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Adsorption Kinetics and Structural Arrangements of Cationic Surfactants on Silica Surfaces

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The adsorption of cetyltrimethylammonium bromide (CTAB) to the silica–aqueous interface has been studied using optical reflectometry. The effect of pH, salt, and surface preparation on the surface excess and adsorption kinetics has been studied. The adsorption kinetics have been measured and compared to the theoretical diffusion limited flux of surfactant, the quotient being the “sticking ratio”. Analysis of the sticking ratio as a function of CTAB concentration reveals that the adsorption process is cooperative above the critical micelle concentration (CMC). At the critical surface aggregation concentration (CSAC), adsorption proceeds slowly in the absence of salt and takes hours to reach an equilibrium value. At all other concentrations and even at the CSAC when salt is present, the adsorption is complete within minutes. These results indicate that, above the CMC, micelles adsorb directly to the silica surface, and this is reflected in the structure of the surface layer. At the CSAC the equilibrium surface structure is analogous to adsorbed micelles, but as only monomers are present in solution, the adsorption proceeds to equilibrium slowly.

Introduction

A thorough understanding of the adsorption of soluble surfactants to the solid–aqueous interface is important in many processes from detergency to froth flotation and oil recovery. Knowledge of the surface excess, the rate of adsorption, and the structural arrangement of the adsorbed layer is required to fully characterize the adsorption behavior. Adsorption isotherms for silica surfaces typically exhibit two steps^{1,2} whereas metal oxide surfaces are known to have adsorption isotherms with four steps.³ The silica surface has a low charge density, and as such, the individual charged sites have only a small influence on neighboring sites. Therefore, at very low surfactant concentrations surface neutralization will occur. Further increases in concentration, in the absence of salt, result in a reversal of the surface charge and then a sharp increase in adsorption. This occurs due to hydrophobic interactions between surfactant chains and produces the first step in the isotherm. This is often called the hemimicelle concentration (HMC).⁴ The term hemimicelle is used to describe monomers that are adsorbed to the surface such that the head groups are next to the surface and the chains are interacting with neighboring monomers forming small aggregates.⁵ As the concentration is increased still further, little change in adsorption is seen until the critical surface aggregation concentration (CSAC) is reached. This typically occurs at a concentration of about 60% of the critical micelle concentration (CMC). At the CSAC the adsorbed amount rises rapidly as admicelles

are formed. The term admicelle is used to describe surface-adsorbed surfactant aggregates that have surfactants oriented with head groups facing both the surface and into solution.⁵

The structure of the aggregates at the silica–water interface, the admicelles, has been described variously as bilayers, patchy bilayers, and interdigitated bilayers. A precise description of the structure of adsorbed surfactants is yet to emerge, but advances are being made by direct imaging and reflectivity studies. Atomic force microscopy has been employed to image surface-adsorbed surfactant structures in equilibrium with surfactant solutions at length scales close to that of a surfactant, but as yet these studies have been limited to bulk surfactant concentrations that are near or above the CMC for silica surfaces.⁶ A study at low bulk surfactant concentrations has imaged adsorbed surfactants at length scales much greater than that for the surfactant molecule.⁷ At these length scales little structural information is available. The structure of surface layers elucidated by reflectivity studies⁸ is model dependent and therefore somewhat ambiguous. However, with increasingly intense radiation sources and the combination of X-ray and neutron radiations, greater differentiation between models is being realized. Determination of the spatial arrangement of adsorbed surfactants at all points on the adsorption isotherm remains an important goal. Until recently,^{9,10} the kinetics of surfactant adsorption have received comparatively little attention, despite the importance of adsorption kinetics in mixed surfactant–polymer systems and minerals' separation processes. This is primarily due to the difficulty of following the fast adsorption of surfactants. The development of

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ellipsometric methods with high temporal resolution has overcome this difficulty.^{9–12}

Here we report measurements of surfactant surface excess and the kinetics of surfactant adsorption to silica surfaces. These measurements are used to probe the structural changes taking place in the adsorbed surfactant layer. This is achieved using optical reflectometry with a stagnant point flow cell, after Dijt.¹¹ Reflectometry allows the surface excess to be followed in real time. The hydrodynamics within the stagnant point of the cell are well defined, enabling the diffusion-limited flux of surfactant to be calculated. Analysis of these results allows conclusions to be drawn regarding the mechanism of surfactant adsorption and the implications for the structure of surface aggregates.

