Interaction Forces on α-Alumina Surfaces with Coadsorption of Anionic/Nonionic Surfactant Mixtures

Kenichi Sakai, Tomokazu Yoshimura, and Kunio Esumi*

Department of Applied Chemistry and Institute of Colloid and Interface Science, Tokyo University of Science, Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan

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Direct measurement of interaction forces between α-alumina surfaces with coadsorbed anionic sodium dodecyl sulfate (SDS) and nonionic hexaoxyethylenedodecyl ether ($C_{12}E_6$) at pH 3.5 is carried out by colloidal probe atomic force microscopy. The strength of interaction forces is found to be dependent on the initial SDS concentrations, whereas the addition of $C_{12}E_6$ alone causes negligible effects on the interaction. This is due to the absence of attractive interactions between $C_{12}E_6$ molecules and α-alumina. On the other hand, the interaction forces are remarkably different for the simultaneous addition of the two surfactants. At lower $C_{12}E_6$ concentrations the observed repulsion induced by the electric double layer is larger than that in the corresponding single SDS solution, suggesting the stronger SDS adsorption as a consequence of the reduction of the electrostatic repulsion between the ionic headgroups of SDS admicelles. By the further addition of $C_{12}E_6$ a steric stabilizing force is detected from the separation of approximately 5 nm. This is attributed to the formation of a closely packed adlayer comparing with the case of the single SDS admicelles. The effects of sequential addition of $C_{12}E_6$ to the α-alumina preadsorbed hydrophobically with SDS are also investigated to understand the complex phenomena that occur at the interface.

Introduction

Adsorption of surfactants at the solid/liquid interface has been a scientific subject of considerable experimental and theoretical interest for many years. The knowledge has been used in the development of various industrial applications in the area of detergency as well as wastewater treatment, oil recovery, and mineral flotation. Because it is generally accepted that the layered structure of surfactants at the interface is the most important factor when the wettability of solid particles is interpreted, many investigators have paid attention to the adsorption behavior of ionic/nonionic surfactant mixtures with a view to study the enhanced surface activity.

Surfactant mixtures provide several advantages over single surfactants because the adsorption of surfactants on the solid surfaces can be controlled using appropriate surfactants and solution properties. It is well-known that regular mixing theory[1] completely describes the thermodynamics of the mixed ionic/nonionic micellization in the bulk phase. However, significant deviations from the predicted behavior have been observed upon the formation of mixed adlayers.[2] This is attributed to the fact that the ionic/nonionic surfactant mixtures often show synergistic effects as the adsorption of one surfactant is sometimes enhanced in the presence of the other surfactant. For example, nonionic octylphenolpoly(oxyethylene) (Triton X-100), which itself does not readily adsorb onto positively charged γ-alumina, is strongly coadsorbed from sodium dodecyl sulfate (SDS) and Triton X-100 binary solutions.[3] Here, it is noted that the adsorbed amount of Triton X-100 is largely dependent on SDS concentration: the adsorption of Triton X-100 reaches a maximum level at a quite low SDS concentration, suggesting the formation of mixed SDS/Triton X-100 hemimicelles on γ-alumina. Similar results have been reported for certain anionic/nonionic surfactant mixtures.[4−6]

We have also investigated simultaneous adsorption behavior of SDS and nonionic oxyethylene surfactants on α-alumina by measuring the adsorbed amount of both the surfactants.[7,8] Taking the individual adsorption isotherms for the mixtures into consideration, it has been shown that the adsorption of the oxyethylene surfactants is enhanced significantly and the isotherm is shifted toward the lower concentration region, whereas the adsorption of SDS is only enhanced at low SDS concentrations. The incremental affinities of the two surfactants for the α-alumina surface indicate that (i) the initial adsorption of SDS provides a number of hydrophobic sites that is sufficient to enable hydrophobic adsorption of the nonionic surfactants and (ii) the presence of the oxyethylene surfactants enhances the SDS adsorption by reducing the lateral electrostatic repulsive force between the ionic headgroups of SDS. On the other hand, for the sequential addition of nonionic surfactants to an α-alumina surface pretreated hydrophobically with an anionic surfactant, the flocculated α-alumina redisperses by the formation of mixed surfactant adlayers via the hydrophobic binding between the two surfactants.[9] These observations provide primary explanations on the adsorption behavior of surfactant mixtures, concomitantly with indirect information on the detailed structure of surface layers.

