

pH-Dependent Interactions of Mica Surfaces in Aqueous Dodecylammonium/Dodecylamine Solutions

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The adsorption of a hydrolyzable surfactant, dodecylammonium chloride, and interactions between layers thereof, has been studied at a surfactant concentration of 10^{-4} M as a function of pH using the surface force apparatus. At low pH the surfaces undergo charge reversal as dodecylammonium ions adsorb to form a sparse monolayer. At pH 8-9, adsorption of neutral dodecylamine molecules becomes important, rendering the monolayer more compact with a thickness close to the length of an extended molecule. A hydrophobic attraction is observed between the surfactant monolayers. At pH 9.5-10.3, a bilayer forms on each surface. The double-layer force decreases gradually with increasing pH and disappears at pH 10.3. At this and slightly higher pH values a multilayer gradually builds up on the surface. At pH values around 12 the multilayer buildup is prevented by a recharging of the adsorbed layer. Both the adsorption behavior and the interactions between the layers are reversible with respect to changes in the pH. The structure of the adsorbed surfactant layer on mica is compared to that on other surfaces.

Introduction

The adsorption of surfactants to solid surfaces is of great technical importance due to a vast number of applications in areas where a low interfacial tension between a solid and a liquid is required, like detergency,¹ or between two liquids, for example in food emulsions.² Surfactants are also used in various separation and dispersion processes. Valuable information on different aspects of surfactant adsorption on solid surfaces can be obtained from techniques such as calorimetric studies³ and neutron-scattering experiments.⁴ We have chosen to use the surface force technique⁵ to investigate how the presence of surfactants influences interparticle forces. From these measurements it is also possible to obtain information about the adsorbed surfactant layer, e.g., its thickness and the preferred orientation of the molecules at the solid/solution interface.

The surface force technique has previously been employed to study a range of surfactant systems. The adsorption of nonionic surfactants to hydrophobic surfaces and the temperature-dependent interaction between such layers has been studied.⁶ The adsorption of nonionic surfactants⁷ and cationic surfactants⁸ on hydrophilic mica surfaces has also been investigated. In particular, Herder⁹

investigated how the solution concentration of dodecylammonium (DAH^+) chloride influences the forces acting between mica surfaces. He limited his study to pH 5.6 where the surfactant exists in cationic form. We have chosen to use the same system as Herder, but we focus our attention on the pH dependence of the adsorption and interaction. In particular, the behavior in weakly alkaline solutions, where several surfactant species are present, has been investigated. Somasundaran¹⁰ gives the pK_b of the dissociation of the DAH^+ ion into a proton and a dodecylamine (DA) molecule as 10.63, and the association constant of a DAH^+ ion and a DA molecule to form a species of the form $\text{RNH}_2\text{H}^+\text{NH}_2\text{R}$ as -3.12. Pugh¹¹ constructed a diagram from the various chemical equilibria involved in alkylamine systems to show the species distribution as a function of pH. At neutral or slightly acidic pH, essentially all the surfactant is charged. As the pH increases, the fractions of uncharged DA and singly charged dimer increase. When the total surfactant concentration is $\sim 10^{-4}$ M, the concentration of the dimer peaks at pH ~ 10 , and at pH 10.3 the aqueous solution phase separates into a water-rich phase and a hydrated dodecylamine phase.

The understanding of the properties of the adsorbed DA/ DAH^+ layer and the interparticle forces under slightly alkaline conditions is of particular importance when one considers separation processes, which often work with optimal efficiency over a limited alkaline pH range. For instance, the recovery of calcium fluorite using DAH^+ /DA as collector in froth flotation shows a sharp maximum around pH 10.¹¹

Flotation is a complex process. It is influenced by surfactant adsorption at the air/water interface as well as to solid surfaces. This in turn is affected by surfactant concentration, pH, and ionic strength. To obtain a good picture of the flotation process, one has therefore to perform a range of studies using various techniques to

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characterize the surfactant behavior in solution, at the air/solution interface and at the solid/solution interface. Interactions between two solid particles, between two air bubbles, and between an air bubble and a particle in the surfactant solution also need to be understood.

The work by Pugh¹¹ and Herder,⁹ and that presented here, can in a broader perspective be regarded as the first steps in collecting the data needed for understanding froth flotation of the model mica system using DAH⁺/DA as collector. Further studies toward this goal, including, of course, flotation of mica, surface elasticity and surface viscosity measurements, measurements of the interactions in free surfactant films, and surface force measurements in surfactant solutions containing added salt, will be reported in future papers.

Experimental Section

Dodecylammonium chloride was obtained from Eastman Kodak and used without further purification. Sodium hydroxide and hydrochloric acid were purchased from Merck. All water used in the experiments had undergone the following treatment: First, it was deionized and prefiltered over activated charcoal and then treated with a reverse osmosis unit. In the next steps the water was passed through two mixed-bed ion exchangers, one activated charcoal cartridge, an in-line filter (0.2 μm), an Organex cartridge, and, finally, another filter (0.2 μm). The units were all Millipore products apart from the filters which were Zetapore. Measurements of pH were performed with a PHM portable pH meter from Radiometer on a small sample drained from the surface force apparatus.