Materials and Methods

KBr (Analytical Grade) and CTAB (purity greater than 99%) were obtained from Aldrich. The CTAB was recrystallized twice from acetone and freeze-dried. The KBr was oven baked for 24 h at 600 °C to remove organic contaminants. All water used was filtered, distilled, and passed through a Millipore filtration unit before use. Silicon wafers were baked at 1000 °C for 100 min in an oxygen atmosphere to produce an oxide layer (SiO₂) 165 nm thick. Baking results in condensation reactions at the silica surface resulting in the formation of siloxane bonds and a lower hydroxyl group density.¹³ The resulting silica surface, when immersed in water, is more highly charged than untreated silica, as the hydroxyl groups are isolated and therefore less likely to participate in hydrogen-bonded stabilization of hydronium ions at the surface.¹³ That is, the density of hydroxyl groups is reduced but their degree of ionization is greatly increased. When used in this state we call the silica pyrogenic. All measurements were conducted on pyrogenic silica unless otherwise stated. The surface slowly rehydroxylates when exposed to atmospheric moisture or immersed in water, giving what we term hydroxylated silica. The hydroxylated silica used here was prepared by soaking pyrogenic silica in water for 48 h, followed by cleaning in 10 wt % NaOH for 30 s and rinsing in water and then ethanol before drying under a nitrogen stream. The layer thickness at various sites on the wafer was determined ellipsometrically, using an Auto EL-II Automatic Ellipsometer produced by Rudolf Research, to be 165 ± 1 nm. These wafers were used as the substrate for all adsorption studies. The oxide layer thicknesses of the hydroxylated silica surfaces were also measured by ellipsometry and found to be unchanged. The reflectometer is entirely contained in an incubator, allowing the temperature to be accurately maintained at 25 ± 0.1 °C. A schematic representation of the reflectometer is presented in Figure 1.

Optical reflectometry utilizes a linearly polarized light beam, which is reflected from the surface under investigation and subsequently split into its parallel (p) and perpendicular (s) components using a polarizing beam splitter. Continuous measurement and acquisition of the intensity of the s and p polarizations is accomplished using signal processing electronics and a PC. Continuous adsorption measurements can be obtained over long time intervals with a temporal resolution of <0.1 s. As material adsorbs to the silica–water interface, the intensities of the reflected p and s polarized beams change. The ratio of the intensity of these beams (p/s) is defined as *S*. The system can be treated by analysis of the Fresnel reflectivities for a four-layer system where each layer is described by a complex refractive index and a layer thickness.¹⁴ The layers are solvent, adsorbed layer, silica, and silicon. When the beam is incident upon the surface at the Brewster angle for the water–silicon interface, the reflectivity of the surface is insensitive to the conformation of the adsorbed layer and is determined by the mass of adsorbed

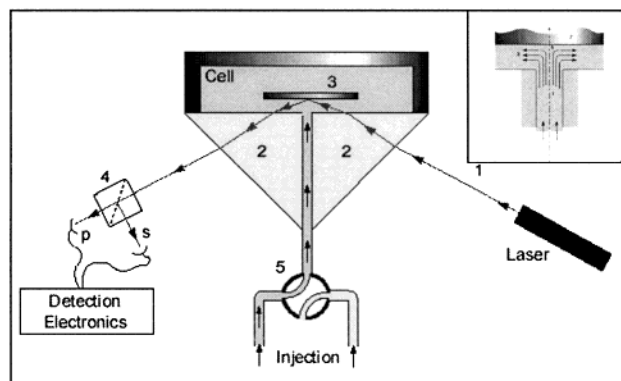


Figure 1. Schematic diagram of the reflectometer (after ref 11). A linearly polarized beam from the He–Ne laser (1) enters the cell through a 45° glass prism (2) and passes through the solution, striking the surface under investigation (3). The reflected beam is split into its p and s components (4). Both components are detected by photodiodes and recorded separately. Solution is passed into the cell by means of an injection system. This consists of two flasks, one containing only solvent and the other containing surfactant solution, and a valve (5) that directs one solution to the cell and the other to waste. Solutions are passed into the cell by Teflon tubing via a cylindrical hole in the glass prism (2). Inset: Schematic diagram of stagnation point flow. The solution is perpendicularly injected toward the flat surface. As the jet stream spreads over the surface, a stagnation point forms at the spot where the axis of the impinging jet intersects with the surface.

material and the refractive index increment of the adsorbing material (0.15 cm³ g^{−1} for CTAB).¹⁵ Application of the theory (using eq 1) yields the sensitivity factor (*A_s*), which is the relative change in *S* per unit surface excess.

$$A_s = \frac{1}{R_s/R_p} \frac{dR_p/R_s}{d\Gamma} \quad (1)$$

The parameter *A_s* is found to be very weakly dependent upon the amount of material adsorbed and in practice is taken to be constant. The surface excess is then obtainable by application of eq 2, where *S*₀ is the initial value of *S* prior to adsorption.

$$\Gamma = \frac{\Delta S}{S_0} \frac{1}{A_s} \quad (2)$$

The hydrodynamics and deposition of colloidal particles in stagnation point flow have been investigated by Dabros and Van de Ven.¹⁶ This work is concerned only with their final equations describing diffusive mass transport, and simplifications that can be made when surfactant molecules are used in place of colloidal particles. The hydrodynamics associated with stagnation point flow are well defined. The geometry is shown in the inset of Figure 1. At the stagnation point there is zero hydrodynamic flow. That is, while the injected solution flows about the stagnation point, any exchange is diffusion limited. Thus, the rate of adsorption of surfactant to the silica surface is diffusion limited and defined in the following equation.

