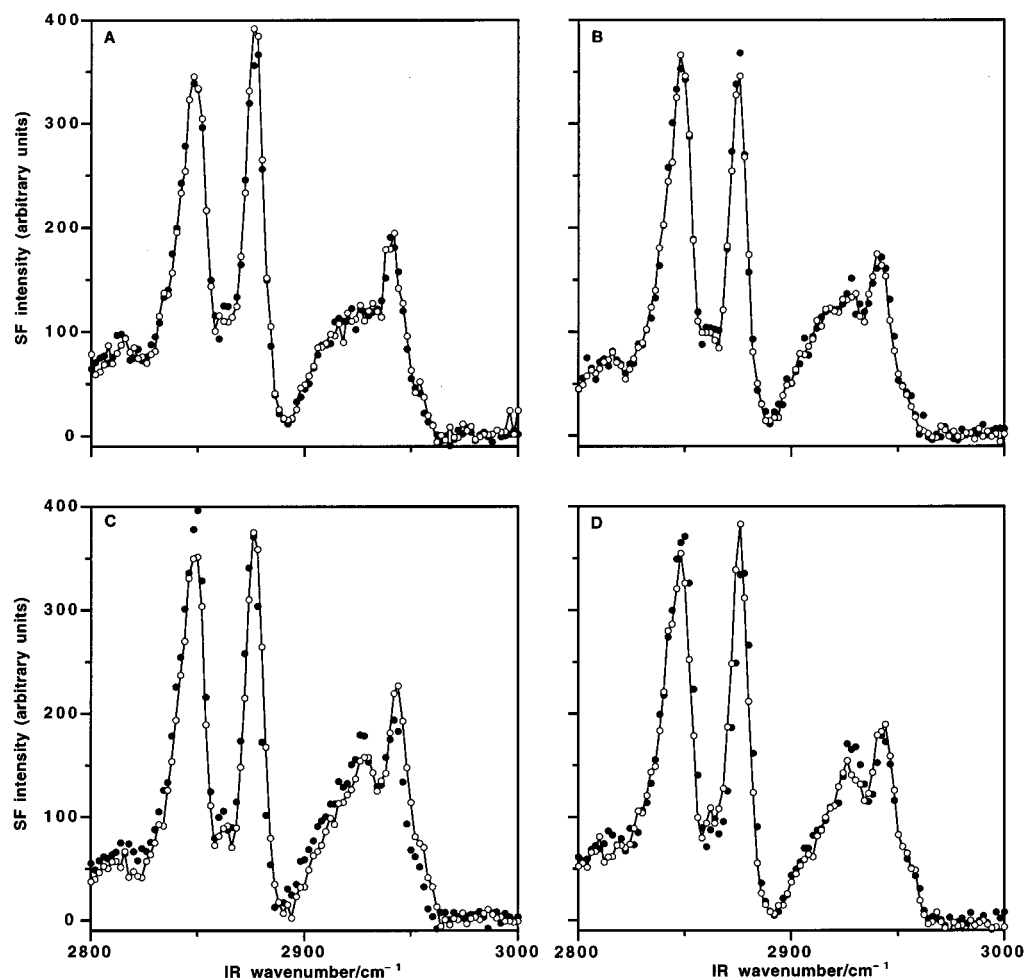*J. Phys. Chem. B, Vol. 102, No. 1, 1998* **219**

Figure 1. SF spectra acquired from the surface of solutions of C$_n$TAB in D$_2$O at an area per surfactant molecule of 44 Å^2. A, C$_{12}$TAB; B, C$_{14}$TAB; C, C$_{16}$TAB; D, C$_{18}$TAB. Filled and solid symbols represent two independent experiments. The solid line is a guide to the eye through the open symbols. Polarizations: sum-frequency (s), visible (s), infrared (p). Temperatures and concentrations are listed in Table 1.

TABLE 1. Temperatures and Concentrations Employed in SF Experiments on C$_n$TAB

n	concn/mM	T/K
12	4.0^a	298
14	4.3	298
16	1.1	301
18	0.37	306

^{a} In presence of 0.15 M NaBr.

