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Adsorption of Gemini Surfactants with Partially Fluorinated Chains at Three Different Surfaces: Neutron Reflectometry Results

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The adsorption of six symmetrical cationic (dimethylammonium bromide) gemini surfactants with four different partially fluorinated chains at three different surfaces—the air/water, the hydrophilic silica/water, and the hydrophobic (octadecyltricholorosilane (OTS))/water—has been investigated by neutron reflectometry. The corresponding single chain trimethylammonium bromides have also been studied at the two solid surfaces. Four of the geminis with a C₆ spacer and chains with differing amounts of fluorocarbon have identical limiting areas per molecule at the air/water interface ($106 \pm 5 \text{ Å}^2$). This is similar to the value for the corresponding hydrocarbon gemini with a C₆ spacer and C₁₂ side chains, but unlike the hydrocarbon gemini, it is significantly more than twice the area per molecule of the corresponding single chain cationic. In adsorbed aggregates on hydrophilic silica the area per molecule decreases from the air/water value by an average of about 25%, indicating a substantial improvement in the packing of these geminis in the aggregates. On the hydrophobic OTS surface the area per molecule in the adsorbed monolayer for three partially fluorinated geminis decreased by about 15% from the air/water value, again indicating much more favorable packing next to the hydrophobic OTS, but for one of the geminis, fC₈C₆-C₆-C₆C₆C₈, the change in area was reversed. This reversal is accompanied by a marked thinning of the layer, which is attributed to a shift in the balance between the interactions of the hydrocarbon spacer and fluorocarbon chain fragments and the OTS surface.

Introduction

Fluorinated carbon surfactants are interesting because their surface activity is superior to hydrocarbon surfactants.¹ The fluorocarbon chain is more rigid than the hydrocarbon chain, the fluorinated carbon segments are both hydrophobic and oleophobic, and the interaction between fluorinated carbon chains is weak. The hydrophobicity of a CF₂ group has been estimated to be ~1.5 times that of a CH₂ group.² As a consequence, fluorinated surfactants have much lower critical micelle concentrations (CMC) than their hydrocarbon counterparts and can decrease the surface tension of water below the lower limit reached by hydrocarbon surfactants. Partially fluorinated chains have the further difference that the presence of a hydrocarbon fragment between fluorocarbon and headgroup keeps the surfactant chain reasonably flexible and hence should improve its chances of packing efficiently while retaining the more powerful surface tension reducing ability of the fluorocarbon.

Gemini surfactants consist of two polar head groups and two hydrocarbon chains connected by a spacer.³ They are better in some important respects than the corresponding monomeric surfactants, such as in their lower CMC and better ability to wet and to promote emulsification of oil in water. It is not easy to estimate the effect of partial fluorination of the side chains in a gemini because it is not clear how the unfavorable hydrocarbon/fluorocarbon interaction will operate. We have shown that for single chain surfactants the fluorinated outer fragment of the chain segregates

 Kissa, E. Fluorinated Surfactants and Repellents, 2nd ed.; Surfactant Science Series Vol. 91; Marcel Dekker: New York, 2001. quite efficiently from the inner flexible hydrocarbon fragment.⁴ However, the two differences in a gemini are that the packing of the chains is strongly affected by the spacer, being generally poorer than in the corresponding single chain surfactant, and the spacer itself is hydrophobic and may interact with the side chains. Oda et al.⁵ and Yoshimura et al.⁶ have shown that the combination of gemini characteristics with the high hydrophobicity of the fluorocarbon chains leads to very low CMCs and unusually low rates of exchange of surfactant between aggregates and solution.

Here we extend our earlier study on single chain partially fluorinated surfactants to the identical series of partially fluorinated chains but in the gemini form, with two spacers of different length. In order to explore the range of different interactions expected to be exhibited by the partially fluorinated surfactants, we also include measurements of the same series of surfactants at two characteristic types of solid/aqueous interfaces: the hydrophilic silica/aqueous interface and the hydrophobic (octadecyltrichlorosilane-coated silica)/aqueous interface. Adsorption at the former will be dominated by a mix of how the surfactants aggregate and the strength of the attachment of this aggregate to the surface. The three surfaces should lead to different effects of the unfavorable fluorocarbon/ hydrocarbon interaction on the structure of the adsorbed layer. Adsorption at the hydrophobic/aqueous interface will be complicated by the unfavorable fluorocarbon interaction with the hydrocarbon-coated surface. For normal hydrocarbon surfactants the surface density of adsorbed layers at the OTS/water has been found to be 0-10% higher than at the air/water surface, e.g. Fragneto et al.,⁷ but it could well be very different for the partially fluorinated

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Figure 1. Synthesis scheme for partially fluorinated gemini surfactants.

surfactants. An issue for the gemini surfactants has been the role of the spacer in the adsorbed layer structure.^{3,8,9} As the length of the spacer increases, it is thought to become more and more part of the hydrophobic region of the surface layer. Such an effect should be strongly enhanced at the hydrophobic/aqueous interface. Finally, in order to make a proper comparison of gemini and single chain surfactants at the two solid surfaces, we have also determined the structures of layers of the corresponding single chain surfactants at these two interfaces.