$$J = 0.766\nu^{1/3} R^{-1} D^{2/3} (\alpha Re)^{1/3} c \quad (3)$$

where *ν* is the kinematic viscosity, *D* is the diffusion coefficient, *Re* is the Reynolds number, *c* is the concentration of adsorbent, and *α* is determined by the ratio *h/R*, where *h* is the distance between the surface and the inlet tube and *R* is the radius of the tube. It provides a measure of the intensity of flow near the surface and is dependent on the radial distance to the stagnation point, the geometry of the cell, and the Reynolds number. The

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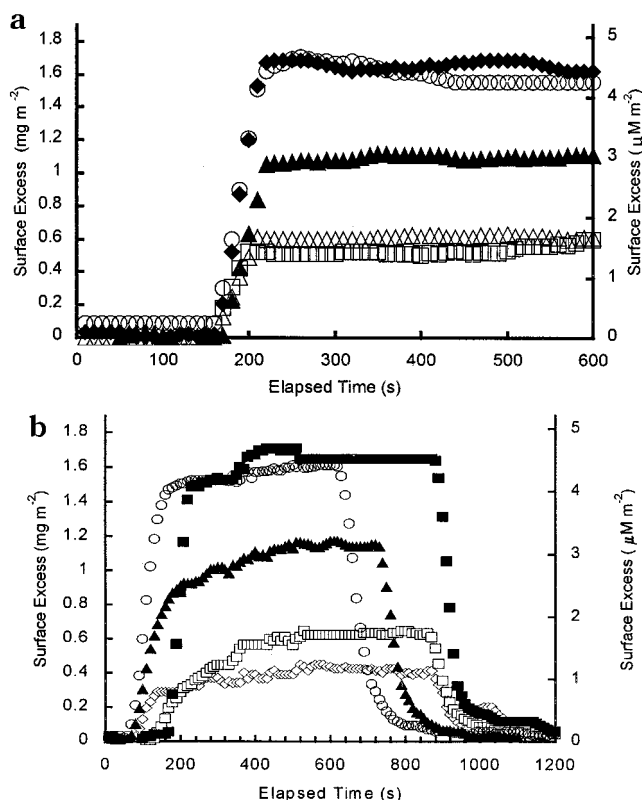


Figure 2. (a) Surface excess of CTAB at the hydroxylated silica–solution interface versus time with no added electrolyte for CTAB concentrations of 0.4 (open squares), 0.5 (open diamonds), 0.7 (filled triangles), 1.0 (open circles), and 3.0 (filled diamonds) mM. The CTAB solution is first passed into the cell at approximately 180 s, leading to surfactant adsorption. The plateau level of adsorption is maintained while the CTAB solution is in the cell. (b) Surface excess of CTAB at the pyrogenic silica–solution interface versus time with 0.01 M KBr for CTAB concentrations of 0.03 (open diamonds), 0.04 (open squares), 0.06 (filled triangles), 0.09 (open circles), and 1 (filled squares) mM. When water is passed into the cell, the adsorbed CTAB is completely desorbed from the surface. Adsorption of surfactant occurs at much lower bulk concentrations of CTAB in the presence of electrolyte.

appropriate value for α was determined to be 6 for our system.¹⁶ In our cell $h/R = 1.7$ and α is approximately proportional to Re . The diffusion coefficient used for the monomers was $2 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, which is the experimentally determined value for dodecyltributylammonium bromide.¹⁷ The diffusion coefficient used for the micelles was $8.36 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$, which was calculated using a micelle radius of 2.9 nm¹⁵. At the concentrations of surfactant and electrolyte used in these studies, the diffusion coefficient of the micelles effectively remains unchanged.¹⁸

Results

Measurements for the adsorption of CTAB onto silica are shown in Figure 2 for a range of solution concentrations. Initially the surface is immersed in pure water until the CTAB solution is introduced after about 180 s (presented in Figure 2a). A rapid increase in adsorption is observed over approximately 20 s until an equilibrium surface excess is reached, which is dependent upon the concentration of CTAB in solution. This plateau is maintained as long as the solution concentration remains constant. When the solution also contains a background electrolyte, the solution concentration of CTAB required to produce a given surface excess is considerably less.