Ellipsometric measurements were performed with a Beagle-hole Instruments ellipsometer by the method of Jasperson and Schnatterly.[11] Readings were taken every second and averaged over 60 s. This process was repeated for 10−15 minutes. The variation in the averaged readings over this period was generally <5 × 10^{-5} but was occasionally as high as 1 × 10^{-4}. The estimated precision in the ellipticities quoted is ±5 × 10^{-5}. The solutions used for the ellipsometry measurements were at the cmc.

For both techniques, solutions were thermostated to a precision of 0.5 K at the temperatures shown in Table 1.

Results

(i) Sum-Frequency Spectra. Sum-frequency spectroscopy is a nonlinear optical method for obtaining vibrational spectra of molecules at interfaces.[8,12] A pulsed visible laser and a tunable pulsed infrared laser are overlapped on the surface of water and the blue light emitted at the sum of the two incident frequencies is detected. Scanning the frequency of the IR laser generates a vibrational spectrum of molecules in the monolayer. Figure 1 shows sum-frequency spectra of the four C$_n$TABs (n = 12, 14, 16, and 18) in the C-H stretching region. Two independent sets of spectra are shown to provide an indication of the experimental variation. The concentrations and temperatures employed are listed in Table 1. The temperatures were chosen to exceed the Krafft point for each surfactant and are close to the temperatures employed in the neutron reflection experiments of Thomas et al.[5−7] For C$_{12}$TAB, the aqueous phase contained 0.15 M NaBr to reduce the area per molecule at the interface to the same value as for the other three surfactants: 44 ± 2 Å^2. The narrow peak at 2850 cm^{-1} and the broad peak at 2890−2930 cm^{-1} in the SF spectra are assigned to the symmetric methylene stretch (d$^+$) and its Fermi resonance with the overtones of the methylene deformation modes. The sharp peaks at 2878 and 2940 cm^{-1} are assigned to the symmetric methyl stretch (r$^+$), which is also split by a Fermi resonance interaction.[13] The remarkable feature of these spectra is that they are virtually identical, irrespective of the chain length.[14]

Since the area per molecule, A = 44 Å^2, is invariant, the relative intensities of the peaks in these spectra are determined by the conformation of the surfactant molecules in the monolayer through the molecular hyperpolarizability β_{yyz}

$$I_{ssp} \propto \langle \beta_{yyz} \rangle^2 \qquad (1)$$

where the angle brackets indicate that the hyperpolarizability is averaged over the orientations of all molecules at the interface. β is enhanced when the IR laser is in resonance with a molecular vibration that is both IR and Raman active. For the r[+] mode, $\langle\beta\rangle$ is a function of the angle θ between the C_3 axis of the methyl group (c) and the surface normal z:

$$\langle\beta_{yyz}\rangle = [\langle\cos\theta\rangle(1+7r) + \langle\cos 3\theta\rangle(r-1)]\beta_{ccc} \quad (2)$$

where $r = \beta_{aac}/\beta_{ccc}$ and the a-axis is perpendicular to the molecular c-axis. Since the first term in eq 2 is very much greater than the second for reasonable values of r, $\langle\beta_{yyz}\rangle$ is approximately proportional to $\langle\cos\theta\rangle$. For surfactant in the bulk solution, $\langle\cos\theta\rangle$ vanishes: only adsorbed molecules are detected. From Figure 1 we see that the intensity of the r[+] mode is independent of chain length to within experimental error.[15] To determine $\langle\cos\theta\rangle$ for the C_nTAB monolayers, we compared the intensity of the r[+] mode in SF spectra of monolayers of C_{14}TAB and dodecanol taken under the same conditions. It is known from X-ray diffraction that the chains in dodecanol monolayer are vertical, and hence, that $\theta = 35°$, and that the area per molecule is 21 Å[2] at room temperature.[16] After correction for the different areas per molecule, the ratio of intensities yields a value of $\langle\cos\theta\rangle = 0.50 \pm 0.05$ in C_{14}-TAB.[17] This value is most easily interpreted in terms of a concrete model for the chain distribution. If we assume that the ends of the hydrocarbon chains have a uniform tilt, χ, from the surface normal, but have a random twist about that direction,[18] then we find that the chain tilt $\chi = 58 \pm 3°$. It is significant that 58° is the angle required to yield a density equal to that of a liquid hydrocarbon near its freezing point (30 Å[3]/ CH_2).[19] While the monolayer is undoubtedly much more disordered than this simple model would suggest,[20] the model does provide a basis for comparison with other experimental data and computer simulations.