The gemini surfactants are 1,6-bis[dimethyl-(perfluoroalkylalkyl)ammonium]hexane dibromides where the lengths of the perfluoroalkyl and alkyl groups are varied. Their structure will be referred to as, for example, fC₆C₈-C₆-C₈fC₆, where fC₆ is a perfluorinated hexyl fragment; the rest of the side chain is an alkyl group with 8 carbon atoms, and the spacer is an alkyl group of 6 carbon atoms (s = 6) (in the tables this is sometimes further abbreviated to $(fC_6C_8)_2$ -C₆)). The spacer is linked to each side chain through a dimethylammonium bromide group. The only compound that deviates from this description is the fC_5C_{10} -C₆-C₁₀fC₅ compound which is branched (two terminal perfluoromethyl groups) rather than an n-alkylperfluoro group. The micellization of this series of partially fluorinated cationic gemini surfactants has been studied by microcalorimetry, using for comparison parallel measurements on the corresponding monomeric surfactants.¹⁰ The values of the CMC decrease with an increase in the number of fluorine atoms on the hydrophobic chain while the micellization enthalpies mostly increase. The corresponding single chain surfactants have already been studied by neutron reflectometry at the air/ water interface. However, no measurements have previously been made on the single chain components at these two solid/aqueous interfaces. Matsuoka et al.¹¹ have also investigated surface tension, CMC, and the size and shape of the related partially fluorinated gemini surfactant 1,2-bis[dimethyl-(3-perfluoroalkyl-2-hydroxypropyl)ammonium]ethane bromide $(fC_nC_3-C_2-C_3fC_n, where n =$ 4, 6, and 8) in aqueous solution.

Experimental Methods

The partially fluorinated chain quaternary ammonium gemini surfactants were prepared by a procedure similar to that used for the alkyl chain gemini surfactants, and the synthesis of the partially fluorinated chains followed the method described by Jackson et al.⁴ The method is shown in Figure 1. The purity of the samples was assessed by surface tension measurements (Kruss K10), the absence of a minimum being the main criterion of purity. The surface characterization of these compounds has already been reported.¹⁰

The neutron reflectivity measurements were made on the SURF reflectometer at the ISIS neutron source UK.¹² The measurements were made using a single detector at fixed angle of $\theta = 1.5^{\circ}$ with neutron wavelengths in the range 0.5-6.8 Å⁻¹ to provide a momentum transfer range 0.048-0.5 Å⁻¹, the momentum transfer Q being defined as $Q = (4\pi \sin \theta)/\lambda$. For the air/water measurements on null reflecting water, where there is no critical edge, the reflectivity was calibrated with respect to pure D₂O. Null reflecting water is a mixure of 92% H₂O and 8% D₂O wiuth a scattering length density of exactly 0 and which is therefore optically identical with air. Flat backgrounds were assumed in all cases and defined with respect to the signal at angles where the reflectivity profiles were fitted using Java programs based on the kinematic approximation, the reflectivity *R* is given as a function of *Q* by

$$R(\kappa) = \left(\frac{16\pi^2}{Q^2}\right) \left[\sum b_i^2 h_{ii} + \sum \sum 2b_i b_j h_{ij}\right]$$
(1)

where the h_{ii} and h_{ij} are the partial structure factors of the different fragments. The h_{ii} are the squared Fourier transforms of the individual fragment distributions normal to the surface, and the h_{ij} are products of the Fourier transforms of fragments *i* and *j*. The Fourier transforms of the fragments were determined numerically, and the distributions are described below. The final reflectivity was obtained from eq 1 by the application of a correction devised by Crowley¹⁶ that essentially allows a conversion from the approximate kinematic reflectivity of eq 1 to the exact value. This method of analysis has been widely used and is fully described by Lu et al.¹⁷

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Table 1. Values	of the CMC	and the Surface	Tension at the	CMC	of Fluorinated	Cationic	Surfactants,	from	Microcalorimetry	at 298	K unless
Otherwise Stated ¹⁰											

gemini	CMC (mM)	$\gamma (mN m^{-1})$	single chain	CMC (mM)	$\gamma \ (mN \ m^{-1})$
fC ₄ C ₁₁ -C ₆ -C ₁₁ fC ₄	0.072	27.3	fC ₄ C ₁₁ TAB	1.13	25.2(30°C)
$fC_4C_{11}-C_{12}-C_{11}fC_4$	0.049	33.6			· · · ·
$fC_5C_{10}-C_6-C_{10}fC_5$	0.060	27.2	fC ₅ C ₁₀ TAB	0.83	22.3 (30 °C)
$fC_5C_{10}-C_{12}-C_{10}fC_5$	0.054	37.4	5 10		· · · ·
$fC_6C_8-C_6-C_8fC_6$	0.049	30.8	fC ₆ C ₈ TAB	1.07	24.0 (30 °C)
$fC_8C_6-C_6-C_6fC_8$	0.023	30.3	fC ₈ C ₆ TAB	0.37	20.2 (35 °C)

Table 2. Volumes^{20,21} and Scattering Lengths²² of Fluorocarbon Gemini Fragments, Substrates, and Water

fragment	volume (Å ³)	$10^5 n_i b_i (\text{\AA})$	fragment	volume (Å ³)	$10^5 n_i b_i (\text{\AA})$
H(D) ₂ O	30	-1.68(19.5)	Si	20	4.15
SiO ₂	47	15.85	-C ₈₁₆ -	200	-6.69
$-C_6H(D)_{12}$	150	-5.0(116.2)	$-C_{11}H_{22}$	275	-9.13
-C ₁₀ H ₂₀ -	250	-8.26	C_4F_9	200	77.45
$-C_{12}H(D)_{24}$	300	-9.96(232.4)	$C_{12}H(D)_{25}$ -	350	-13.7(238.7)
$-N(CH(D)_3)_2Br$ -	100	7.0 (69.5)	C_6F_{13} -	275	113.4
$(CF_3)_2 CF(CF_2)_2$	230	95.4	C ₈ F ₁₇ -	350	149.3