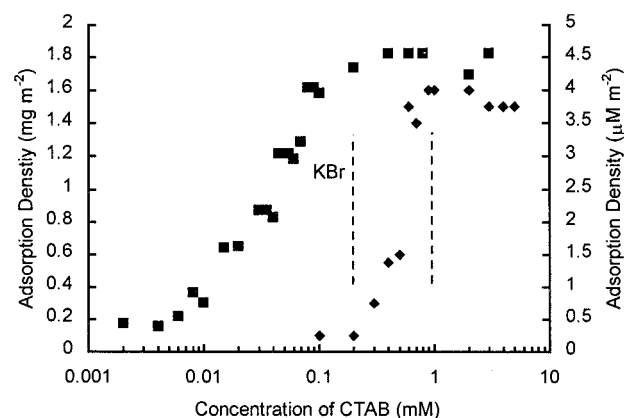


Figure 3. Surface excess versus CTAB concentration in the presence (squares) and absence (diamonds) of 0.01 M KBr. The dotted lines show the position of the CMC for each system. In the absence of electrolyte, adsorption occurs in a two-step process. This is not observed in the presence of electrolyte.

Figure 2b shows adsorption data for a range of CTAB concentrations in the presence of 0.01 M KBr. The baseline is obtained with 0.01 M KBr in the absence of CTAB. At around 100 s the CTAB solutions with electrolyte are introduced and adsorption takes place. Also included in Figure 2b is the "wash-off" which occurs when the CTAB solution is replaced by 0.01 M KBr. The surface excess is seen to rapidly decrease and return to zero as all the adsorbed surfactant is removed from the surface. This was found to be the case in all measurements, both with and without electrolyte present.

An adsorption isotherm can be constructed by performing a series of adsorption experiments to determine the equilibrium surface excess for different concentrations of CTAB in solution. The adsorption isotherms for CTAB without added salt and in the presence of 0.01 M KBr are shown in Figure 3. In the absence of salt the classical two-step isotherm is observed. The first step, which occurs between 0.2 and 0.4 mM, leads to a surface coverage of $\sim 0.6 \text{ mg m}^{-2}$. The second step occurs sharply at 0.6 mM and results in a surface coverage of $\sim 1.6 \text{ mg m}^{-2}$. This concentration is associated with the formation of admicelles and is termed the critical surface aggregation concentration (CSAC). As previously reported, the second step is considerably larger ($\sim 50\%$) than the first.¹⁹ When salt is added, adsorption takes place at lower concentrations of CTAB and the steps in the isotherm are no longer observed. Further, the adsorbed amount above the CSAC is slightly greater at 1.8 mg m^{-2} .

A surprising result was obtained for 0.6 mM CTAB in the absence of salt, with the adsorption of surfactant continuing for several hours (presented in Figure 4). The adsorption initially takes place rapidly, up to an adsorption density of $\sim 0.6 \text{ mg m}^{-2}$, but then increases very slowly until it reaches the final equilibrium adsorption value of $\sim 1.6 \text{ mg m}^{-2}$. The significance of this result is discussed below.

The surface charge of silica increases on raising the pH from 6.5 to 10.0, as a greater proportion of surface hydroxyl groups are ionized.¹³ Measurements of CTAB adsorption have been conducted using pH values of 6.5, 8.0, and 10.0, using 0.01 M KBr as a background electrolyte, as shown in Figure 5. The isotherms are essentially unchanged, indicating that the surface charge has little effect on the surface excess of CTAB at equilibrium. The adsorption isotherms for pyrogenic and hydroxylated silica are shown

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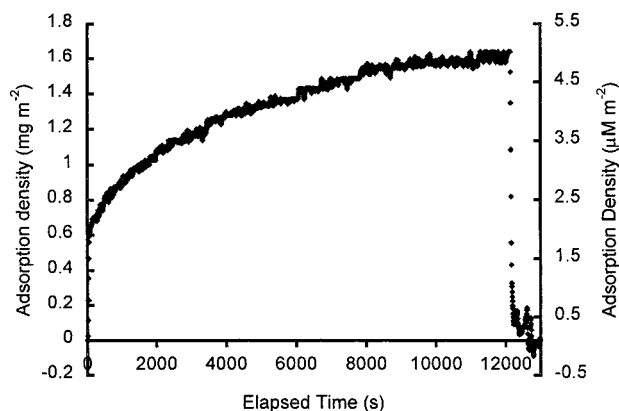


Figure 4. Surface excess of CTAB at the pyrogenic silica-solution interface versus time for a CTAB concentration of 0.6 mM. Adsorption occurs over a much greater time period than those for other concentrations. The surface excess initially increases rapidly to 0.6 mg/m² (which equals the equilibrium excess achieved at slightly lower concentrations), and then over a number of hours adsorption increases to the plateau level obtained for slightly higher concentrations. At these higher concentrations, equilibrium adsorption levels are obtained within minutes. Upon introduction of pure water at 12000 s (~3 1/3 h), the adsorption returns to baseline levels.