With the advent of the AFM imaging technique, it is now possible to focus on the self-assembly of surfactant molecules at the solid/liquid interface. Until now a few studies have been carried out to elucidate the coadsorption behavior of surfactants mixtures, where the interaction between the surfactants in bulk solution plays a key role. Certain surfactant combinations exhibit a weak interaction, whereas others interact strongly in a more specific manner. In the former case, the structural transformation

* To whom correspondence should be addressed. E-mail: kuesumi@rs.kagu.tus.ac.jp.

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of adlayers takes place in a stepwise fashion as a function of the mole fraction of surfactants in bulk. A typical example is the behavior of cationic dodecyltrimethylammonium bromide (DTAB) and amphoteric (dodecyldimethylammonio)propanesulfonate (DDAPS) on mica.[10] In contrast, in the latter case, one would expect that the mixed adlayer shows a quite different structure in comparison to the individual structural pattern of the surfactant adlayers.[11] Thus, our aim in this investigation is to understand the relationship between the association behavior of surfactants in bulk solution and the formation of mixed adlayers on a specific surface at the nanoscopic scale.

In the present work, we measured the interaction forces between α-alumina surfaces with the adsorption of anionic/nonionic surfactant mixtures by colloidal probe atomic force microscopy. This technique has been utilized to study the adsorption of single surfactants,[12−14] linear polymers,[15−19] or dendritic macromolecules.[14] In addition, a few recent publications describe the coadsorption behavior of ionic surfactants and linear polymers.[20−25] However, interaction forces between adlayers consisting of two surfactants have not been reported systematically despite their scientific importance. Surfactants used in this study were anionic SDS and nonionic hexaoxyethylenedodecyl ether ($C_{12}E_6$). Two experiments were carried out for force measurements: (i) simultaneous addition of both the surfactants with variable concentrations and (ii) sequential addition of the surfactants for elucidating the complex phenomena that occur at the interface. Furthermore, the association behavior of the two surfactants in bulk solution was also assessed through surface tensiometry.

Experimental Section

Materials. α-Alumina spheres with an average diameter of 20 μm were obtained from Showa Denko Co. Single-crystal sapphire windows, used as flat plates for AFM measurements, were kindly supplied by Saint-Gobain Crystals and Detectors Co. The root-mean-square roughness of the plates, measured over an area of 1 μm^2, was 0.25 nm. The α-alumina spheres and the sapphire windows were ultrasonicated for 10 min in concentrated H_2SO_4. The materials were then rinsed with water, kept overnight in an aqueous 0.1 mol dm^{-3} KOH solution, and finally rinsed thoroughly with water.

SDS obtained from Nacalai Tesque Inc. was recrystallized three times from ethanol. $C_{12}E_6$ (Nikko Chemicals Co.) was used as received. All other reagents were of analytical grade. Water was deionized using a Milli-Q Plus system.

Methods. The static surface tension of aqueous surfactant solutions was measured using a Krüss K100 tensiometer by the Wilhelmy plate technique. All solutions contained 1 mmol dm^{-3} 1:1 background electrolytes (NaCl + HCl), and the pH was adjusted to 3.5.

Surface force measurements were carried out using a TMX2100 atomic force microscope (TMmicroscopes Inc.). A detailed description of the force measurement technique is given elsewhere.[26] Data were collected using commercial silicon nitride cantilevers (Digital Instrument Inc.) with a spring constant of 0.58 N m^{-1}, modified by attaching an α-alumina sphere, as described by Ducker et al.[27]

Prior to force measurements, the colloidal probe attached to the cantilever was immersed overnight in 0.1 mol dm^{-3} KOH, followed by a thorough deionized water rinse. Sapphire windows were washed following the same procedure. After washing, the probe and the plate were both set at their fixed positions on the AFM and immediately immersed in the sample solution. The system was allowed to equilibrate for 30 min prior to the initial injection and force runs. In sequential adsorption, force acquisition was resumed only after a lapse of 120−150 min following the replacement of the preadsorbate solution with the postadsorbate solution. The temperature was maintained constant at 25 °C using a thermomodule controller (MT862-04C12, Netsu Denshi Co., Ltd.).