The solid/liquid interface experiments used silicon single crystals of dimensions $125 \times 50 \times 25$ mm³ which were polished on the (111) face. The experimental solution was held in a Teflon container with a volume of ~25 mL, which was clamped against the silicon block between temperature-controlled aluminum and magnetic stirrer plates. Sample changes were made through inlet and outlet ports located on opposite sides of the container, which could be connected to plastic tubes for injection by syringe. The silicon blocks were cleaned by immersion in piranha solution (a 5:4:1 mixture of $H_2O:H_2SO_4:H_2O_2$) at 70 °C followed by UV/ ozone treatment. They were used for the hydrophilic/aqueous experiments after rinsing and soaking in clean water (Elgastat Ultrapure). Following this treatment, the silicon (111) surface typically has a layer of oxide of about 15 A in depth. Hydrophobic surfaces were generated from surfaces that had been freshly treated with UV/ozone. The clean silicon blocks were immersed in a solution of 2×10^{-3} M perdeuterated octadecyltrichlorosilane (d-OTS) in n-hexadecane (Sigma 99%, used without further purification) at 20 °C overnight. Upon removal of the blocks, the excess d-OTS was removed by wiping the surface with a Kodak lens paper soaked in dry dichloromethane, followed by wiping with ethanol to remove the dichloromethane and the blocks were finally rinsed with UHQ water. Following several rinses in the order dichloromethane, ethanol, and UHQ water until the residual patches of bulk polymerized OTS on the surface were removed, the hydrophobic layer was robust enough to withstand rubbing without introducing scratches or other defects detrimental to neutron reflection experiments. The d-OTS (isotopic purity 92%) was synthesized from perdeuterated octadecyl bromide as described elsewhere.

Results and Discussion

Adsorption at the Air/Aqueous Interface. The CMC values at 298.15 K of all the compounds studied are listed in Table 1 for reference (the concentrations selected for the neutron measurements are mainly defined relative to the CMC).

The main purpose of the neutron reflection measurements was to determine the composition and structure of the layers. Measurements of the reflectivity of the partially fluorinated surfactants in null reflecting water (NRW) give the surface coverages of the surfactants. In order to study the structure of the layers, it is necessary to measure the reflectivity of a number of different isotopic compositions (contrasts), as has been described elsewhere.¹⁸ The isotopic compositions used here were the protonated surfactant and

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that with the spacer and the two dimethylamino groups deuterated, each run in NRW and D₂O. For the fC₄C₁₁-C₆-C₁₁fC₄ surfactant the additional composition where just the dimethylamino groups were deuterated was also used.

The surfactant layer was modeled using five structural components: the fluorocarbon segment, fC, the hydrocarbon segment, hC, the headgroup, H, the spacer segment, S, and water, W. The surfactant components were represented by Gaussian distributions, and the water was represented by a distribution that is space filling up to a cutoff value and then decays as a half-Gaussian.¹⁹ The numbers of independent parameters needed to fit a particular set of data are the four thicknesses of the fragments, τ_{fC} , τ_{hC} , τ_{H} , and $\tau_{\rm S}$, the area per molecule A, and the four fragment center-tocenter separations, δ_{fC-H} , δ_{hC-H} , δ_{S-H} , and δ_{W-H} . As well as these parameters the scattering lengths and volumes of the fragments are required to calculate the reflectivities, and these are given in Table 2. The volumes of the fragments are important in the calculation because the fragments displace water in the interfacial region and this affects the reflectivity. The values of the fragment volumes are not easy to estimate and typically have an uncertainty of 10%, which introduces a comparable uncertainty in the final parameters. A Java program in which the parameters could be adjusted interactively was used to fit all contrasts simultaneously for a given surfactant. The most stringent test of the quality of a fit is to make the comparison between calculated and observed data using the plots of RQ^4 against Q. These remove the Q^4 dependence of the reflectivity, and hence the comparison can be made on a linear rather than a log scale. Examples of the best fits to the neutron reflectivity profiles using this program are shown in Figures 2 and 3, and the fitted parameters are given in Table 3.

Before comparing the results, we assess which parameters have the most impact on the fitting. The value of the area per molecule is independent of the model structure used and is therefore the most robustly determined parameter of the layer. However, at the values of the widths observed here, the fitting is not very sensitive to the widths of the individual fragments. Previous work indicates that the minimum thickness of the smallest fragment is determined by thermal fluctuations (capillary waves). This depends on the surfactant, but the minimum seems to be in the range 8-10 Å.

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Figure 2. Neutron reflectivity of C_6C_8 - C_6 - C_8fC_6 for four contrasts at three isotopic compositions. fC_6 is shorthand for C_6F_{13} , and hC_8 , hC_6 , and dC_6 are shorthand for C_8H_{16} , C_6H_{12} , and C_6D_{12} , respectively. The concentration was 0.08 mM (a) reflectivity profiles, (b) RQ^4 profiles, and (c) the individual fragment profiles used to fit the data. The continuous lines in (a) and (b) are calculated for the best fits using the parameters in Table 3, which were fitted to six contrasts, two of which are not shown. The dimethyl groups are only shown in the formula when they are deuterated.

This tends to smear genuine effects that might arise from differences in the mean geometry at the interface, which makes the fragment thickness a less interesting parameter. This is indicated by the spread of ± 5 Å given as the error. The simultaneous fitting of all the profiles is most sensitive to the separations between fragments, the δ values in Table 3, but the relative sensitivity to the individual δ values depends on the contrasts used. In general, the present data are sensitive to all the separations except that the limited range of contrasts does not allow a good distinction between head groups and spacer. Most importantly, there is little correlation between the δ values; i.e., they are independent of each other in the fitting.



Figure 3. Neutron reflectivity of fC_5C_{10} - C_6 - $C_{10}fC_5$ for four contrasts at three isotopic compositions. fC_5 is shorthand for C_5F_{10} , and hC_{10} , hC_6 , and dC_6 are shorthand for $C_{10}H_{20}$, C_6H_{12} , and C_6D_{12} respectively. The concentration was 0.09 mM: (a) reflectivity profiles, (b) RQ^4 profiles, and (c) the individual profiles used to fit the data. The continuous lines in (a) and (b) are calculated for the best fits using the parameters in Table 3. The zero in (c) has been chosen to be the position of the Gibbs plane for zero surface excess of water. The dimethyl groups are only shown in the formula when they are deuterated.