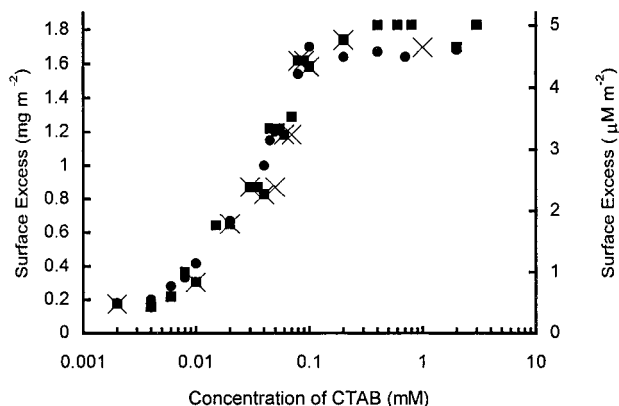


Figure 5. Surface excess of CTAB at the pyrogenic silica-solution interface versus concentration, for solutions of pH 6.5 (squares), pH 8.0 (circles), and pH 10.0 (crosses). The pH was adjusted using NaOH.

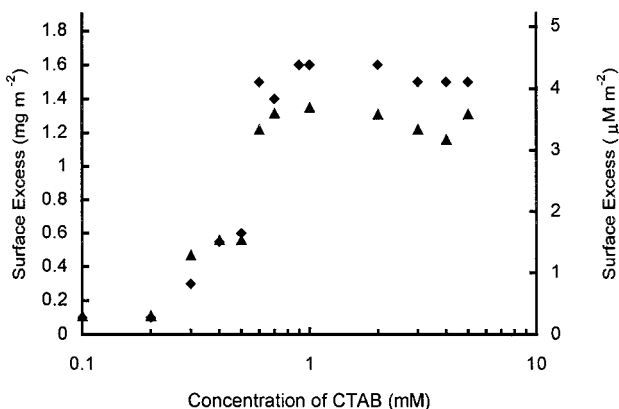


Figure 6. Surface excess of CTAB at the silica-solution interface versus concentration, for pyrogenic (diamonds) and hydroxylated (triangles) silica. For details of the silica preparation see text.

in Figure 6. Up to the CSAC the isotherms are similar, but beyond this the surface excess for hydroxylated silica is somewhat lower than that for pyrogenic silica. These surfaces differ both in their surface charge and in their

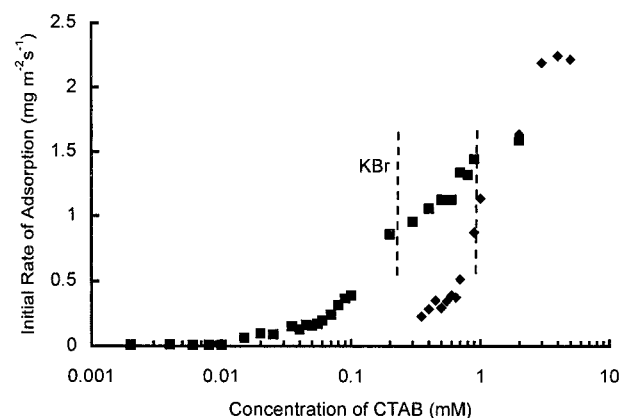


Figure 7. Initial rates of CTAB adsorption to the pyrogenic silica-solution interface in the presence (squares) and absence (diamonds) of salt. The vertical lines indicate the CMC of each solution.

hydrophobicity. The relative contributions of these differences on the adsorption isotherms are discussed later.

While reflectometry is a useful tool for equilibrium studies, it is highly suited to study the fast kinetics associated with surfactant adsorption that cannot be followed using traditional techniques. The adsorbed amount can be followed with high temporal resolution. By examination of the rate of increase in surface excess that occurs upon injection of the surfactant solution, the initial rate of adsorption can be determined. These rates are shown in Figure 7 for CTAB with and without the addition of salt. As expected, below the CMC the rate of adsorption increases with concentration. However, this trend continues even above the CMC, where the monomer concentration in bulk is no longer increasing. This indicates that the micelles must be playing a role in the initial adsorption process, either by direct adsorption to the surface or by acting as a transport mechanism for monomers. To clarify this, the data for the initial rate of adsorption can be converted to a "sticking ratio". When a stagnant point flow cell is employed, the hydrodynamics are well defined and the observed adsorption can be compared to the theoretically derived diffusion-limited flux to the interface. The ratio of the two is reported as the sticking ratio. This can be thought of as the fraction of molecules that, upon reaching the surface, stick to it. It must be remembered that this is an oversimplification, as the adsorbed surfactant is freely exchanging with the surfactant in solution. Trends in the sticking ratio with concentration can, however, reveal the character of the adsorption process. The sticking ratios for CTAB and CTAB with 10 mM KBr are shown in Figure 8. In this figure the concentration of surfactant has been normalized by the CMC for each system (1.25×10^{-4} M²⁰ with 0.01 M KBr, 9.0×10^{-4} M without salt²¹). For concentrations above the CMC the theoretical flux consists of two components, the flux due to monomers and the flux due to micelles. Any increase in the concentration above the CMC is reflected only in the flux due to micelles, as the monomer concentration is assumed to be constant. In Figure 9 we have evaluated the sticking ratio for three pH values at a range of CTAB concentrations in 0.01 M KBr. Here it can be seen that an increase in pH results in a higher sticking ratio below the CMC, but the sticking ratio above the CMC remains unchanged.