The intensity of the d[+] mode in SF spectra is sensitive to the conformation of the hydrocarbon chains. In an all-trans polymethylene chain, the d[+] mode is sum-frequency inactive due to the local inversion symmetry of the chain. Gauche defects lower the symmetry and give rise to SF-active conformations. It is not yet possible to interpret the intensity of the d[+] mode in terms of a quantitative measure of conformational defects, except in densely packed monolayers. The d[+] mode does, nevertheless, provide a valuable qualitative measure of conformational disorder. In the SF spectra in Figure 1, the intensity and line shape of the d[+] mode is independent of chain length, to within the sample-to-sample variation. These spectra therefore suggest that the chain conformations in the four C_nTABs are similar and that the addition of successive C_2H_4 groups does not generate additional SF-active conformational defects.

(ii) Ellipsometry. In ellipsometry, a laser beam is reflected from a surface and the change in polarization of the reflected beam is determined.[21] In our experiments, we operated at the Brewster angle θ_B defined by $\text{Re}(r_p/r_s) = 0$, where r_p and r_s are the reflection coefficients for p- and s-polarized light, respectively. We report the coefficient of ellipticity, $\bar{\rho} = \text{Im}(r_p/r_s)$ at θ_B. Ellipsometry is an extremely sensitive technique for measuring interfacial properties. It is, however, information poor and can only be interpreted in terms of a specific model of the surfactant monolayer. Figure 2 shows the coefficient of ellipticity $\bar{\rho}$ for the four C_nTAB monolayers.[22] Two terms contribute independently to $\bar{\rho}$. The capillary wave roughness of the surface, which scales approximately as $\gamma^{-0.5}$, gives a
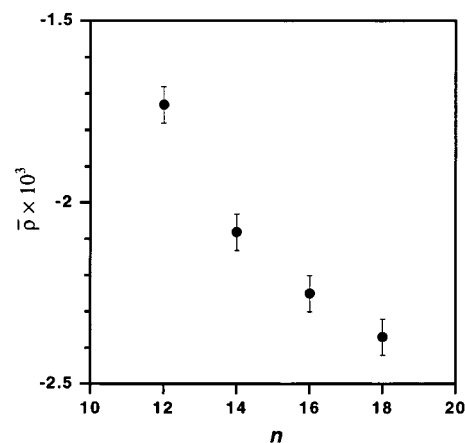

Figure 2. Coefficient of ellipticity of solutions of C_nTAB in H_2O at an area per surfactant molecule of 44 Å[2] as a function of chain length n. The ellipticity for $n = 12$ has been corrected for the presence of 0.15 M NaBr in the subphase. Temperatures as in Table 1; concentration = cmc. The upper bound to the figure represents the expected contribution to the ellipticity from roughness alone.

positive contribution to the ellipticity $\bar{\rho}^R \sim 0.5 \times 10^{-3}$.[23] The thickness of the interface gives a (usually) negative contribution to the ellipticity, which depends on the relative permittivity profile, $\epsilon(z)$, through the interface. To a first approximation, the surfactant monolayers can be assumed to be optically isotropic,[24] in which case the thickness contribution $\bar{\rho}^d$ is given by[25]

$$\bar{\rho}^d = \frac{\pi}{\lambda}\frac{\sqrt{(\epsilon_{H_2O}+1)}}{1-\epsilon_{H_2O}}\int\frac{(\epsilon(z)-1)(\epsilon(z)-\epsilon_{H_2O})}{\epsilon(z)}dz \quad (3)$$

where λ is the wavelength of the light at which $\bar{\rho}$ and $\epsilon(z)$ are measured.