The limiting areas per molecule for the four geminis with the C_6 spacer are identical within error at $106 \pm 5 \text{ Å}^2$. For the two geminis with the C_{12} spacer and fC_4C_{11} and fC_5C_{10} side chains this limiting area changes to 122 and $132 \pm 5 \text{ Å}^2$, respectively. The nearest comparison is with the hydrocarbon geminis studied by Li et al.,²³ who obtained values of 95 and 140 Å² for geminis with dodecyl side chains and C_6 and C_{12} spacers, respectively. Andelman and Diamant⁹ have produced a model that attempts to account for the variation of the limiting areas of geminis in terms of the

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Table 3. Structure of Layers of Partially Fluorinated Gemini Surfactants at the Air/Water Interface

surfactant	$c (\mathrm{mM})$	$\tau_{\rm fC}(\pm5{\rm \AA})$	$\tau_{\rm hC}(\pm5{\rm \AA})$	$\tau_{\rm H}(\pm5{\rm \AA})$	$\tau_{\rm S}(\pm5{\rm \AA})$	$\delta_{\rm fCH}(\pm 1~{\rm \AA})$	$\delta_{\rm hCH}(\pm 1~{\rm \AA})$	$\delta_{\rm SH}(\pm 2~{\rm \AA})$	$\delta_{\rm WH}(\pm 1~{\rm \AA})$	$A \ (\pm 5\% \ /\text{\AA}^2)$
$(fC_4C_{11})_2-C_6$	1.5	8	12	8.75	6.75	-14	-4.5	1.0	0.5	106
$(fC_4C_{11})_2 - C_{12}$	1.05	7.5	11.5	8.5	8.75	-14	-6.25	-0.25	0.8	122
$(fC_5C_{10})_2-C_6$	0.9	8	11	8.75	6.5	-14	-7.5	1.75	2.1	106
$(fC_5C_{10})_2 - C_{12}$	0.35	7.25	10.75	8.75	9	-14	-3.75	-1.75	0.3	132
$(fC_6C_8)_2-C_6$	0.08	9	9.5	8.75	6.75	-14	-8.5	1.25	3.4	105
$(fC_8C_6)_2-C_6$	0.08	10.75	8.75	8.75	6.75	-14	-6.5	-1.5	3.0	106

varying interaction of the spacer with the aqueous subphase as it increases in length. The longer the spacer, the more it will tend to try to position itself in the same region of the interface as the chains. The geminis with fluorocarbon side chains will differ in that the side chains will interact more strongly with each other than with the hydrocarbon fragments, and the fluorocarbon fragments will interact unfavorably with the purely hydrocarbon spacer. The limiting area of the hydrocarbon geminis with a C_6 spacer is approximately double the limiting area for the equivalent single chain cationic surfactants. Thus, the C₆ spacer seems to allow the hydrocarbon side chains to pack at their natural separation. However, the single chain fluorocarbon trimethylammonium bromides pack more tightly than their hydrocarbon counterparts,⁴ and the limiting area of the corresponding fluorocarbon geminis is significantly more than double the single chain compounds. The C₆ spacer is evidently constraining the side chains at separations greater than the natural separation. This is presumably because the spacer is too short to be able to adopt the bent configurations that could allow a closer approach of the side chains. On the other hand, the stronger side chain interaction between fluorinated carbons is able to force the longer C₁₂ spacer into a bent configuration so that the C_{12} fluorocarbon geminis have a smaller limiting area than their hydrocarbon counterparts. Andelman and Diamant showed that there could be a maximum in the limiting area as a function of spacer length depending on the model they used for the spacer/water interaction. The results of Li et al. suggested that there is not a maximum in the hydrocarbon series. However, the stronger interaction of the side chains in the fluorocarbon compounds suggests that the fluorocarbon series would be more likely to show a maximum, and this would therefore be worth further exploration.

The observation that the C_6 spacer is preventing the optimum packing of the fluorocarbon chains at the surface is also demonstrated strikingly in the values of the limiting surface tension (Table 1). For the fC_8C_6 side chain the limiting surface tension is about 8 mN m⁻¹ higher than the value for the single chain compound, indicating that the gemini chains are a long way from optimum packing. This difference drops sharply as the number of fluorinated carbons decreases, and for the fC_4C_{11} chains the difference is only 2 mN m⁻¹. We return to this point in the discussion of the structure of the layer.

Table 3 at first indicates that the structures of the six partially fluorinated carbon chain cationic gemini surfactants at the air/ water interface are similar. The outer region of the surfactant layer is largely composed of the fluorocarbon segments, and the centers of their distributions are well away from the water. This is expected from the greater hydrophobicity and lower surface tension of the fluorocarbon segment. However, the fact that the fluorocarbon—headgroup separation stays approximately constant across the series indicates a more subtle pattern of behavior when one takes into account the decreasing distance between heads and centers of fluorocarbon fragments in the molecule as the fluorination increases. This distance drops from about 16 Å in fC_4C_{11} to about 12.5 Å in fC_8C_6 . The constancy of the value of $\delta_{\rm fH}$

Table 4. Overlaps of Hydrocarbon Fragments with Fluorocarbon and with Water for Gemini and Single Chain Surfactants

gemini	$(fC_4C_{11})_2$ -C ₆	$(fC_5C_{10})_2$ -C ₆	$(fC_6C_8)_2-C_6$	$(fC_8C_6)_2-C_6$
$\Delta_{hC-fC} (\pm 0.002)$	0.014	0.035	0.036	0.014
$\Delta_{hC-W} (\pm 0.02)$	0.31	0.27	0.28	0.39
single chain	fC ₄ C ₁₁ -TAB	fC ₅ C ₁₀ -TAB	fC ₆ C ₈ -TAB	fC ₈ C ₆ -TAB
$\Delta_{hC-fC} (\pm 0.002)$	0.023	0.018	0.012	0.009
$\Delta_{hC-W} (\pm 0.02)$	0.26	0.31	0.26	0.44