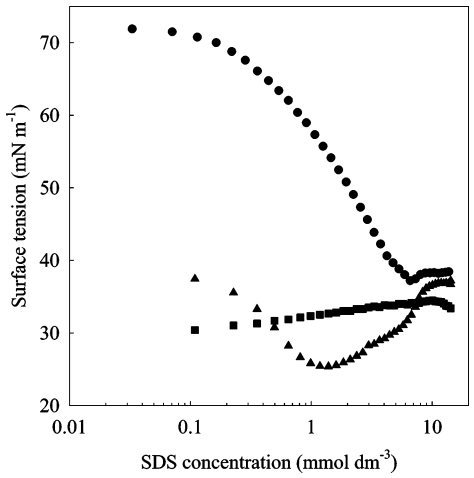

Figure 1. Surface tension of aqueous solutions of SDS and $C_{12}E_6$. Initial concentrations of $C_{12}E_6$ are set to 0 (●), 0.02 (▲), and 0.2 mmol dm^{-3} (■), respectively. Each solution contains 1 mmol dm^{-3} 1:1 background electrolytes (NaCl + HCl) and the pH values are adjusted to 3.5.

Results and Discussion

Figure 1 shows the surface tension data for aqueous SDS−$C_{12}E_6$ solutions as a function of SDS concentrations. Feed concentrations of $C_{12}E_6$ are 0.02 and 0.2 mmol dm^{-3}, and all the solutions contain 1 mmol dm^{-3} 1:1 background electrolytes (NaCl + HCl) at a pH of 3.5. The critical micelle concentration (cmc) of $C_{12}E_6$ is 0.068 mmol dm^{-3} under this experimental condition, which is in good agreement with the literature value.[28] The surface tension of SDS alone (circular symbols in Figure 1) decreases monotonically with the concentration and reaches a plateau at about 6 mmol dm^{-3} (cmc). The surface tension curve is divided into three parts for the mixtures of SDS and $C_{12}E_6$ (0.02 mmol dm^{-3}): (i) C_{SDS} < 1 mmol dm^{-3}, the surface tension decreases with increasing SDS concentration in a manner similar to that of SDS alone; (ii) 1 mmol dm^{-3} < C_{SDS} < 8 mmol dm^{-3}, the surface tension increases progressively through further adsorption of SDS at the air/solution interface; (iii) 8 mmol dm^{-3} < C_{SDS}, the surface tension remains relatively constant. This result indicates that the mixed micelles start to form at and above 1 mmol dm^{-3} of SDS concentrations and the driving force for the micellization is believed to be the surfactant's tail-to-tail association in the bulk phase. In addition, the electrostatic attractive force is also relevant because the oxyethylene chain of $C_{12}E_6$ might be proton-donated at this pH. Akasu et al.[29] have measured the surface tension of aqueous mixtures of SDS and pentaoxyethylenedodecyl ether ($C_{12}E_5$) at neutral pH and found an appearance of a flat portion instead of the observed deep minimum. This difference corroborates that the attractive interaction between SDS and nonionic oxyethylene surfactants can be influenced by the solution pH and the energetically more favorable micellization takes place from the acidic solution. On the other hand, for the mixtures of SDS and 0.2 mmol dm^{-3} $C_{12}E_6$ the surface tension increases gradually with increasing SDS concentration, suggesting that the mixed micelles exist in the whole range of SDS concentrations investigated.