Surface force measurements⁵ were performed using a Mark IV surface force apparatus.¹² Two molecularly smooth mica sheets (with silver backing) were glued with an epoxy resin (Epon 1004) onto cylindrical silica disks (radius ~ 2 cm) and mounted in a crossed cylinder configuration. The separation of the surfaces, D , is determined interferometrically to within 0.2 nm, using fringes of equal chromatic order. The force is measured by the deflection of a double cantilever spring supporting one of the surfaces. The results from the measurements are reported as the force, F , normalized by the geometric mean radius of curvature of the surfaces (R), and plotted as a function of surface separation. The zero separation is taken as the adhesive contact position of the surfaces in pure water. The measured force is related to the free energy of interaction per unit area (G_f) via the Derjaguin approximation:¹³

$$F(D)/R = 2\pi G_f(D) \quad (1)$$

This relation holds provided that $D \ll R$. All measurements were carried out at $20 \pm 2^\circ\text{C}$.

The measured forces were analyzed using DLVO theory. The van der Waals force was, when not otherwise stated, approximated with the nonretarded van der Waals interaction for mica across water (with a Hamaker constant of 2.2×10^{-20} J⁵). This gives the upper limit of the van der Waals attraction in this system since adsorption of surfactants, screening by electrolyte, and retardation effects will result in a weaker van der Waals interaction. The double-layer force was calculated using the nonlinear Poisson-Boltzmann approximation, neglecting ion/ion correlation effects. The analyses were performed according to the algorithm of Chan et al.¹⁴ The fitted Debye lengths were in all cases within 20% of the expected from considering the surfactant and electrolyte concentrations. In these analyses it has been assumed that the origin of the van der Waals force and the plane of charge are located at the surface of any adsorbed layer.

Results

The forces acting between two muscovite mica surfaces immersed in pure water are dominated by repulsive double-

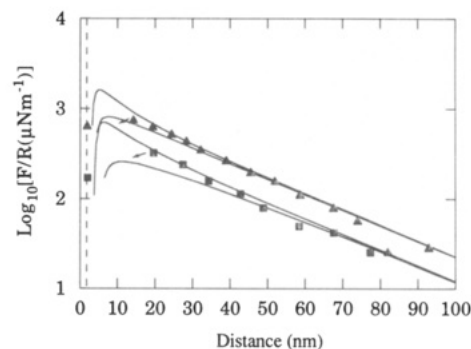


Figure 1. Force normalized by radius as a function of separation between mica surfaces immersed in aqueous solutions at pH 5.6. Squares and triangles represent forces measured in a 10^{-4} M DAH-Cl solution ~ 1 h and ~ 1 day, respectively, after the surfactant was injected. The solid lines are force curves calculated from the DLVO theory. The lower curves correspond to interaction at constant potential and the upper to interaction at constant charge. The apparent double-layer potentials and Debye lengths used for the calculated force curves are ± 45 mV and 24 nm after 1-h adsorption and $+72$ mV and 24 nm after ~ 1 -day adsorption. The layer thickness on each surface is 0.7 ± 0.2 nm. Arrows indicate jumps into adhesive contact.

layer forces at large distances, and by attractive van der Waals forces at separations below ~ 3 nm. The contact position between the surfaces in pure water defines zero separation. As DAH-Cl is injected into the solution to a concentration of 10^{-4} M, the magnitude of the surface charge density first decreases and then increases again. This is a result of adsorption of cationic surfactants to the negatively charged surfaces that initially leads to a charge neutralization and, as the adsorption proceeds due to hydrophobic interactions, to charge reversal. How rapidly this process takes place depends on how thoroughly the solution is mixed after the surfactant has been introduced into the aqueous solution. The forces measured ~ 1 h and ~ 1 day after injection are displayed in Figure 1. The forces observed after 1 day correspond to the equilibrium adsorption case.

A measure of the apparent double-layer potential can be obtained by fitting double-layer forces calculated in the nonlinear Poisson-Boltzmann approximation to the measured forces. The apparent surface potential after ~ 1 -h adsorption was ± 45 mV, whereas the equilibrium value, reached after prolonged adsorption (12–24 h), varied between $+60$ and $+100$ mV in different experiments over a pH range of 4.7–5.8. The corresponding apparent area per charge is 75 – 38 nm². The value for the apparent surface potential previously reported by Herder⁹ is at the lower limit of the range of values observed by us. He also found that charge neutralization occurred at a DAH⁺ concentration of $\sim 1 \times 10^{-5}$ M. (It should be noted that one cannot directly obtain the sign of the surface charge from surface force measurements but it can usually be inferred quite easily from the trends, in this case the change in magnitude of the double-layer force with time.) In each case the double-layer force was calculated for the two extreme ion adsorption cases, constant surface potential and constant surface charge. The more correct case of interaction between regulating surfaces (interaction at constant chemical potential) lies in between these two cases. As is apparent from the figure, the ion adsorption characteristics influence the interaction significantly only at separations less than 1–2 Debye lengths.

