Interactions between Nonpolar Surfaces Coated with the Nonionic Surfactant Hexaoxyethylene Dodecyl Ether $\text{C}_{12}\text{E}_6$ and the Origin of Surface Charges at the Air/Water Interface

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The interactions between nonpolar surfaces coated with the nonionic surfactant hexaoxyethylene dodecyl ether, $\text{C}_{12}\text{E}_6$, were investigated using two techniques and three different types of surfaces. As nonpolar surfaces, the air/water interface, silanated negatively charged glass, and thiolated uncharged gold surfaces were chosen. The interactions between the air/water interfaces were measured with a thin film pressure balance in terms of disjoining pressure as a function of film thickness. The interactions between the solid/liquid interfaces were determined using a bimorph surface force apparatus. The influence of the nature of the surface on the interaction forces was investigated at surfactant concentrations below and above the cmc. The adsorption of the nonionic surfactant on the uncharged thiolated surface does not, as expected, lead to any buildup of a surface charge. On the other hand, adsorption of $\text{C}_{12}\text{E}_6$ on the charged silanated glass and the charged air/water interface results in a lowering of the surface charge density. The reduction of the surface charge density on the silanated glass surfaces is rationalized by changes in the dielectric permittivity around the charged silanol groups. The reason for the surface charge observed at the air/water interface as well as its decrease with increasing surfactant concentration is discussed and a new mechanism for generation of OH− ions at this particular interface is proposed.

1. Introduction

To understand interaction forces generated between surfactant coated surfaces, several topics have to be addressed. First, the adsorption of the surfactant at the surface is of outstanding importance as each adsorbed molecule alters the properties of the surface and thus the respective interaction forces. Second, the nature of the surface has to be considered because it influences the interaction forces. This is due to both forces generated between the surfaces themselves (e.g., double-layer forces generated by charged surface groups) and the influence of the surface on the structure of the adsorption layers. For example, the adsorption of surfactants at hydrophilic and hydrophobic surfaces, respectively, results in adsorption layers of completely different structure, which, in turn, generates different interaction forces. Additionally, the nature of the surfactant is crucial for the nature and the magnitude of the interaction forces. These forces are mainly due to repulsive short-range confinement, repulsive long-range electrostatic, and attractive short-range van der Waals interactions.1–2 In addition, the presence of an attractive long-range force, often referred to as the "hydrophobic interaction", is observed between nonpolar surfaces in aqueous solutions.3,4 For the investigation of these forces, different surface force techniques can be employed. The choice of the appropriate technique depends on the type of surface dealt with. For solid/liquid interfaces, the atomic force microscope (AFM), the surface force apparatus (SFA), and the MASIF-technique5–7 and for both air/water and oil/water interfaces the thin film pressure balance (TFPB) (refs 8 and 9 and references therein) have proved to be suitable techniques. In this study, we used the MASIF and TFPB techniques to probe the interactions between surfactant coated surfaces across the corresponding aqueous surfactant solution.

The present study is concerned with the interactions between nonpolar surfaces coated with the nonionic surfactant hexaoxyethylene dodecyl ether, $\text{C}_{12}\text{E}_6$. One aim is to clarify the influence of the nature of surface on the interaction forces. Our approach is to directly measure the interaction forces between three different kinds of nonpolar surfaces, namely, air/water, silanated glass, and thiolated gold surfaces, with respect to the surfactant concentration. As nonpolar surfaces, the air/water interface, silanated negatively charged glass, and thiolated uncharged gold surfaces were chosen. The interactions between the air/water interfaces were measured with a thin film pressure balance in terms of disjoining pressure as a function of film thickness. The interactions between the solid/liquid interfaces were determined using a bimorph surface force apparatus. The influence of the nature of the surface on the interaction forces was investigated at surfactant concentrations below and above the cmc. The adsorption of the nonionic surfactant on the uncharged thiolated surface does not, as expected, lead to any buildup of a surface charge. On the other hand, adsorption of $\text{C}_{12}\text{E}_6$ on the charged silanated glass and the charged air/water interface results in a lowering of the surface charge density. The reduction of the surface charge density on the silanated glass surfaces is rationalized by changes in the dielectric permittivity around the charged silanol groups. The reason for the surface charge observed at the air/water interface as well as its decrease with increasing surfactant concentration is discussed and a new mechanism for generation of OH− ions at this particular interface is proposed.