The observed values of $\bar{\rho}^d$ are substantially negative, which indicates that the relative permittivity is greater than that of water over the larger part of the interfacial profile. The ellipticity of the C_nTAB monolayers decreases with increasing n. The decrease is not smooth (the change, $\Delta\bar{\rho}$, between C_{12} and C_{14} is larger than between other chain lengths), but one should not read too much into small variations in $\Delta\bar{\rho}$, given the uncertainty in the area per molecule. The average value of $\partial\bar{\rho}/\partial n$ is -0.10×10^{-3}. If we take a simple model of the monolayer in which methylene groups are added with a liquid-like density ($\epsilon = 2.05$), but the monolayer structure is otherwise unchanged, eq 3 yields $\partial\bar{\rho}/\partial n = -0.10 \times 10^{-3}$, in agreement with the experimental results.[26]

To illustrate the effect of the density of the monolayer on the ellipticity, we have calculated $\bar{\rho}^d$ for films composed of 12−18 carbon chains, $(CH_2)_{n-1}CH_3$, as a function of the volume fraction of the film (Figure 3). We define the volume fraction as the density divided by the density of a liquid hydrocarbon just above its melting point. The molecular volumes in a liquid were taken to be 365, 425, 485 and 545 Å[3] for the 12-, 14-, 16-, and 18-carbon chains, respectively,[19] and the relative permittivity was calculated from the Clausius−Mossotti equation.[27] Figure 3 shows that $\bar{\rho}^d$ is very sensitive to density and even changes sign for volume fractions of less than 0.8. The observed ellipticities are only consistent with monolayers having a density approaching that of a liquid hydrocarbon.
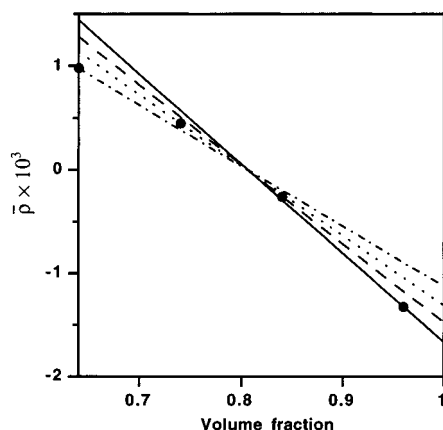
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Figure 3. Calculated contribution to $\bar{\rho}$ of a hydrocarbon layer, $(CH_2)_{n-1}CH_3$, as a function of the volume fraction of the layer at an area per molecule of 44 Å^2. $n = 18$ (solid line), 16 (dashed line), 14 (dotted line), 12 (dash−dot line). Solid circles represent a layer with a constant thickness of 13 Å.

Discussion

The SF spectra provide strong evidence that the chain conformations are very similar in the four surfactants studied. On a uniform tilt model, the chain angle χ near the methyl terminus varies by no more than ±1°. The observed chain angle is that expected for a hydrocarbon of liquid-like density. Ellipsometric data confirm this picture. Both the ellipticities themselves and the variation in ellipticity with chain length suggest densities in the chain region approaching that of a liquid hydrocarbon for all four chain lengths.

How do we reconcile these observations with the neutron-reflection experiments? In order to fit the reflectivity profiles of chain-deuterated surfactants, Thomas and co-workers[5] modeled the surfactant chain as a Gaussian distribution of almost constant thickness whose maximum volume fraction increased from 0.58 for C_{12}TAB to 0.81 for C_{18}TAB.[28] The effect of a constant thickness model on the ellipticity is shown by the solid circles in Figure 3 for a thickness of 13 Å. The variation expected in $\rho^d(n)$ is much greater than that observed experimentally (Figure 2), even after allowing for the crudeness of a single slab model of the monolayer.