The forces measured after injection of the DAH-Cl are not consistent with the DLVO theory (in contrast to those observed in pure water or dilute electrolyte). After an adsorption time of ~ 1 h, a force maximum was located

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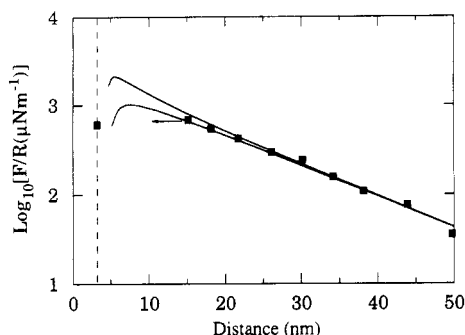


Figure 2. Force normalized by radius as a function of separation between mica surfaces immersed in an aqueous 10^{-4} M DAH-Cl solutions at pH 8.3. An apparent potential at the monolayer surface of +62 mV with a Debye length of 12 nm was deduced from DLVO analysis. An attractive deviation from DLVO theory is observed at separations below 15 nm. The layer thickness on each surface is 1.5–2 nm. This pH value was reached by addition of HCl to a surfactant solution held at pH 10.5. The arrow indicates the point at which the surfaces jumped into monolayer/monolayer contact.

at a separation of ~ 20 nm, from which the action of an attractive force considerably stronger than the van der Waals force pulled the surfaces into monolayer contact. This attraction is consistent with the hydrophobic attraction measured between other surfactant-coated surfaces.^{8,9,28} After equilibrium had been established, a net attractive deviation from DLVO theory remained at distances below ~ 20 nm. The adhesion force ($F(0)/R$) in monolayer contact (about 1.2–2 nm from mica/mica contact) varied in different experiments between 200 and 300 mN m^{-1} . The adhesion force is related to the interfacial tension (γ_{SL}) according to

$$F(0)/R = \alpha\gamma_{\text{SL}} \quad (2)$$

The value assigned to the constant α varies between 3π (for soft surfaces) and 4π (for hard surfaces).¹⁵ The surfaces used by us deform considerably in contact (due to flattening of the glue), so by using the factor 3π we deduce an interfacial tension of $27 \pm 5 \text{ mN m}^{-1}$.

At pH 8.3 (Figure 2) a 1.6–2-nm-thick, essentially hydrophobic layer has adsorbed on each surface. The extended length of a DAH⁺ ion is only 1.8 nm, indicating that either a very tightly packed monolayer has adsorbed or some molecules in a partially formed outer layer remain trapped between the surfaces in contact. At large separations a repulsive double-layer force dominates the interaction whereas a hydrophobic attraction dominates at separations below ~ 15 nm (Figure 2). Once again the adhesion force between the adsorbed layers was in the range 200–300 mN m^{-1} .

The forces observed at pH 9.5 are displayed in Figure 3. At this pH the force wall is located at a separation of 6 nm from mica/mica contact, which is considerably larger than that at lower pH. Instead of the attractive deviation from DLVO theory observed at lower pH, a short-range, repulsive, non-DLVO force operates between the surfaces at pH 9.5. Clearly, a bilayer has adsorbed on each surface. The short-range repulsion has a range of ~ 1 nm (Figure 4). The bilayer remains on the surface even when a high compressive force of $>10 \text{ mN m}^{-1}$ is applied. When the surfaces are separated, an attractive minimum with a

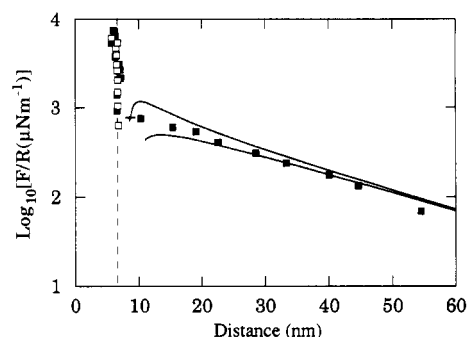


Figure 3. Force normalized by radius as a function of separation between mica surfaces immersed in an aqueous 10^{-4} M DAH-Cl solutions at pH 9.5. Filled squares represent forces measured on approach and open squares forces measured on separation. The solid lines are theoretically calculated force curves assuming interaction at constant surface charge (upper curve) and constant surface potential (lower curve). The apparent potential at the bilayer surface is 55 mV and the Debye length is 20 nm. The layer thickness is 3–3.5 nm on each surface. The arrow indicates the small jump into bilayer/bilayer contact.

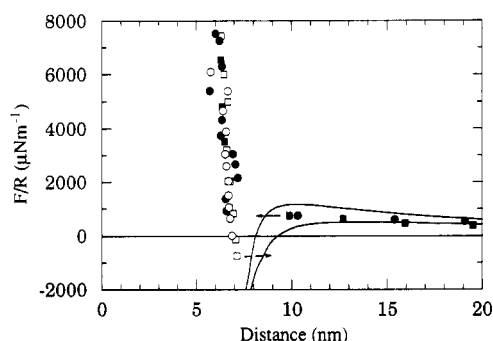


Figure 4. Force normalized by radius as a function of separation between mica surfaces immersed in an aqueous 10^{-4} M DAH-Cl solutions at pH 9.5 plotted on a linear scale. Results from two separate force measurements are shown. Filled symbols represent forces measured on approach and unfilled symbols forces measured on separation. The solid lines have the same meaning as in Figure 3. The depth of the attractive minimum located at $D = 6.7$ –7 nm observed when the surfaces are separated is less than 1 mN m^{-1} . The unbroken arrow indicates the jump into adhesive bilayer/bilayer contact and the dashed arrow indicates at which point the surfaces jump apart.

magnitude slightly less than 1 mN m^{-1} is observed ~ 1 nm from bilayer contact (at $D = 7$ nm). At large separations, a significant double-layer force dominates the interaction, and regulation of the surface charge is indicated as the interaction falls between calculated interactions, assuming constant charge and constant potential. The apparent bilayer potential at large separation is 55 mV, corresponding to an area per charge of 73 nm^2 .