must therefore be caused by the chains becoming more tilted toward the surface normal as the fluorination increases. The value of 14 Å for fC_8C_6 is close enough to the intramolecular separation as to suggest that these chains are approximately normal to the surface. This effect is also observed in a corresponding increase in the hydrocarbon chain-headgroup separation, which is largest for the fC₈C₆ compound, although this has the shortest intramolecular separation. The increasing orientation of the hydrophobic chains toward the normal direction with extent of fluorination was also observed in the single chain compounds.⁴ However, in the single chain compounds this is associated with an increase in the packing density. For the geminis the packing density is significantly lower than optimum and would not be expected to force the chains toward the normal. It may be that the hydrocarbonfluorocarbon interaction, especially when the contribution from the hydrocarbon spacer is included, is what is driving the orientation toward the normal. Whatever the driving force, the combination of the normal orientation with the relatively large separation of the chains will expose nonfluorocarbon entities to the air, resulting in a high surface tension, as observed.

There is some mixing (overlap) of the distributions of the fluorocarbon and hydrocarbon segments, which can be examined more quantitatively by calculating the overlaps, Δ_{ij} , between the different fragments. For an overlap of two fragments, e.g., hydrocarbon and fluorocarbon, Δ_{fC-hC} , is given by

$$\Delta_{\rm fC-hC} = \frac{\int_{-\infty}^{\infty} \phi_{\rm fC}(z) \phi_{\rm hC}(z) \, \mathrm{d}z}{\int_{-\infty}^{\infty} \phi_{\rm fC}(z) \, \mathrm{d}z \int_{-\infty}^{\infty} \phi_{\rm hC}(z) \, \mathrm{d}z} \tag{2}$$

where ϕ represents volume fraction and z is the normal distance to the surface. The denominator is included to normalize the overlaps. Overlaps involving water have to be treated slightly differently. For example, the overlap of hydrocarbon and water, Δ_{hC-W} , is defined as

$$\Delta_{\rm hC-W} = \frac{\int_{-\infty}^{\infty} \phi_{\rm water}(z) \phi_{\rm hC}(z) \, \mathrm{d}z}{\int_{-\infty}^{\infty} \phi_{\rm hC}(z) \, \mathrm{d}z} \tag{3}$$

The parameters of the fitted profiles in Table 3 can be converted into values of Δ_{ij} and give the values in Table 4. We have not given errors in this table because there are two types. The large uncertainty in the thicknesses of the fragments leads to a large absolute error in the calculated overlaps. However, the inaccuracies in the fragment thicknesses are likely to be such that they

Table 5. Adsorption of Partially Fluorinated Gemini and Single Chain Surfactants at the Hydrophobic (OTS)/Water Interface

surfactant	<i>c</i> (mM)	$ au_1 (\pm 1 \text{ \AA})$	$ au_2 (\pm 1 \text{ \AA})$	$\theta \pm 0.03$	σ (±0.5 Å)	$A(\text{\AA}^2\pm5\%)$	$\Gamma~(\pm 0.1~mg/m^2)$
$(fC_4C_{11})_2 - C_6$	1.05	12.0	2.75	0.87	6.0	89	2.1
$(fC_5C_{10})_2 - C_6$	0.86	12.5	1.75	0.86	6.5	89	2.2
$(fC_6C_8)_2-C_6$	0.075	11.0	2.0	0.96	6.5	90	2.2
$(fC_8C_6)_2 - C_6$	0.08	9.0	1.25	0.94	5.0	120	1.9
fC ₅ C ₁₀ -TAB	0.83	12.0	1.75	0.95	6.5	42	2.2
fC ₆ C ₈ -TAB	1.07	19.0	2.75	0.88	7.0	28	3.4
fC ₈ C ₆ -TAB	0.37	16.0	2.5	0.87	6.5	36	3.0

converge to a common value becuase they are largely determined by thermal fluctuation and local roughness. This means that the good accuracy in the values of the fragment separations means that they are relatively very accurate and can usefully be compared.

Table 4 shows that the overlap of hydrocarbon and fluorocarbon is smallest at the two extremes of fluorination. This suggests that there is competition between a greater tendency for larger fluorocarbon groups to segregate from the hydrocarbon and the restriction imposed by shortening the length of the hydrocarbon group. Thus, the long hydrocarbon chain in the fC₄C₁₁ system allows the fluorocarbon more freedom than in the other compounds and it can segregate efficiently, but in the fC₈C₆ system the greater extent of fluorination drives a stronger segregation. However, the really striking difference is between the single chain compounds and the gemini. In the former there is clearly much more efficient segregation of fluoro- and hydrocarbon fragments, as would be expected from the closer packing of the chains. The differences in $\Delta_{\rm hC-W}$ within each system and between single and gemini surfactants show no clear trends.

Finally, we note that the sublayer that was invoked to interpret the data from the hydrocarbon geminis obtained by Li et al. was not found to be necessary here. The data are fitted satisfactorily with only a single molecular layer.

Adsorption at the Hydrophobic Solid/Aqueous Interface. The d-OTS surface was first characterized by measuring reflectivity profiles in three different water contrasts, D₂O, and water of scattering length density 3.4×10^{-6} and 4.0×10^{-6} Å⁻². As always occurs with these layers in contact with water, there is a very thin layer which some attribute to contamination and others to an "air" layer.^{24–27} This disappears in the presence of a surface active adsorbate. It is therefore necessary to include this layer in the basic characterization but not when the adsorbed surfactant layer is present. The surfactant layers were all studied at concentrations either equal to or slightly larger than their CMC.