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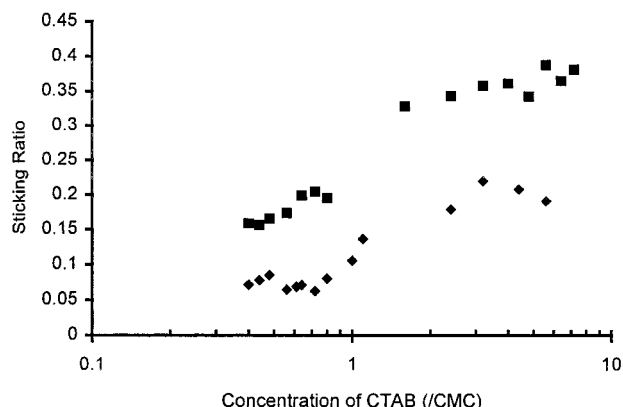


Figure 8. Sticking ratio (determined from the initial rate of adsorption) versus concentration for solutions of CTAB, normalized by the corresponding CMC, with (squares) and without (diamonds) added 10 mM KBr. The values of the variables used in the calculation of the theoretical diffusion-limited flux were as follows: $u = 0.0022$, $R = 0.0013$, $\nu = 8.93 \times 10^{-7}$, $Re = 3.37$, $a = 2 \times 10^{-9}$, $D(\text{monomer}) = 1.21 \times 10^{-10}$, $D(\text{micelle}) = 8.36 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$, $h = 0.0015$, and $\alpha = 6$. The concentration was in kilograms per cubic meter of the surfactant solution. The sticking ratio increases at the CMC for both systems.

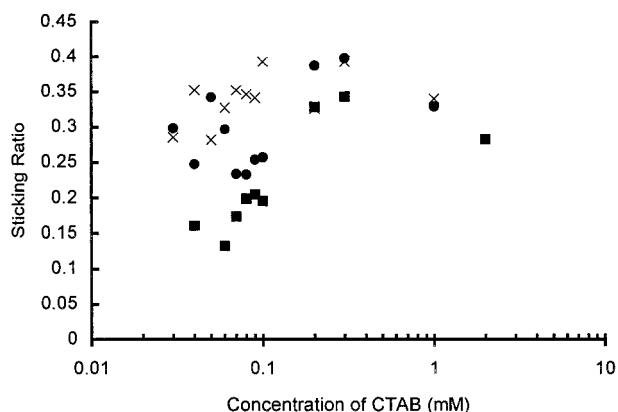


Figure 9. Sticking ratio (determined from the initial rate of adsorption) versus concentration for solutions of CTAB in 10 mM KBr with pH 6.5 (squares), pH 8.0 (circles), and pH 10.0 (crosses).

Discussion

The adsorption isotherm for CTAB onto silica has been extensively studied, revealing a two-step isotherm, in which the steps correspond to hemimicelle and admicelle formation, respectively.^{3,22} The first step is found to be smaller than the second. In our measurements the first step corresponds to $\sim 35\%$ of the adsorption plateau achieved at high surfactant concentrations. The measured adsorption density of $\sim 1.6 \text{ mg m}^{-2}$ is typical for CTAB on silica, with literature values ranging from 1.5 mg^{-2} to 2.1 mg^{-2} .^{10,12} The level of adsorption was found to be slightly higher in the presence of electrolyte at $\sim 1.8 \text{ mg m}^{-2}$. This is a result of the screening of the head-group charge by electrolyte. This reduces the surfactant head-group area and allows more tightly packed surfactant aggregates to form. Upon addition of electrolyte, the steps in the isotherm are no longer observed (see Figure 3).

Silica surfaces are known to differ in surface chemistry depending on the preparation method and on the presence of metal ions within the silica. Our surface is uncomplicated by the presence of metal ions within the silica, as the silicon wafers from which they are made are of high

purity. We have investigated the adsorption of CTAB on silica with different surface properties, termed pyrogenic and hydroxylated silica. In Figure 6 the isotherms for CTAB adsorbed to pyrogenic and hydroxylated silica are compared. The adsorbed amounts at low concentrations are similar, but at high concentrations of CTAB the surface excess is greater for the pyrogenic silica. We have also investigated the effect of surface charge on the surface excess by altering the pH of the solution. The results are shown in Figure 5 for CTAB in the presence of salt. Over a pH range of 6.5 to 10, silica is known to become progressively more negatively charged,¹³ yet the surface excess remains largely unchanged. Therefore, it is unlikely that the increase in surface excess for pyrogenic silica over hydroxylated silica is due to surface charge. The difference must then be due to the greater hydrophobicity of the pyrogenic silica surface. This hydrophobicity will lead to an increased interaction with monomer hydrocarbon chains and a change in structure of the admicelles. We propose that this change in aggregate structure is responsible for the observed increase in surface excess.