When the pH is raised further to 10.1 (Figure 5), the magnitude of the double-layer force decreases (apparent surface potential 38 mV corresponding to an area per charge of 87 nm^2), and the steepness of the short-range force increases (Figure 6). At pH 10.3 the solution becomes cloudy, due to phase separation of hydrated dodecylamine from the bulk solution. At the same pH the double-layer force between the adsorbed bilayers disappears. Initially, the forces are well described by a van der Waals attraction followed by a very steep repulsion close to bilayer contact (Figure 7). With time, a long-range repulsive force showing hysteresis develops between the surfaces. Clearly, additional surfactant molecules have adsorbed to the surfaces, presumably due to precipitation of phase-separated hydrated dodecylamine droplets. Once the multilayer has developed, only the general features of the force

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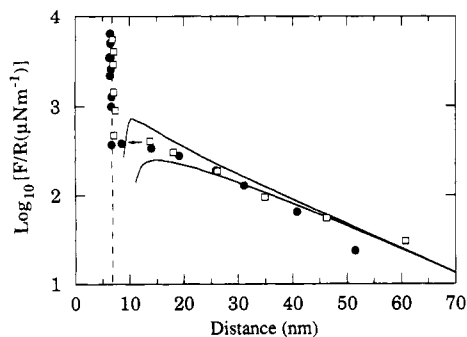


Figure 5. Force normalized by radius as a function of separation between mica surfaces immersed in an aqueous 10^{-4} M DAH-Cl solutions at pH 10.1. The measurements were performed 2 h (filled circles) and 17 h (open squares), respectively, after the pH was raised from 9.5. The solid lines are calculated force curves assuming interaction at constant surface potential (lower curve) and constant surface charge (upper curve), an apparent potential at the bilayer surface of 38 mV, and a Debye length of 16 nm. The layer thickness is 3.5 nm on each surface. The arrow indicates the small jump into bilayer/bilayer contact.

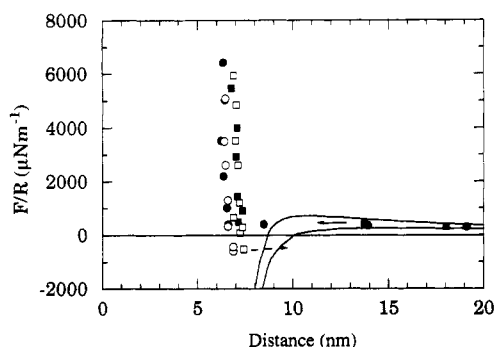


Figure 6. Force normalized by radius as a function of separation between mica surfaces immersed in an aqueous 10^{-4} M DAH-Cl solutions at pH 10.1 plotted on a linear scale. Filled symbols represent two different force measurements on approach and open symbols the corresponding forces measured on separation. The lines have the same meaning as in Figure 5. The attractive minimum is located at a separation of 7 nm. The unbroken arrow indicates the jump into adhesive bilayer/bilayer contact and the dashed arrow indicates at which point the surfaces jump apart.

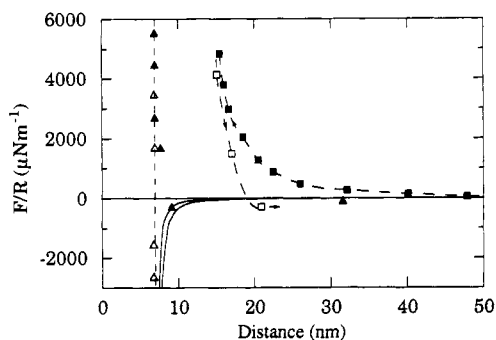


Figure 7. Force normalized by radius as a function of separation between mica surfaces immersed in an aqueous 10^{-4} M DAH-Cl solutions at pH 10.3. Triangles represent forces measured 45 min after the pH was increased from 9.5; squares represent forces measured 2.5 h after the pH was increased. Filled symbols represent forces measured on approach and unfilled symbols forces measured on separation. The solid lines are (upper) the van der Waals force using a Hamaker constant of 1.0×10^{-20} J (a typical value for hydrocarbon across water) and (lower) the van der Waals force using a Hamaker constant of 2.2×10^{-20} J.

curve are reproducible whereas the multilayer thickness and onset of the force vary somewhat between each force run. An adhesion with a magnitude similar to that between bilayers is observed on separation, indicating that the

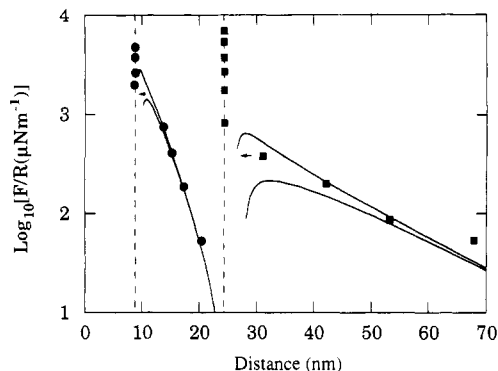


Figure 8. Force normalized by radius as a function of separation between mica surfaces immersed in an aqueous 10^{-4} M DAH-Cl solutions at pH 10.5 (squares) and 12.3 (circles). Solid lines are theoretical DLVO force curves calculated by assuming a surface potential of ± 35 mV and a Debye length of 14.5 nm (pH 10.5), and -47 mV and 2.6 nm (pH 12.3).