The deuterated OTS has a similar scattering length density to D_2O . Adsorption of a layer containing hydrocarbon therefore gives a very strong signal. If a partially fluorinated surfactant were to adsorb with its fluorocarbon fragment attached to the OTS surface, the initial part of the surfactant layer would contrast only weakly with the OTS. The main contribution to the reflectivity would then come from the hydrocarbon part of the layer and the protonated TAB group. In principle, the reflectivity profile is therefore quite sensitive to the relative distribution of these two groups within the layer. However, this was not found to be the case and the adsorbed layer could be modeled in terms of a hydrophobic region next to the OTS (layer 1) containing both

hydrophilic region on the outside of the layer (layer 2), which contained the head groups and the spacer (for the geminis). The parameters of the silica layer and the OTS were constrained to the values obtained in the absence of surfactant. The data were fitted using the optical matrix method with the usual constraints on the total volume fraction at any point in the layer. To allow for disorder in the layer, the fractions of heads and spacers in the chain region were used as additional fitting parameters. The need to include these mixing parameters confirms that the layers are not well ordered, but no useful quantitative conclusions can be drawn from them. In addition, it was necessary to include the roughness (σ) between the surfactant layers and between the last surfactant layer and water. The best fits of the main geometrical parameters plus the coverage (θ) , surface excess and area per molecule, are given in Table 5 (we have omitted the mixing parameters). The reflectivity profiles for the corresponding gemini and single chain cationics for the fC_6C_8 chain just above their respective CMCs are shown in Figure 4. Sometimes a shift to lower Q of the sharp dip in the reflectivity of dOTS and protonated surfactant systems can be attributed to a thickening of the overall layer and hence of the surfactant layer. Here, the situation is complicated by other factors, namely the different contrast of the partially fluorinated systems, the very different coverage of the two layers, and a slight difference in the thickness of the OTS layer used in the two cases. Table 5 shows that the single chain surfactant forms a thicker layer at a much higher coverage. Figure 4 also shows that there is some penetration of water into the OTS (and underlying silica) at a level of about 15%. Neutron reflectometry is particularly sensitive to this effect, and we have usually observed it at a level in the range 10-20%.

fluorocarbon and hydrocarbon chain fragments and a narrow

In general, it is expected that adsorption of an amphiphile on a hydrophobic surface of this type should be stronger than at the hydrophobic air—water interface. This is the case for most of the surfactants here but not for the gemini containing the fC_8C_6 chain, for which adsorption is actually weaker, and not for the single chain fC_5C_{10} -TAB, for which adsorption at the two surfaces is about the same. Although there is a very strong hydrophobic effect driving this adsorption, it requires direct contact between the fluorocarbon fragment and the hydrocarbon OTS surface, and this will become progressively less favorable as the extent of fluorination increases. Adsorption will therefore be driven by a competing mix of the increasing hydrophobicity with extent of fluorination and an increasing repulsion between fluorocarbon and the OTS hydrocarbon.

Given that the layer is disordered, there is the possibility of some contact of the hydrocarbon fragment (and spacer) with the OTS and the system should adjust to optimize this contact. The optimization of hydrocarbon OTS contact would result in a thinning of the layer, which would be expected to be greater for the gemini because of the hydrocarbon spacer. Because only one contrast was used for the OTS experiments, it is not possible to make a clear separation of the layer into its components. However, a comparison of the overall thickness of the layers at OTS/water

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Figure 4. (a) Neutron reflectivities of fC_6C_8 -dTAB and fC_6C_8 - C_6 - C_8fC_6 on a dOTS-coated silicon surface at 30°C in D₂O. (b) and (c) show the respective structural profiles in terms of the volume fractions of the fragments. The continuous lines are calculated for the best fits using the parameters in Table 5.

and at air/water interfaces can be made as follows. At the air surface the separation between centers of the fluorocarbon distribution and heads is 14 Å for the four geminis. There is the additional thickness of the head and fluorocarbon distributions, but much of this is attributable to capillary waves. The thickness of the layer is therefore a bit greater than 14 Å. At the OTS surface the sum of chain and headgroup thickness drops from 14.75 for fC_4C_{11} through 14.25 and 13 to 11 Å for fC_8C_6 . The thinning effect is therefore very marked, and although the lower adsorption would also generate a thinning effect for the fC_6C_8 compound, this occurs without any diminution in adsorption. The thinning of the layer must therefore be accompanied by large tilts of the chains away from the normal direction. For the single chain surfactants the fluorocarbon repulsion evidently has strong effects on the adsorption and structure at fC_5C_{10} and fC_8C_6 . In the former case the layer is thin, and adsorption per chain is almost the same as for the gemini. For the latter, adsorption is strong relative to the gemini, but the layer is more tilted than for the fC_6C_8 compound and adsorption is also weaker than for the latter.

Silica (Hydrophilic)/Water Interface. The oxide layer on the Si(111) substrate was first characterized using the neutron reflectivity profiles from Si/SiO₂/D₂O, Si/SiO₂/water_{2.07}, and Si/SiO₂/water_{4.00} interfaces, where the subscripts indicate the scattering length densities of the water. Three silicon blocks were used for the measurements. The profiles were almost exactly the same as those obtained by Fragneto et al.⁷ and could be well fitted by a single uniform layer of silica of thickness 14 ± 1 Å, scattering length density of $3.4 \times 10^{-6} \text{ Å}^{-2}$, and roughness of $3 \pm 0.5 \text{ Å}$.