Kinetics of Adsorption and Surface Aggregate Structure

The precise structure of the hemimicelles and admicelles is not yet known and is of great interest. Traditionally, these structures were thought to be uniform, corresponding initially to a monolayer coverage and then with increasing concentration to bilayer coverage, but recent studies have revealed that patchy layers or collections of individual aggregates provide a more accurate description of the adsorbed structures. Neutron reflection and atomic force microscopy (AFM) studies have greatly enhanced our understanding in this area; however, both methods have their limitations. Reflectivity is inherently model dependent, as the reflectivity profile is necessarily fit with a scattering model that may not be a unique solution. Currently, AFM has only been successfully applied to the elucidation of surfactant structures on silica surfaces at concentrations above the CSAC; therefore, hemimicellar structures on silica have not yet been imaged.²³

Many previous studies of surfactant adsorption required large adsorbing surface areas in order to obtain the desired sensitivity. Such techniques yielded valuable information on the degree and energetics of adsorption but were inherently unsuitable for kinetic measurements. Ellipsometric measurements are now available that enable the kinetics of surfactant adsorption to be studied on a single interface of low surface area. Kinetic data can be applied to the elucidation of adsorbed surfactant aggregate structures and how these structures evolve with increasing concentration. The initial rate of adsorption for CTAB adsorbing to silica is shown as a function of CTAB concentration with and without added electrolyte in Figure 7. The adsorption rate increases with concentration of surfactant, as would be expected. The dotted lines indicate the CMC for each system. The initial rate of adsorption continues to increase above the CMC for both systems. A remarkable result, given that the monomer concentration is no longer increasing. These data are easily interpreted if they are compared to the theoretical rate of adsorption. We define the ratio of the experimentally determined initial adsorption rates to the theoretical diffusion-limited adsorption rate as the sticking ratio. For the initial adsorption of surfactant, the sticking ratio is equivalent to the fraction of molecules reaching the surface that

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adsorb. An analysis of the variation in sticking ratio with concentration can reveal much about the adsorption process. If the sticking ratio were to decrease as the concentration of surfactant increases, this would indicate competition between surfactant molecules for the surface. Alternatively, if the sticking ratio increases with concentration, this would indicate cooperativity between surfactant molecules during adsorption. A constant sticking ratio describes an adsorption process where the surfactant molecules behave independently.

The measured sticking ratios for the CTAB-silica system reveal a general trend of increasing sticking ratio with concentration. In the absence of salt, the sticking ratio is constant up to the CMC, indicating that the monomers are adsorbing independently. With 0.01 M KBr present, the sticking ratio is higher than that in the absence of salt and is seen to gradually increase even below the CMC, indicating that adsorption of monomers is cooperative in this case. Cooperativity is clearly aided by the screening of the head-group charge by electrolyte. Perhaps such screening allows hydrophobic interactions to play a greater role in adsorption? At the CMC the sticking ratio increases sharply and continues to increase, but more gradually, as the concentration of CTAB is increased both with and without added salt. The sharp increase must be attributed to the presence of micelles in solution and clearly indicates that they play a role in the adsorption process. This is discussed further below. Above the CMC the sticking ratio is a combination of the sticking ratio of monomeric surfactant and the sticking ratio of surfactants within micelles. The contribution of each is determined by the mole fraction of surfactant in that form. Continuing above the CMC, the sticking ratio continues to increase, not because the sticking ratio of the monomers or the sticking ratio of surfactant within the micelles is changing but because the contribution of the latter to the overall value is increasing.

In Figure 9 we have evaluated the sticking ratio for three pH values at a range of CTAB concentrations in 0.01 M KBr. Here it can be seen that an increase in pH results in a higher sticking ratio below the CMC, but in Figure 5 we presented data that indicated that solution pH has no effect on the surface excess at equilibrium. Therefore, while pH has no effect on the equilibrium surface excess, it does affect the rate of surfactant adsorption. This may arise from the larger negative electrostatic potential of the silica surface in high pH solution conditions resulting in a greater driving force for initial adsorption. However, the surface excess at equilibrium is unchanged with pH, supporting the view that the driving force for aggregation is the hydrophobic interaction not electrostatics. While hydrophobic attraction is the driving force for aggregation, the surface excess is limited by the electrostatic repulsions between adsorbed surfactant monomers. Above the CMC, the sticking ratio appears to be unaffected by the solution pH. This is further evidence that the adsorption process above the CMC is substantially different.