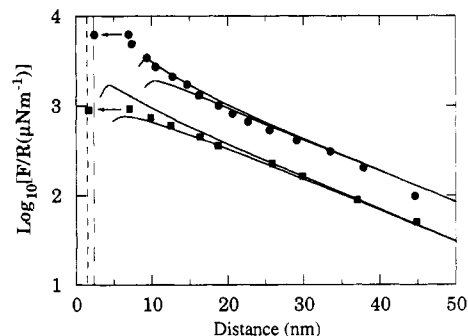


Figure 9. Force normalized by radius as a function of separation between mica surfaces immersed in an aqueous 10^{-4} M DAH-Cl solutions at pH 3.8. This pH was reached by adding HCl to a surfactant solution at pH 10.3. Forces measured after 15 min (filled circles) and 1 day (squares) are shown. The Debye length is 12 nm and the apparent potential after 15 min was 80 mV (assuming a plane of charge a total 7.0 nm from mica/mica contact). After 1 day the apparent potential was 55 mV and the layer thickness was ~ 0.8 nm on each surface. The arrows indicate the small jump into monolayer/monolayer contact.

outermost molecules are adsorbed with the polar group toward the solution. When the pH is reduced again, reproducible forces consistent with those previously measured at low pH are observed. A typical force curve measured at pH 10.5 is shown in Figure 8. However, when the pH is increased directly from 10.1 to 12.3, no multilayer buildup is observed. Instead a strong repulsive double-layer force dominates the long-range interaction, followed closer in by an adhesive minimum and a steric/hydration repulsion (Figure 8).

When HCl is added to the alkaline solution, changing the pH from 10.3 to 3.8, the multilayer dissolves and a repulsive electrostatic double-layer force reappears (Figure 9). The second layer does not desorb immediately, but its presence is observed as a strong double-layer force and a repulsive deviation from DLVO theory at short separations. This indicates that at this stage the molecules forming the bilayer have charged up somewhat, commensurate with the pH in the system, but have not yet completely desorbed from the surface. Unlike the case at high pH, the outer layer can now be squeezed out easily from between the surfaces by application of a compressive force. An example of such a force curve measured before the new adsorption equilibrium has been established (10–20 min after lowering the pH and thoroughly mixing the solution) is illustrated in Figure 9. The adhesion force between the monolayers (at 2.4 nm from mica/mica

contact) was $\sim 240 \text{ mN m}^{-1}$. As the system approaches the new equilibrium situation the double-layer force decreases and the short-range repulsion disappears. At equilibrium, a monolayer is present on each surface, and the forces observed are similar to those recorded initially at pH 5.6 (except for the reduced Debye length caused by the addition of NaOH and HCl). Hence, the adsorption/desorption process is reversible with respect to changes in pH. The adhesion force at monolayer contact (1.6 nm from mica/mica contact) was 200 mN m^{-1} .

Discussion

The forces measured between mica surfaces in DAH-Cl solutions depend strongly on the pH. From these measurements, we are able to draw some firm conclusions about the structure of the adsorbed layer and about the nature of the forces acting between adsorbed DAH-Cl/DA layers.

State of the Adsorbed Layer on Mica. Muscovite mica is a layered aluminosilicate mineral.¹⁶ Each layer is strongly negatively charged (0.48 nm^2 per charge) due to isomorphous substitution of aluminum for silicon. In the crystal, this charge is compensated by potassium ions (and to a lesser extent sodium ions) located between the aluminosilicate sheets. When mica is immersed in water, the potassium ions on the surface are easily exchanged for other types of inorganic¹⁷ or organic cations.¹⁸ Hence, it is to be expected that the cationic DAH⁺ ion will adsorb strongly to the mica surface, thereby reducing the effective surface charge density. That this indeed is the case is confirmed by the reduction in double-layer force in dilute surface solutions.⁹ By considering the size of the DAH⁺ ion, Herder⁹ estimated the thickness of the monolayer to be 0.7–0.8 nm when one surfactant molecule is adsorbed for each negative surface site. He also observed that at pH values between 5 and 6 the surfaces became uncharged at a DAH-Cl concentration of $\sim 10^{-5} \text{ M}$, and that the corresponding layer thickness was slightly less than expected (0.5–0.6 nm) when one surfactant is adsorbed on each surface site. He also observed that upon increasing the surfactant concentration at this pH the monolayer thickness remained essentially unchanged up to at least a surfactant concentration of $3 \times 10^{-3} \text{ M}$, at which point an outer surfactant layer adsorbed.

In our measurements, in five experiments at a surfactant concentration of 10^{-4} M at pH 4.7–5.8, we obtained a monolayer thickness varying between 0.5 and 0.9 nm. Considering the experimental difficulties in determining the thickness of adsorbed layers discussed in a previous paper,⁶ we regard this as consistent with the layer thickness expected when one surfactant is adsorbed at each negative surface site.