The effective thickness of the monolayer measured by NR is determined not only by the characteristics of the monolayer but also by the roughness of the surface. The roughness is unusually larger for monolayers of charged surfactants. For example, for C_{16}TAB the roughness was measured to be 14 Å,[29] greater than the calculated width of the chain distribution (10.5 Å). The effective thickness measured by NR is therefore insensitive to the intrinsic thickness of the monolayer, and small errors in the evaluation of the roughness can lead to much larger errors in the calculated width of the chain distribution.[30] A further effect of roughness in a NR experiment is to convolute the density profile of the hydrocarbon chain with the material bounding the chains on either side: headgroups, solvents, and air. This convolution reduces the apparent volume fraction of the chains, particularly for thinner monolayers.[28]

The use of isotopic substitution allows the determination of the mean separation δ in the z-direction between different parts of the chain.[6] These separations are unaffected by roughness. In a detailed study on C_{16}TAB, Thomas and co-workers broke the chain down into blocks of two methylene units in order to reconstruct the hydrocarbon chain profile (Figure 4).[6] Using the same uniform tilt model that we employ, they found that the outer half of the chains was tilted by 58° from the surface
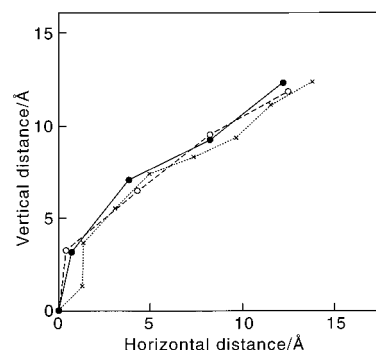

Figure 4. Mean structure of the alkyl chain in C_{16}TAB derived from neutron reflection studies of Thomas and co-workers. The origin represent the position of the headgroup. The horizontal axis represents the length of the projection of the chain in the horizontal plane. Crosses and circles show separations obtained from different isotopic labelling schemes. (Reprinted with permission from ref 5. Copyright 1995 American Chemical Society.)

normal, in perfect agreement with the angle calculated from the SF spectra. Their chain profile yields a density in the centre of the monolayer equal to that of a liquid hydrocarbon. Near the headgroups, Thomas et al. found that the chains were less tilted. In this region, the hydrocarbon chains overlap the headgroup and water distributions and the total volume fraction remains close to one.

In a less detailed study of C_{12}TAB at 44 Å^2 per molecule, the chain was broken down by H/D substitution into two blocks and the separation between the lower and upper halves of the chain was found to be 4.5 Å.[5] A value of 4.2 Å would be expected in the uniform tilt model if the monolayer had the density of a liquid hydrocarbon, within experimental error of the observed separation. In a study of C_{12}TAB at the slightly larger area of 48 Å^2 per molecule, Thomas and co-workers[30] reconstructed the chain profile by subdividing the chain into three blocks of four methylene units. The mean chain tilt of 59° near the methyl terminus is once again in good agreement with the SF spectra.

A final point of comparison is provided by the separation between the centre of the chain distribution and the headgroup, δ_{ch} which was measured for all four chain lengths. δ_{ch} increased from 6.5 Å for C_{12}TAB to 9 Å for C_{18}TAB.[5] On a constant thickness model, this separation would be approximately independent of chain length; if the added methylene groups had a liquid-like density δ_{ch} would increase by 2.0 Å between C_{12}-TAB and C_{18}TAB. The measured values of δ_{ch} are clearly consistent with the latter model.

Conclusion

Sum-frequency spectra of the homologous series of C_nTABs ($n = 12$, 14, 16, and 18) at a constant area per molecule of 44 Å^2 are virtually indistinguishable, suggesting similar conformations for all chains lengths. The intensity of the symmetric methyl stretch can be interpreted in terms of an average chain tilt of 58°, in excellent agreement with measurements on C_{16}-TAB and C_{12}TAB by neutron reflection. This tilt generates a liquid-like density in the monolayer. The large, negative values of the coefficient of ellipticity require that the monolayer has a density close to that of a liquid hydrocarbon for all chain lengths. The variation in ellipticity with chain length is also consistent with this model.