The adsorption experiments were done at a single contrast (protonated surfactant in D_2O) at a single concentration above the CMC. As with other surfactants on the hydrophilic surface, the use of a single monolayer to fit the data shows that the thicknesses of all the adsorbed surfactants studied are too large to be considered as a monolayer. For these fluorocarbon systems the coverage is also far too high to be accommodated in a monolayer. We therefore assume that the layer consists of three sublayers corresponding to some kind of bilayer structure. The central layer (layer 2) consists mainly of the hydrophobic chains, and the outer two layers (layers 1 and 3) consist of heads and spacers or just heads in the case of the single chain surfactants. The bilayer is assumed to occur in patches so that the average scattering length density of a sublayer is weighted by the volume fractions of bilayer and water.²⁸ The coverage (θ in Table 6) is then defined as the volume fraction of surfactant at the center of the bilayer. The calculation of the reflectivity was based on the optical matrix method and the main adjustable parameters are the thicknesses of the three layers and the coverage of the bilayer. The numbers of headgroups in inner and outer layers were constrained only to be approximately identical. In addition, the interfacial roughness, the parameter σ , was the same for all sublayers and could be adjusted. The scattering properties of fragments of the layer used to fit the reflectivity profiles have already been listed in Table 2. As always with neutron reflectometry, the fits are most sensitive to the coverage. In this case, because of the thicker layers, they are also sensitive to the overall thickness. However, they are not generally sensitive to the division into the three sublayers unless the water fraction in the outer layers is very different from that in the inner layer. This was not found to be the case for the geminis, so it was not possible to identify where the spacer is located within the layer. Finally, the parameters of the silica layer were fixed as determined for the bare silica surface. The fits to the observed profiles of the same pair of single chain and gemini surfactants as shown for the hydrophobic surface are shown in Figure 5, and the fitted parameters are given in Table 6. In Figure 5, the position of the sharp dip in the reflectivity is inversely related to the overall thickness of the layer and is evidently much thicker for the single chain surfactant. Neutron reflectometry only measures the average distribution in the plane, and the presence of water as a significant part of the layer indicates that both single chain and gemini surfactants form aggregates rather than a continuous bilayer. Note that the natural silica layer on silicon is different for the two blocks used for the two experiments. This does not affect the fitting because it is fixed independently from measurements on the clean surface.

The adsorption of the single chain compounds is both very high, higher than for hydrocarbon TABs at comparable relative concentrations,²⁸ and higher per chain than for the geminis. There are two parameters related to the area per molecule in the table. The first, A, refers to the mean area per molecule on the surface.

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surfactant	c (mM)	$\tau_1(\pm 0.5~{\rm \AA})$	$\tau_2(\pm 1~{\rm \AA})$	$\tau_3(\pm 0.5\text{\AA})$	$\theta \pm 0.03$	$\sigma\pm 0.5$	$A (\pm 4 \text{ Å}^2)$	$\Gamma~(\pm 0.1~{\rm mg~m^{-2}})$	A^* (±4 Å ₂)
$(fC_4C_{11})_2 - C_6$	1.05	7.0	25	4.0	0.76	3.0	51	3.5	77
$(fC_5C_{10})_2 - C_6$	0.86	6.5	26	3.0	0.79	3.0	45	4.1	71
$(fC_6C_8)_2-C_6$	0.075	6.0	21	5.5	0.68	3.0	65	3.0	88
$(fC_8C_6)_2 - C_6$	0.08	4.5	26	2.3	0.72	3.0	53	4.2	76
fC ₅ C ₁₀ -TAB	0.83	7.0	27	5.0	0.85	3.0	21	4.3	36
fC ₆ C ₈ -TAB	1.07	4.5	31	5.0	0.74	3.0	21	4.6	31
fC ₈ C ₆ -TAB	0.37	6.0	30	5.0	0.92	3.0	18	5.9	33



Figure 5. (a) Neutron reflectivities of fC_6hC_8 -dTAB (red) and fC_6hC_8 -C₆-hC₈fC₆ (blue) on a silicon surface at 30 °C in D₂O. (b) and (c) show the respective structural profiles in terms of the volume fractions of the fragments. The continuous lines are calculated for the best fits using the parameters in Table 6.

The second area parameter, A^* , is the average area per individual molecule in the aggregate. This can be obtained on the assumption that the water in the center of the layer $(1 - \theta)$ corresponds to areas of the surface where there is no surfactant, in which case the actual area per molecule in an aggregate is given by $A^* = 2A\theta$. Both, like the values at the hydrophobic OTS surface, are all much

less than at the air/water interface. This indicates that the interaction of chains with other chains is much more favorable than the interaction of chains with air, although there could also be a contribution from a reduction in the charge repulsion at the hydrophilic surface. For the partially fluorinated geminis the area per molecule in the aggregates in three out of the four compounds is substantially lower than at the OTS surface, and this must reflect the unfavorable fluorocarbon/hydrocarbon interaction in the latter. The thicknesses of the bilayer aggregates are comparable with twice the thickness of the monolayer on OTS but less than twice the fully extended chain length. This could mean either that they are interdigitated or that they remain tilted and pack end-to-end. The gemini layers are again all thinner than the single chain layers, the most marked being the fC₆C₈-C₆-C₈fC₆ layer, which has an overall thickness of 32.5 Å as compared with 40.5 Å for the single chain compound.

Comparisons and Conclusions

The motivation for studying this series of surfactants was to explore the effects of competition between fluorocarbon and hydrocarbon and the geometrical constraints imposed by the gemini structure. We first examine the effects on the limiting surface tension at the air/water interface. For the purely hydrocarbon surfactants, C12TAB and C12-C6-C12, the limiting surface tensions (at the CMC) are 40.5 and 43.2 mN m^{-1} , respectively. On the basis that the lowering of the surface tension is largely caused by screening the high tension bare water/air interface, one might expect that the extra screening from the spacer would give the gemini a lower tension than that of the single chain surfactant (the limiting area per chain is within error identical). That the gemini tension is higher suggests that the geometric constraints within the gemini lead to a more disordered gemini structure and hence less effective screening of the water, although there could also be an electrostatic contribution. The failure of the gemini to lower the surface tension is more marked for the fluorocarbons (see Table 1) and becomes stronger with the proportion of fluorination, so much so that the order of decreasing surface tension with increasing fluorocarbon content is largely reversed compared with the equivalent single chain compounds. To obtain the maximum lowering from the presence of fluorocarbon requires screening both of the bare water/air and of the hydrocarbon/air interfaces. These gains will be offset by the unfavorable mixing of hydrocarbon and fluorocarbon. It is then interesting that the fC₄C₁₁-C₆- $C_{11}fC_4$ is the most effective of the geminis at lowering the surface tension. In this compound the more flexible hydrocarbon chain reduces the geometric constraints of the gemini architecture, the fluorocarbon/hydrocarbon mixing is also minimized, and the fluorocarbon is naturally situated right at the outer surface.