When the pH is increased, the concentration of neutral DA molecules and the ratio of DAH⁺ to H⁺ increases. This results in an increased surfactant adsorption. At the same time, the surface charge density is nearly constant up to pH 9.5 from which point it decreases to zero at pH 10.3. This demonstrates that the additional adsorption is due to neutral DA molecules. The additional adsorption takes place both in the inner layer, as observed by the increase in monolayer thickness with pH, and by the formation of an outer layer. The fact that there is further adsorption in the inner layer when the pH is increased but not when the surfactant concentration is increased (at a constant pH of 5.6, see ref 9) is further evidence for the

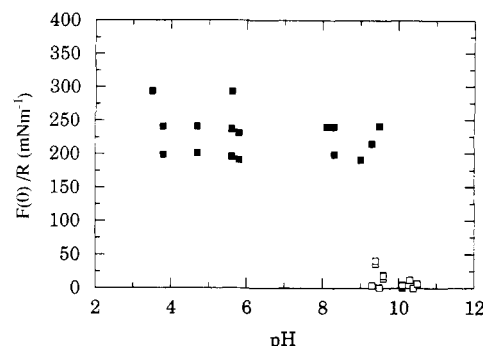


Figure 10. The pull-off force, $F(0)$, normalized by the local radius of curvature, R , as a function of pH. The filled symbols are forces measured in monolayer/monolayer contact and the open symbols in bilayer/bilayer contact.

adsorption of uncharged DA molecules. This effect is prominent already at pH 8.3, as is evident from the large layer thickness and the small surface charge density. At this pH only $\sim 0.5\%$ of the molecules in bulk solution are uncharged. Since the positively charged DAH⁺ ions are depleted near the positively charged surface, the ratio of uncharged to charged species next to the surface is larger, $\sim 3\%$. Nevertheless, it is clear that uncharged DA molecules adsorb much more readily to the neutralized or slightly positively charged surface than charged DAH⁺ ions.

When "monolayers" are present on the surface, a strong attractive force is observed in monolayer contact, indicating that the surfaces have a hydrophobic character (Figure 10). However, the interfacial energy deduced from these measurements is less than that expected for a pure hydrocarbon/water interface, and also less than observed between deposited Langmuir–Blodgett layers ($F(0)/R = 350\text{--}500 \text{ mN m}^{-1}$).^{19,20} The pull-off force is a measure of the difference in surface energy between the monolayers in contact with one another and the monolayers in contact with the solution. Our adhesion values may be lower than those of LB films as a result of some surfactant molecules adsorbing weakly onto the monolayer when it is exposed to solution. The low surface charge density at pH 5–6 indicates that the number of molecules in a possible "outer layer" must be small, and it is possible that these molecules therefore would not be observed by the surface force technique, either as a secondary force wall or as an increased monolayer thickness. Also, it is likely that some molecules adsorbed on the surface are oriented with the polar group toward the solution. Hence, the structure of the adsorbed layer is not that of a perfect monolayer but contains imperfections, related to the submicellar surface aggregate structures increasingly invoked in the explanation of surfactant adsorption to solid surfaces.^{21–26}

The concentration of DA and DA/DAH⁺ dimers increases as the pH is increased. The larger concentration of these more surface active species causes the adsorption to increase significantly. At pH values between 9.5 and 10.3, the thickness of the adsorbed layer, possibly including

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some tightly bound water, is 3.2–3.5 nm on each each surface. This is close to twice the extended length of DA (3.6 nm), showing that the adsorbed structure is essentially a bilayer. The low surface charge density indicates that the inner layer is built up of a mixture of DAH^+ and DA, whereas DA predominates in the outer layer. The adhesion between the bilayers, which carry only a small charge, is 2 orders of magnitude lower than that observed between the monolayers, demonstrating that the orientation of the molecules in the outer layer is preferentially with the polar group toward the solution. We note that the thickness of the almost neutral bilayers at high pH in 10^{-4} M surfactant solutions is significantly larger than the bilayer thickness (2.7 nm) observed by Herder for strongly charged bilayers at high surfactant concentrations at pH 5.6. This is to a large extent due to the difference in adsorption in the innermost layer as discussed above and further emphasizes that the structure and composition of the adsorbed layer obtained by increasing the pH is different from that obtained by increasing the surfactant concentration at low pH.