What is the role of micelles in surfactant adsorption? It has generally been thought that micelles do not adsorb directly to a surface but act as a reservoir for the adsorption of monomers.²⁴ In this scenario, the micelles transport surfactant monomers to a surface layer whereby they leave the micelles and adsorb to the surface as monomers. For this process to lead to the observed trend in sticking ratio, the greater success of CTAB monomers borne in micelles in adsorbing to the surface must be due to the more

effective penetration of the surface layer by micelles when compared to monomers. Opposing penetration of the surface layer is the repulsion due to the electrical double layer. As a micelle carries a large number of counterions, it is reasonable to postulate that monomers of CTAB borne in a micelle will penetrate the surface layer more effectively than a lone monomer, as they carry a much smaller charge per monomer. However, this effect would be somewhat reduced in the presence of electrolyte, where the range of the electrical double layer is diminished. We observe a similar increase in sticking ratio at the CMC, in the presence or absence of electrolyte; this is contrary to what would be expected in the above model. Adsorption of micelles, in part or wholly, directly to the surface must be considered. AFM images of CTAB adsorbed to silica, utilizing similar methods of substrate preparation, reveal spherical aggregates, which are interpreted as surface-adsorbed micelles.²⁵ Each spherical structure may arise from an adsorbed micelle rather than a gradual aggregation of monomers.

At a concentration of 0.6 mM CTAB in the absence of salt, the adsorption of surfactant occurs over a period of several hours. This is shown in Figure 4. The adsorption initially takes place rapidly up to an adsorption density of $\sim 0.6 \text{ mg m}^{-2}$ but then proceeds very slowly until it reaches the final equilibrium adsorption value of $\sim 1.6 \text{ mg m}^{-2}$, which is equivalent to that reached at all higher concentrations of CTAB. It is extremely difficult to conclusively rule out a role for contaminants in the slow adsorption process, but several observations lead us to believe that they are not the cause of this phenomenon. The slow adsorption process only occurs at a concentration of $0.6 \pm 0.05 \text{ mM}$, and it is unaffected by purification of the surfactant. The change in surface excess that takes place during this process corresponds to a transition from the first step to the second step in the isotherm. Further, the material is rapidly and completely washed free of the surface upon introduction of water. Slow adsorption has been reported in the same system previously.^{12,15} In this prior work the equilibrium surface excess of CTAB was found to be higher than previously reported at $\sim 3 \text{ mg m}^{-2}$ for concentrations below the CMC, and the accepted value of $\sim 1.6 \text{ mg m}^{-2}$ was found above the CMC. The adsorption of CTAB below the CMC was found to occur very slowly. Recently, it has been found that these results were affected by contamination arising from PVC tubing.²³ The slow adsorption process we report here is different in that it only occurs over a very narrow concentration range and that it corresponds to a transition in surface excess from the first to second step of the adsorption isotherm. The measured surface excess is equal to the accepted literature values throughout the concentration range.

If micelles adsorb directly to the surface and the aggregate structure is that of a surface adsorbed micelle, then this may explain the slow adsorption process observed for $0.6 \pm 0.05 \text{ mM}$ CTAB. At this concentration sufficient surfactant is present to result in equilibrium levels of adsorption that correspond to those obtained above the CMC. However, at this concentration there are no micelles present in bulk. Clearly adsorption must take place by monomers and these monomers must undergo structural arrangements at the surface in order to form a surface structure that is analogous to a bulk micelle. This process will be strongly hindered, as the monomers must sample many sites in order to be successfully incorporated into the surface structure. It is conceivable that this process could take hours to reach the final equilibrium concentra-

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tion, as we observe in Figure 4. This observation supports a model where complete micelles adsorb to the surface rather than adsorption proceeding by the adsorption of micelle parts.

Why then is this process not observed in the presence of salt? Two changes could account for this. The presence of electrolyte will reduce the head-group area of the surfactant and lower the curvature of structures that it forms.²⁶ In the case of CTAB, this would drive the structure of the admicelles away from spheres²⁷ to elongated structures.²⁸ This transition has been observed by atomic force microscopy.²³ Monomers may pack into such structures more readily and thereby reach the final equilibrium concentration rapidly. Also, changes to the micelles in solution could lead to more rapid adsorption. The presence of salt in micellar solutions alters the structure of the micelles. Spherical micelles become elongated and worm-like. Concurrently, the size polydispersity of the micelles increases dramatically.²⁸ The onset of micellization will also be less sharp. Thus, even at a concentration below the accepted CMC, a few micelles may still be present. Any such micelles may then participate in adsorption at

the surface and negate the need for monomeric surfactants to pack into a surface aggregate.

Conclusion

Optical reflectometry has been used to investigate the adsorption of CTAB to the silica–water interface as a function of CTAB concentration, with and without added salt, and as a function of pH. The adsorption isotherms obtained agree with those in the literature obtained using other methods. The kinetics of adsorption have been followed, and the experimentally determined adsorption rates have been compared to calculated diffusion-limited adsorption rates. The sticking ratio is defined as the ratio of the experimental flux to the diffusion-limited flux and is used to interpret the structure of the adsorbed surfactant layer. An unusually slow adsorption process at a CTAB concentration of 0.6 ± 0.05 mM has been observed. This is interpreted as arising from a slow structural change in the adsorbed surfactant layer. Slow adsorption behavior is not observed in the presence of 0.01 M KBr. At concentrations above the CMC, micelles participate in the adsorption process and the surfactant layers formed reflect the structure of the component micelles.

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