TABLE 1: Surface Potential and Decay Length Estimated from Force Curves in Aqueous SDS−$C_{12}E_6$ Solution[a]

	SDS alone			SDS−$C_{12}E_6$ (0.02 mmol dm^{-3})			SDS−$C_{12}E_6$ (0.2 mol dm^{-3})		
C_{SDS} (mmol dm^{-3})	Ψ_0 (mV)	κ^{-1} (nm)	κ_c^{-1} (nm)	Ψ_0 (mV)	κ^{-1} (nm)	κ_c^{-1} (nm)	Ψ_0 (mV)	κ^{-1} (nm)	κ_c^{-1} (nm)
0	13	9.7	9.6	14	9.8	9.6	15	9.8	9.6
0.3	attractive		8.4	attractive		8.4	steric		8.4
3	−9.1	5.1	4.8	−13	6.6	4.8−6.8	−14	6.5	4.8−9.6
12	−22	4.1	2.7−3.6	−20	3.8	2.7−6.8	−20	3.6	2.7−6.8

[a] Key: C_{SDS} is the initial concentration of SDS, Ψ_0 is the surface potential, κ^{-1} is the decay length estimated from force curves, and κ_c^{-1} is the calculated Debye length; $\kappa_c^{-1} = 0.304/C_{eff}^{1/2}$ (C_{eff} is the effective electrolyte concentration).

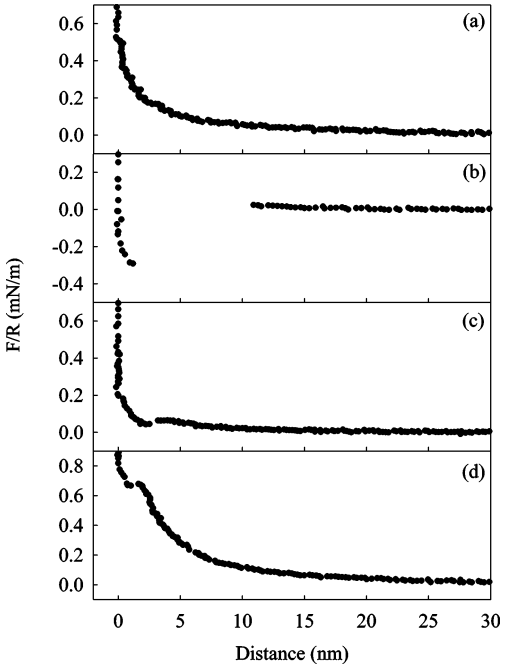

Figure 2. Normalized forces between α-alumina surfaces in aqueous SDS solutions containing 1 mmol dm^{-3} 1:1 background electrolytes (NaCl + HCl) at pH 3.5. Initial SDS concentrations are (a) 0, (b) 0.3, (c) 3, and (d) 12 mmol dm^{-3}, respectively.

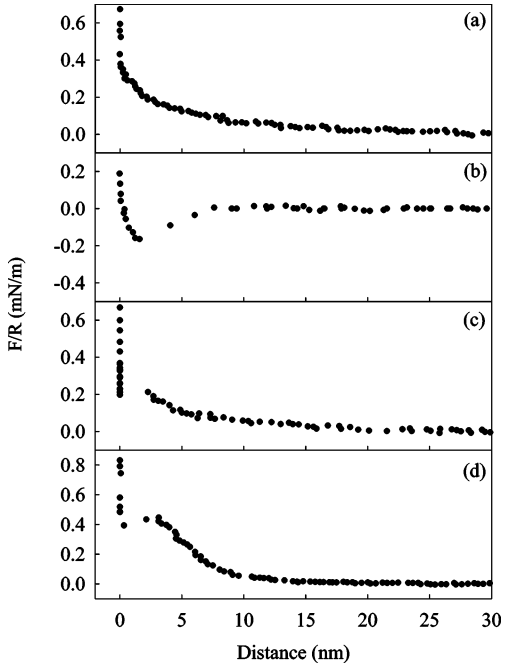

Figure 3. Normalized forces between α-alumina surfaces in aqueous SDS and 0.02 mmol dm^{-3} $C_{12}E_6$. Each solution contains 1 mmol dm^{-3} 1:1 background electrolytes (NaCl + HCl) at pH 3.5. Initial SDS concentrations are (a) 0, (b) 0.3, (c) 3, and (d) 12 mmol dm^{-3}, respectively.