Comparison of Adsorption on Mica and Other Hydrophilic Mineral Surfaces. It is reasonable to assume that the driving forces for adsorption of charged surfactants to oppositely charged hydrophilic surfaces are essentially the same in all cases. Hence, the observation that the initial stage of the adsorption is driven by electrostatic forces and the later stage by hydrophobic interactions should be quite general. However, the structure of the adsorbed layer is likely to vary from case to case. The most important factors affecting the adsorption structure of a particular cationic surfactant (the size of the charged group and of the hydrophobic tail influence the adsorption) to a negatively charged surface are the surface charge density and the surface roughness. Mica is a highly charged homogeneous surface and consequently a rather homogeneous "monolayer" can form due to electrostatic interactions. For surfaces with a lower surface charge density this will not be the case and it is possible that adsorption to such surfaces is patchy, with a tendency to form surface aggregates.²¹ The fact that the mica surface has atomic smoothness over macroscopic distances allows surfactant molecules to pack together due to hydrophobic association into a monolayer structure over essentially infinite sheets. Hence the "edges" of the monolayer, which necessarily have a higher energy associated with them, are insignificant. If, on the other hand, the surface is rough on a molecular scale (consisting of microscopic cliffs and chasms), edge effects may become relatively large and surfactant molecules may be unable to pack in parallel. Such situations would tend to preclude monolayer and hemimicellar adsorption (with the polar charged group toward the surface) and would thus tend to impose an adsorption regime of smaller aggregates (which effectively would remove edge and protrusion effects). There is still a great deal of debate about the structure of adsorbed cationic surfactant aggregates^{4,21–27} and the picture is by no means clear yet. The first model proposed in 1955 by Gaudin and Fuerstenau,²¹ which is still widely invoked, envisages an adsorption of "hemimicelles"—two-dimensional aggregates with the polar groups toward the surface of the adsorbent. This was later modified to include the possibility of adsorption into the hemimicelle of molecules with the polar group toward the solution.²² More recently, bilayer and micellar structures have been proposed.^{23,24,26} Other work²⁵ on silica gels has suggested that closed, three-dimensional aggregates

of low aggregation number (6–18) are formed, which the authors have nonetheless labeled "hemimicelles". (Though it would seem that the pore size must largely dictate the size and shape of aggregates in such systems.) The surfaces onto which these often conflicting structures have been proposed to adsorb vary greatly in terms of roughness, charge density, chemistry, and curvature and it seems ever more likely that a range of adsorbed aggregate or "solloid"²⁷ structures exist—perhaps as many structures as there are systems. The difference in observed structure from equally valid experimental techniques using the same surfactant is exemplified below. Rennie et al.⁴ investigated cetyltrimethylammonium bromide (CTAB) adsorption below the cmc on amorphous quartz using specular reflection of neutrons. Their data are consistent with surfactants adsorbing in incomplete bilayers or in flattened micelles covering 35% of the surface at a CTAB concentration of 3×10^{-4} M and 80% at a concentration of 6×10^{-4} M, but not with adsorption in monolayers. It was concluded that both the dimension and the separation of the patches were less than $1 \mu\text{m}$. As a comparison, surface force data²⁸ are consistent with adsorption of CTAB to mica below the cmc in a monolayer having most polar groups oriented toward the surface. Above $\sim 1/2$ the cmc, CTAB adsorbs as a bilayer onto mica. The difference between the structures of the surfactant layers deduced for the adsorption of CTAB on mica and quartz can have two explanations. First, the surface charge on silica is lower than that on mica at low pH (the pH of the neutron reflectance experiment was not reported), reducing the importance of electrostatic forces. (It would be interesting to see the neutron reflectance experiment repeated on mica or quartz at different pH values.) Second, in the surface force experiment the average surface properties over several square micrometers are observed, and a weakly adsorbed outer surface layer of CTAB could be removed by pressing the surfaces together leaving only a monolayer between the surfaces in contact. (It should perhaps be observed that, if the adsorbed layer on mica were in patches of monolayer or bilayer and at high coverages, it would not necessarily be distinguishable from a complete monolayer/bilayer by the surface force technique.)

Pugh investigated the adsorption of DAH^+/DA on calcium fluorite (isoelectric point 10.8) using electrophoresis and determination of the total carbon content on the surface.¹¹ Adsorption of the surfactant was very low below pH 9 and did not change the ζ potential. At high pH, a coverage of $\sim 80\%$ of a full monolayer was observed. No detailed information of the structure of the adsorbed layer was determined, but the results were interpreted in terms of submicellar aggregate adsorption. The very clear difference compared to adsorption on mica is due to the very different nature of the mineral surface, particularly that mica is strongly negatively charged whereas calcium fluorite is positively charged up to pH 10.8.

Comparison of the Adsorption of Dodecylamine with Other Structurally Similar Surfactants. It is of some interest to compare the adsorption of DAH^+/DA at high pH with the adsorption of dimethyldodecylamine oxide (DDAO), dimethyldodecylphosphine oxide (DDPO), and penta(oxyethylene) dodecyl ether (C_{12}E_5) onto mica. These molecules have the same hydrophobic part but different polar groups. DAH^+/DA adsorbs readily due to electrostatic interactions between the charged species and mica. DDAO has a weak tendency to exist in a cationic

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form ($pK_a = 4.65^{29}$). This is sufficient to allow a rather strong adsorption onto mica in "monolayers" and, at higher concentrations, "bilayers".³⁰ DDPO is a poor proton acceptor and adsorbs much more weakly to mica. However, "monolayers" with many polar groups toward the surface are formed and, at high concentrations, on top of that an outer layer.³¹ $C_{12}E_5$ does associate weakly with the mica surface, but the association is so weak that no evidence for a mono- or bilayer structure could be deduced from surface force measurements.⁷