The data we report from sum-frequency spectroscopy and ellipsometry are in excellent agreement with the model proposed by Thomas and co-workers from their detailed studies of C_{16}-

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TAB and C_{12}TAB by neutron reflection (Figure 4). These studies collectively suggest that all four homologues share nearly the same structure. Increasing the chain length simply adds methylene groups into the central part of the monolayer without perturbing the average conformation of the chains. We infer that, for this range of n, the principal factors determining the structure of the monolayer are the headgroup and the area per molecule. Chain length *per se* does not play an important role.

References and Notes

(1) The effectiveness of adsorption is defined as the maximum surface excess Γ_m and is normally determined from the Gibbs equation. The efficiency of adsorption is widely quoted as the concentration of surfactant required to reduce the surface tension by 20 mN/m.

(2) For example, see: Gillap, W. R.; Weiner, N. D.; Gibaldi, M. *J. Phys. Chem.* **1968**, *72*, 2218. Nearn, M. R.; Spaull, A. J. B. *Trans. Faraday Soc.* **1969**, *65*, 1785.

(3) For the excellent monograph by Rosen, see; Rosen, M. J. *Surfactants and Interfacial Phenomena*, 2nd ed.; Wiley: New York, 1989.

(4) The structure of the monolayer is not the sole determinant of interfacial properties. From a thermodynamic perspective, it is often useful to consider the surface tension and other surface thermodynamic parameters as properties of the whole system, not just of the interface. Many applications of surfactants also involve nonequilibrium conditions where mass transport to the interface plays an important role.

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(14) The appearance of a small, sharp peak at 2922 cm^{-1} in the longer chains is experimentally significant. This peak appears at a frequency characteristic of the antisymmetric methylene stretch, but the specific conformation that gives rise to it is not known.

(15) The absolute error in the areas per molecule determined by neutron reflection is quoted as ± 2 Å^2. Much of this error is attributable to systematic errors and the variation in A among the four C_nTABs is likely to be considerably less than this, perhaps ± 1 Å^2. Since $I_{ssp} \propto A^{-2}$, the maximum variation in I_{ssp} due to differences in A would be <10%. Thus the observed variation in the intensity of the r$^+$ mode of <5% falls within the limits of error engendered by uncertainty in A.

(16) Renault, A.; LeGrand, J. F.; Goldmann, M.; Berge, B. *J. Phys. II (France)* **1993**, *3*, 761.

(17) In this calculation, we used the full expression for $\langle\beta_{yyz}\rangle$ and line strengths obtained from a computer fit to the whole sum-frequency spectrum, but excluded local field effects (see ref 9).

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(24) All-trans chains are significantly anisotropic. Conformational disorder will, however, reduce the anisotropy of the chains. Furthermore, a monolayer composed of chains tilted at the magic angle (55°) will be optically isotropic, even though the chains themselves are anisotropic, if the direction of the tilt is random. The mean tilt in these monolayers is close to the magic angle and so any anisotropy will be small.

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(26) The ellipticity extrapolates to a value of about -0.5×10^{-3} at $n = 0$, suggesting that the quaternary ammonium headgroup or its counterion makes a surprisingly large negative contribution to the ellipticity: $\sim -1 \times 10^{-3}$.

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(28) These numbers differ from those quoted in ref 5 due to the use of different values for the molar volumes of CH$_2$ and CH$_3$ groups in liquid alkanes. If the broadening effect of a capillary wave roughness on these distributions is removed, the maximum volume fraction ranges from 0.68 for C_{12}TAB to 0.95 for C_{18}TAB.

(29) The roughness, w, is obtained from the density profile $n = (2n_0/\omega\sqrt{\pi}) \exp(-4z^2/w^2)$ of a deuterated fragment whose intrinsic thickness is negligible compared to w.

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