Interaction forces between α-alumina surfaces with the adsorption of SDS are shown in Figure 2. The initial SDS concentrations are fixed at 0, 0.3 (0.05 cmc), 3 (0.5 cmc), and 12 mmol dm^{-3} (2 cmc). All sample solutions contain 1 mmol dm^{-3} background electrolytes (NaCl + HCl) and the pH value of each solution is 3.5. As was pointed out in our previous paper,[24] the strength of interaction forces depends on the SDS concentration: (i) the electric double layer repulsion between positively charged α-alumina surfaces can be observed in the absence of SDS (Figure 2a), (ii) the hydrophobic attraction is detected at the surface-neutralizing SDS concentration (Figure 2b), and (iii) the repulsive force originating from the electric double layer interaction once again appears due to the formation of SDS adlayers (Figure 2c,d). The estimated surface potentials based on the force measurements and empirical decay lengths are summarized in Table 1. The analysis of force curves does not always provide information about the sign of the surface potentials. However, we addressed in our previous paper[25] that, by the addition of SDS to α-alumina suspensions, the positive ζ potential decreases to zero and then a charge reversal occurs with increasing SDS concentration. Because this result correlated well with the stability test of α-alumina suspensions and the resultant force data, the negative sign is relevant above the SDS hemimicellar concentration region.

Figures 3 and 4 provide interaction forces between α-alumina surfaces for the coaddition of SDS and $C_{12}E_6$. The initial $C_{12}E_6$ concentrations are 0.02 mmol dm^{-3} (Figure 3) and 0.2 mmol dm^{-3} (Figure 4) whereas SDS concentrations are set to 0, 0.3 (0.05 cmc), 3 (0.5 cmc), and 12 mmol dm^{-3} (2 cmc), respectively. All solutions contain 1 mmol dm^{-3} 1:1 background electrolytes (NaCl + HCl), and the pH values are adjusted to 3.5. In the absence of SDS (Figures 3a and 4a) the force data match the results obtained for the surfactants free solution. This corroborates that the nonionic $C_{12}E_6$ causes negligible effects on the interaction between the bare surfaces, meaning a very low adsorption of $C_{12}E_6$ alone at the interface. It is accepted[30,31] that for adsorption to occur on polar surfaces the nonionic surfactants must have a moiety that has adsorption force sufficient to overcome the strong interaction between water molecules and the oxyethylene groups. Accordingly, it is conceivable that in the case of the strong hydrated α-alumina surface, $C_{12}E_6$ cannot displace enough water molecules to enable adsorption. Furthermore, this low adsorption may be due to electrostatic repulsion between the positively charged α-alumina and the proton-donated oxyethylene headgroup at pH 3.5.

In aqueous 0.3 mmol dm^{-3} SDS and 0.02 mmol dm^{-3} $C_{12}E_6$ solution (Figure 3b) a weak attraction is detected at a separation of 10 nm. This attractive force is significantly smaller than that in the 0.3 mmol dm^{-3} SDS single solution (Figure 2b). This suggests that the adsorbed $C_{12}E_6$ molecules, whose oxyethylene segment protrudes into the bulk, partially shield the SDS hemimicellar layer from the aqueous phase. A similar implication has been reported in the flocculation studies on kaolinite:

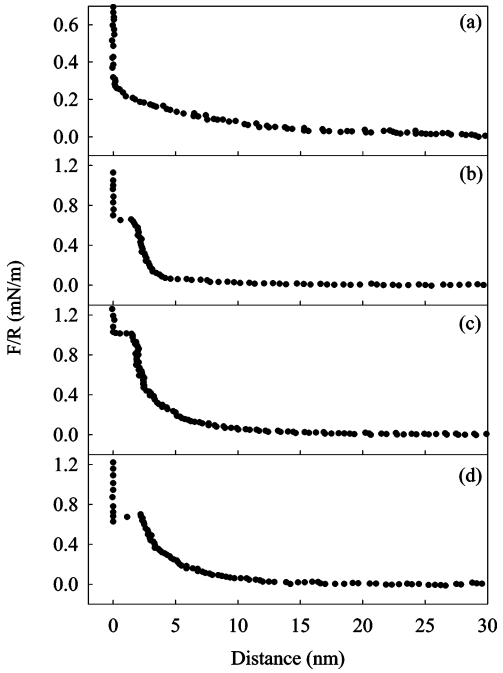

Figure 4. Normalized forces between α-alumina surfaces in aqueous SDS and 0.2 mmol dm^{-3} $C_{12}E_6$. Each solution contains 1 mmol dm^{-3} 1:1 background electrolytes (NaCl + HCl) at pH 3.5. Initial SDS concentrations are (a) 0, (b) 0.3, (c) 3, and (d) 12 mmol dm^{-3}, respectively.

for the mixture of SDS and an oxyethylene surfactant, the dispersion stability of kaolinite suspensions increases when the adsorption of the nonionic surfactant increases.[4] In contrast to that when SDS concentration is increased to 3 mmol dm^{-3}, a repulsive interaction is observed at a separation of 15 nm (Figure 3c). The empirical decay length of this repulsion is 6.6 nm, which is within the range of the theoretical Debye lengths (4.8−6.8 nm). Thus, the origin of this repulsion is the electric double layer interaction between the SDS−$C_{12}E_6$ coadsorbed layers on the two surfaces. Here, it is noted that the Debye length is calculated through the nonlinear Poisson−Boltzmann equation with a constant charge limit. A detailed description of the force analysis is given elsewhere.[32] In addition, our calculations assume that the nonionic surfactant in the bulk phase does not influence the electrolyte concentration. In this case the lower length (4.8 nm) corresponds to the value that SDS behaves as a simple 1:1 electrolyte capable of dissociating fully, where the total electrolytes concentration is 4 mmol dm^{-3} (3 mmol dm^{-3} SDS + 1 mmol dm^{-3} background electrolytes). On the other hand, the upper length (6.8 nm) is obtained from the sum of the background electrolytes concentration (1 mmol dm^{-3}) and the SDS monomer concentration determined by the surface tensiometry (1 mmol dm^{-3}; it is worth recalling that the mixed micelles start to form above 1 mmol dm^{-3} of SDS concentration).

In Figure 3c one can see that the two surfaces jump into adhesive contact. This jump-in corresponds to the fusion of adsorbed surfactant layers under a limiting compression, accompanying the squeeze-out of the surface layer in admicelles.[13,14] As described in our previous papers,[7,8] in the range of low SDS concentrations the incorporation of nonionic surfactants into SDS adlayers reduces the electrostatic repulsion between ionic headgroups and hence promotes the SDS adsorption on α-alumina. Also in the present case, the fact that the surface potential in the mixed micellar solution is higher than that in the absence of $C_{12}E_6$ suggests that a more favorable adsorption of SDS occurs in the presence of $C_{12}E_6$ and 3 mmol dm^{-3} SDS.

The behavior presented in Figure 4b,c is of interest in the mixed admicelle formation on α-alumina because a more compact arrangement of mixed adlayers would take place at around 1:1 molar ratio of the individual surfactants.[4] In fact, interaction forces are dramatically altered by the further addition of $C_{12}E_6$. In aqueous 0.3 mmol dm^{-3} SDS and 0.2 mmol dm^{-3} $C_{12}E_6$ solution (Figure 4b) a very weak repulsion is detected at a separation of 10 nm and reaches a hard wall at 4 nm. The normalized force values increase steeply with decreasing surface separation and then the surfaces come into adhesive contact. The appearance of this extra repulsive force implies the steric hindrance occurs due to the overlapping adlayers formed on the surfaces. Similar force profiles are obtained from the measurement in the 3 mmol dm^{-3} SDS and 0.2 mmol dm^{-3} $C_{12}E_6$ solution (Figure 4c), but the range of repulsion extends to 15 nm. The decay length of this long range repulsion is 6.5 nm, suggesting that the observed repulsion in the range 5−15 nm originates from the electric double layer interaction. This result means that the observed repulsion is composed of electrostatic and steric forces, contributing to the fact that a closely packed adlayer forms at the interface through the oxyethylene surfactant adsorption.