Interactions at pH Values below 9. At pH values below ~ 8.5 , the surfactant adsorbs in essentially a monolayer, rendering the surface hydrophobic. The long-range repulsion is due to an electrostatic double-layer force having a decay length to within 20% of the value expected from DLVO theory. By fitting forces calculated in the PB approximation to the measured forces, one obtains a value of the apparent surface charge density. Due to, among other things, the neglect of ion/ion correlations the surface charge density obtained in this way underestimates the real surface charge density.³² For the rather weakly charged surfaces in this study this is expected to cause an error of less than 20% in the determined surface charge density.³³ At separations below ~ 15 nm, a considerably more attractive force than expected from DLVO theory is observed. An attractive force with a similar range has also been observed between other hydrophobic surfaces obtained by surfactant adsorption.^{8,9,28} There is then no controversy about the existence of this unexpectedly long range attraction. The same cannot be said about the molecular origin of this force. A number of explanations, invoking a wide range of mechanisms, have been put forward. These include attractive solvation forces,³⁴ charge fluctuation forces,³⁵ the collapse of the double-layer force,³⁶ and forces originating from the fact that the thin water film between the hydrophobic surfaces is in a metastable state.³⁷⁻³⁹ It must be emphasized that the attraction between the surfaces in contact is not unexpectedly strong, but in fact is weaker than expected for a pure hydrocarbon/water interface. The theoretical and experimental challenge is to explain the mechanism of the long-range part of the force.

One measure of the surface hydrophobicity is the pull-off force, which is related to the interfacial tension. The value measured in 10^{-4} M DAH-Cl solutions ($200\text{--}300$ mN m^{-1}) is roughly independent of pH (up to pH 9), as illustrated in Figure 10. This range agrees with that observed by Herder at pH 5.6⁹ and is similar to that observed for CTAB²⁸ and dihexadecyldimethylammonium bromide.⁸ Even longer range attractive forces have been observed for hydrophobic surfaces prepared by silanation^{40,41} or Langmuir-Blodgett deposition.^{19,42}

Interactions at pH Values between 9 and 10.3. Charged DAH⁺ ions are more abundant than uncharged DA molecules up to a pH of 10.3, above which the solution phase separates into one water-rich and one hydrated dodecylamine phase.¹¹ At pH values above 9.5 a surfactant bilayer, which cannot be removed on compression, is adsorbed on each surface. The interaction between these bilayers is characterized by a long-range double-layer force, the magnitude of which decreases with increasing pH. We note that the double-layer force between the adsorbed bilayers disappears at essentially the same pH as phase separation takes place in bulk solution. At short separations, the force becomes attractive over a small distance regime, and close to bilayer contact, a short-range strongly repulsive force is observed. In fact, the forces acting between the bilayers at these pH values are very similar to those observed between other nonionic surfactant layers.⁶ In contrast, the forces acting between DAH⁺ bilayers at pH 5-6⁹ are purely repulsive.

As the pH is increased from 9.5 to 10.3 the attractive minimum remains located at a separation of 6.6-7.1 nm from mica/mica contact, whereas the slope of the short-range force becomes significantly steeper at higher pH. This indicates an increased adsorption. There are at least two contributions to the short-range force: dehydration of the polar group⁴³⁻⁴⁷ and steric confinement of adsorbed surfactants.⁴⁸ To distinguish between these two contributions is (as discussed in a previous paper⁶) very difficult when the adsorbed amount may vary as a result of changing conditions.

Interactions at pH Values above 10.3. At pH values at and above 10.3, the bulk solution has phase separated into one water-rich phase and hydrated dodecylamine droplets. The properties of DA solutions at these pH values have been investigated,⁴⁹ and it was found that a precipitate was formed which was redispersed at a pH of ~ 12 . ζ potential measurements indicated a positive potential of the colloidal droplets below pH 11 and a negative potential above this pH value. Our observations are consistent with those results. At pH values around 10.5, hardly any repulsive double-layer force acts between the hydrated dodecylamine droplets and the surfactant-coated surface. Consequently, the droplets precipitate on the surface, giving rise to long-range, repulsive, and poorly reproducible forces. At pH values above 12, strong, repulsive double-layer forces are again present between the adsorbed layers. The sign of the surface charge cannot be inferred from surface force measurements directly. However, since there is no precipitation of negatively charged dodecylamine droplets onto the surface at this pH, it follows that the surfaces must be negatively charged. In all probability the negative surface charge has partly the same origin as that of the dodecylamine droplets; adsorption of hydroxide ions has been suggested,⁴⁹ but there also is a contribution from the negatively charged mica lattice, which can no longer be effectively neutralized by DAH⁺ ions or protons.

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Conclusion

The adsorption to mica in the DAH-Cl system is dramatically dependent on the pH of the system and the resulting concentrations of the different species present in solution. At low pH, essentially all the surfactant is charged and at a surfactant concentration of 10^{-4} M adsorption occurs only to the extent of one molecule per negative site on the mica surface, forming a sparsely packed, "tilted" monolayer. As the pH increases, so does the concentration of DA that, at pH 8–9, is able to coadsorb into the monolayer thus increasing the adsorbed layer thickness. At this stage a long-range hydrophobic attraction is observed, which is consistent with that found by previous workers, as are the measured adhesion values. At high pH values (≥ 9.5), the concentrations of DA and the highly surface active associated species are sufficiently high to allow the formation of a bilayer on each surface. The bilayer is uncharged at pH 10.3 but redevelops a significant charge at higher pH values.

Our results contribute to the debate over the structure of adsorbates as they show that on an "ideal" highly charged, smooth, homogeneous mineral surface it is possible to come close to the classical monolayer/bilayer adsorption behavior. However, as discussed, not even in this case are perfect monolayers obtained, and it is even less likely that such a simple adsorption behavior is observed for less ideal surfaces.

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