At the hydrophobic OTS surface the adsorbed amount and the thickness of the gemini layers vary strongly from surfactant to surfactant, but the ratio of the two is more or less constant. At the air/water interface such a result might indicate that these two parameters cannot be fitted independently. However, the resolution

at the deuterated OTS surface is such that the two parameters are genuinely independent. The reason for the strong correlation can be attributed to the unfavorable interaction between hydrocarbon and fluorocarbon. The OTS is a hydrocarbon surface and interacts most strongly with the hydrocarbon component of the surfactant. The spacer has more freedom to interact with the surface than the chain hydrocarbon fragment, and a strong interaction of spacer with the surface will tend to thin the layer. Thus, the more fluorinated the chains, the more the spacer dominates and the thinnner the layer, as observed, the fC₈C₆-C₆-C₆fC₈ having the lowest τ_1 of 9 Å. This effect is similar to that proposed by Diamant and Andelman for the change in area per molecule with spacer⁹ and is similar to what has been discussed above in the comparison of the gemini with their single chain counterparts.

The coverage of all the surfactants on silica is high, and the fC₈C₆TAB comes close to forming a complete bilayer. The variation in coverage and in area per molecule in the aggregate varies with the hydrophobicity more systematically than for the layer on OTS, suggesting that the mixing of fluorocarbon and hydrocarbon fragments is able to be optimized in the bilayer aggregates. This together with the result that the thicknesses of the single chain surfactant bilayers are all significantly larger than the length of a fully extended chain indicates that the single chain bilayers are probably not interdigitated structures. However, the issue is more complicated for the geminis because of the presence of the spacer. Interdigitation is unlikely because of the unfavorable fluorocarbon/hydrocarbon interaction and because of the volume mismatch between the two fragments. Two limiting structures are shown schematically in Figure 6a,b. Taking fC_6C_8 -TAB as an example, the cross section of the fluorocarbon is \sim 32 Å² (volume of 275/length of 8.5; see Table 2), and that of the hydrocarbon is ~ 20 Å². If the fluorocarbon is aligned normal to the surface, the hydrocarbon fragments will have to be aligned at about 50° away from the surface normal. This would give an overall thickness of the chain region of the layer of $2 \times 8.5 + 10 \cos 50 = 30$ Å, close to the 31 Å observed. This suggests that the single chain compounds do form end-to-end packed layers, and then the pattern of results suggests that the cohesion of the layer increases with fluorination. The gemini are again very different. In particular, the fC_6C_8 - C_6 - $C_8 f C_6$ has a chain region that is only 21 Å thick. Following the same argument as for the single chain TAB, the fluorocarbon fragments could pack end-to-end with tilted hydrocarbon fragments, but now the spacer can also help to fill the hydrocarbon space and reduce the amount of tilt relative to the single chain compounds. The presence of the spacer also makes the volume mismatch in an interdigitated structure less unfavorable, as illustrated schematically in Figure 6c,d. For the thickness of the gemini bilayer to be as low as observed for $fC_8C_6-C_6-C_6fC_8$ requires either that the fluorocarbon fragments are also very highly tilted from the surface normal or that the structure is interdigitated. For the fluorocarbon compounds the overall hydrophobic effect will favor interdigitation, and this will be opposed by the unfavorable fluorocarbon/hydrocarbon interaction. The observations suggest that interdigitation may be occurring in the $fC_6C_8-C_6-C_8fC_6$ compound, but the other three partially fluorinated geminis form thicker layers which could fit with either partial interdigitation or end-to-end packing with strong tilts.

Finally, we examine the limiting coverage of the surfactants. For the four fluorogeminis studied the limiting areas per molecule at the CMC are fC_4C_{11} - C_6 - $C_{11}fC_4$ (106, 89, 77 Å²), fC_5C_{10} - C_6 - $C_{10}fC_5$ (106, 89, 71 Å²), fC_6C_8 - C_6 - C_8fC_6 (105, 90, 88 Å²), and fC_8C_6 - C_6 - C_6fC_8 (106, 120, 76 Å²) where the areas per molecule in parentheses are respectively for the air/water and OTS/water and for the area within an aggregate for the silica/water interface.



Figure 6. Schematic limiting structures for single chain and gemini bilayers of partially fluorinated surfactants adsorbed on a hydrophilic surface (silica). The structures correspond to end-to-end packed bilayers for (a) a single chain surfactant and (d) a gemini surfactant and to interdigitated structures for (b) a single chain surfactant and (c) a gemini surfactant. The colors of the blocks are fluorocarbon fragment (green), hydrocarbon fragment (blue), and gemini spacer (brown).

Apart from the last compound, where the value at the OTS surface is anomalously high, the values are consistent with the expectation that adsorption should be stronger at the more hydrophobic OTS surface than at the air/water interface and that the interactions within an aggregate (on silica) are also more favorable. As noted earlier, the limiting areas of these geminis with the C₆ spacer at the air/water interface are also very close to the neutron reflectometry value for a hydrocarbon gemini with the same spacer, C12-C6-C12. In our previous paper on C12-C6-C12 the neutron value was found to be substantially lower than that obtained from surface tension (using a Gibbs prefactor of 3), and the similarity of the present values for the parallel fluorocarbon geminis is consistent with the neutron value. We have not attempted a surface tension analysis for the fluorocarbons here partly because of the ambiguity concerning the appropriate Gibbs prefactor to use to analyze the gemini surface tension data and partly because the much lower CMC of the fluorocarbon geminis makes the measurement of the surface tension below the CMC measurement more prone to experimental error.

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