A similar repulsion caused by the steric hindrance between nonionic $C_{12}E_5$ adlayers on silica has been presented in previous literature,[12] where the repulsion is detected in the range of $C_{12}E_5$ concentrations above the cmc and the layered structure of the surfactant seems to be intercalated bilayers with a large headgroup area. Furthermore, force measurements between a silicon nitride AFM cantilever and a muscovite mica sheet have demonstrated that $C_{12}E_5$ molecules form loosely bound bilayers or continuous bilayers on the two surfaces.[33] However, these descriptions of the bilayer formation could not be applied to our results because the interactions are quite different in our case; namely, nonionic surfactants hardly adsorb on α-alumina by itself. From this point of view, a comparison with adsorption of nonionic surfactants onto hydrophobic surfaces would be more in order because the surfactant adsorbs to the hydrophobic anchor parts in our case: for the adsorption of oxyethylene surfactants the AFM imaging technique has shown the formation of a laterally homogeneous adlayer on the hydrophobically modified silica surface.[34] One would expect from these findings that $C_{12}E_6$ adsorbs via the tail-to-tail association between the two surfactants and then forms a closely packed adlayer on α-alumina.

As the SDS concentration increases to 12 mmol dm^{-3} the force curves (Figures 3d and 4d) resemble that observed in the case of only SDS solution (Figure 2d). In fact, the surface potentials determined by best curve fitting are in agreement with each other (Table 1). Accordingly, it is obvious that the force curve for the simultaneous addition of 12 mmol dm^{-3} SDS and $C_{12}E_6$ is predominantly determined by the interaction of α-alumina with SDS at longer separation distances. On the other hand, the discrepancy between these curves arises near the constant compliance. This is probably due to the difference in compactness between the adsorbed surfactant layers. However, detailed claims could not be obtained from our experiments.

It is useful to consider the relationship between the adlayer formation and solution properties. Previous literature[32] has shown that the decay length determined experimentally from the force results can be influenced by the effective electrolyte concentration in bulk solution. In addition, as found in our

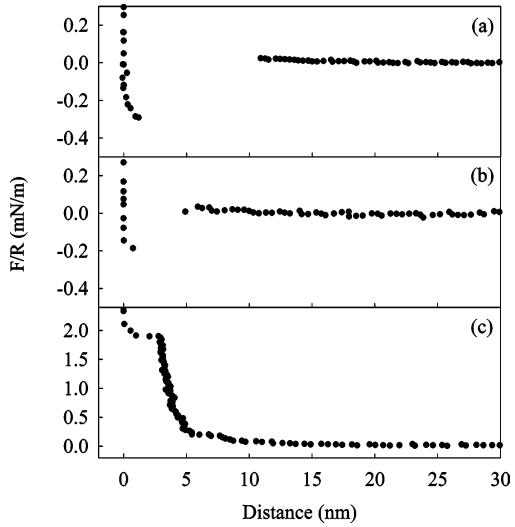

Figure 5. Sequential addition of $C_{12}E_6$ to the preadsorbed SDS at pH 3.5: (a) SDS alone; (b) sequential addition of 0.3 mmol dm^{-3} SDS and 0.02 mmol dm^{-3} $C_{12}E_6$; (c) sequential addition of 0.3 mmol dm^{-3} SDS and 0.2 mmol dm^{-3} $C_{12}E_6$. Each solution contains 1 mmol dm^{-3} 1:1 background electrolytes (NaCl + HCl).

previous study,[24] the decay length is also affected by the existence of single surfactant micelles due to the counterion binding to the micelle surfaces. As a result, the reduction of the effective electrolyte concentration leads to an increase in the decay length. In the present work, one can see that the decay length values for the coaddition of 3 mmol dm^{-3} SDS and $C_{12}E_6$ are considerably larger than that for the addition of SDS alone (Table 1). It is worth recalling that the mixed micelle formation occurs above 1 mmol dm^{-3} of SDS concentration even in the presence of 0.02 mmol dm^{-3} $C_{12}E_6$ (Figure 1). Thus, the decrease in the SDS monomer concentration due to the mixed micellization causes an increase in the decay length value. On the other hand, in the presence of 12 mmol dm^{-3} SDS the decay length value decreases with increasing $C_{12}E_6$ concentration. This result indicates that the formation of the mixed micelles causes the reduction of the effective electrolyte concentration in a manner similar to the single SDS micellization. It has been reported[35] that for the mixture of anionic/nonionic surfactants the ionization degree of mixed micelles increases as the proportion of the nonionic surfactant increases. This is due to a decline in the electrostatic repulsion between ionic headgroups through the incorporation of nonionic surfactants into the anionic micelles. Therefore, the decrease in the decay length can be attributed to the high dissociation of the mixed micelles compared with the SDS regular micelles.

Figure 5 presents the effect of the sequential addition of $C_{12}E_6$ from (b) 0.02 and (c) 0.2 mmol dm^{-3} to a system containing preadsorbed SDS at 0.3 mmol dm^{-3} (a). The initial SDS concentrations are fixed at 0.3 mmol dm^{-3} to prevent desorption of preadsorbed SDS. All solutions are adjusted to a pH of 3.5. As described above, an attractive force is detected due to surface neutralization and hydrophobic interactions in the 0.3 mmol dm^{-3} SDS single solution. The resultant force curve for the sequential addition of 0.02 mmol dm^{-3} (Figure 5b) is purely attractive at a separation distance of 6 nm, which is significantly shorter than that for the SDS alone (Figure 5a). This is because the adsorbed $C_{12}E_6$ molecules leaving the oxyethylene segments protruding into the solution phase reduce the hydrophobic interaction. In contrast, as the concentration of $C_{12}E_6$ increases to 0.2 mmol dm^{-3} a strong repulsion caused by the steric hindrance is observed near 5 nm. One can see that the force curve for the sequential adsorption is analogous to that for the simultaneous adsorption (Figure 4b); however, the magnitude of the repulsion in the former case is much larger than that of the latter. The explanation lies in their different structures of adlayers: the addition of $C_{12}E_6$ to α-alumina pretreated hydrophobically with SDS leads to the formation of a $C_{12}E_6$ outer layer and hence the steric stabilizing force appears instead of the electrostatic interaction. We believe that the system reaches the kinetically stable state because the bilayer formation consisting of the SDS inner layer and the $C_{12}E_6$ outer layer takes place even in the presence of mixed micelles in solution. As a result, a sequential addition of nonionic surfactants to α-alumina particles with anionic surfactant hemimicelles causes the enhancement of dispersion stability, even though the corresponding ζ potentials are almost zero.[9]

Conclusion

Coadsorption behaviors from anionic/nonionic surfactant mixtures on α-alumina have been presented through surface force measurements. It can be pointed out that the synergism for the simultaneous adsorption of surfactants mainly arises from the hydrophobic interaction of the surfactants at the solid/solution interface as well as in the bulk solution. The closed packed adlayers are formed in the mixed solutions of 0.3 or 3 mmol dm^{-3} SDS and 0.2 mmol dm^{-3} $C_{12}E_6$ because the oxyethylene headgroup of $C_{12}E_6$ reduces the electrostatic repulsion between SDS anionic headgroups in admicelles. In addition, a force wall appears upon the sequential addition of 0.2 mmol dm^{-3} $C_{12}E_6$ to α-alumina pretreated with 0.3 mmol dm^{-3} SDS in a manner similar to the case of the simultaneous addition. These results corroborate the finding that SDS monomers adsorb onto the positively charged α-alumina, overcoming the mixed micellization in bulk solution. On the other hand, in the presence of 0.02 mmol dm^{-3} $C_{12}E_6$ the adlayer−adlayer interaction consisting of the two surfactants is predominantly governed by the adsorption of SDS at the interface. Thus, colloidal probe atomic force microscopy becomes a useful technique for correlating surface forces and coadsorption phenomena on a nanoscopic scale.

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