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thiolated gold surfaces. Investigations with solid surfaces are of particular interest since we are able to modify the surface. For example, the silanization of glass surfaces leads to a nonpolar surface that is slightly charged, whereas the thiolated gold surfaces are completely uncharged. We took advantage of the possibility to adjust the surface charge of the (nonpolar) solid surfaces to compare the interaction forces with those existing between air/water interfaces. For that purpose, the interaction forces across aqueous solutions of C12E6 were investigated at three different surfactant concentrations (two below and one above the cmc). These measurements shed further light on the origin of the surface charges at the air/water interface.

Figure 1. Surface tension \( \sigma \) as a function of the C12E6 concentration \( c \) at \( T = 22 \pm 1 \, ^\circ C \). The error is about the size of the symbols. The line represents the best Langmuir–Szyzkowski fit (eq 3), leading to a cmc of 7.3 \( 10^{-5} \, M \).

Supporting Information

2. Experimental Section

2.1 Solution Preparation. The nonionic surfactant hexa- oxyethylene dodecyl ether (C12E6) was purchased from Fluka (Germany) and used as received. The purity was checked by measuring the surface tension as a function of the concentration \( c \) at 22 \, ^\circ C \) by the DuNoüy ring method using a Kruüss K10ST tensiometer (see Figure 1). Sodium chloride was obtained from Merck (Germany) and roasted at 500 \, ^\circ C \) before use to remove organic impurities. Water used for the preparation of all solutions was purified with a Millipore Milli-Q Plus 185 water purification system. For the MASIF measurements, the water was deaerated using a water jet pump for 2 h immediately before use which is essential to minimize the formation of air bubbles in the vicinity of highly hydrophobic solid surfaces. All glassware (except the film holder of the TFPB) was cleaned with deconex from Borer Chemie (as a replacement for chromic sulfuric acid) and rinsed thoroughly with Milli-Q water before use. The film holders used in the TFPB (see below) were boiled two times in the autoclave for six times in water, and at least 0.5 L of hot water was sucked through each disk. Three different surfactant solutions at concentrations of \( 10^{-5} \, M \), \( 5 \, 10^{-5} \, M \), and \( 10^{-4} \, M \), respectively, were prepared in \( 10^{-4} \, M \) NaCl background electrolyte concentration. It was made sure that the pH of the investigated solutions was equal to the usual pH of 5.5 \pm 0.3, which is due to the dissolution of \( CO_2 \) present in air.

2.2 Thin Film Pressure Balance. The disjoining pressure \( \Pi \) was measured as a function of the film thickness \( h \) with the TFPB technique. Experimental details have been published only recently.15 In brief, with a TFPB free-standing horizontal liquid films are investigated. These films are formed in a film holder that consists of a glass tube, which is connected to a porous glass frit so that the solution is free to move. A hole of 1-2 \, mm diameter, in which the film is formed, is drilled in the frit. The film holder is sealed in a cell in which the gas pressure can be adjusted in a controlled manner. \( \Pi(h) \)-curves are generated by interferometrically measuring the equivalent film thickness \( h_{eq} \) after applying a fixed pressure in the cell. The true film thickness \( h \) is obtained according to the three-layer model16 where the film is considered as a solution layer of refractive index \( n_s \) plus two adsorbed surfactant layers of different refractive index, that is,

\[
h = h_{eq} - 2h_{head} \left( \frac{n_{tail}^2 - n_s^2}{n_s^2 - 1} \right) - 2h_{head} \left( \frac{n_{head}^2 - n_s^2}{n_s^2 - 1} \right) \quad (1)
\]

where \( h_{eq} \) and \( h_{head} \) are the thicknesses of the hydrocarbon tail and the headgroup, respectively, \( n_{head} \) and \( n_{head} \) are the corresponding refractive indices, \( n_{tail} = 1.3 \, nm \) and \( n_{head} = 1.2 \, nm \) were derived from neutron reflectivity measurements.17,18 \( n_{head} \) was approximated to that of 1,4-dioxane \( (1.4216) \) and \( n_{head} \) to that corresponding to hexaoxyethylene \( n_{head} = 1.4650 \). The error margins in the reported \( \Pi(h) \)-curves are \( \pm 30 \, Pa \) which is a result of uncertainty in the measurement of hydrostatic pressure in the glass tube of the film holder and \( \pm 5\% \) for the film thickness. The latter results from the uncertainty in the determination of the equilibrium intensity from which the film thickness is calculated.15

2.3 Surfaces Used for MASIF Measurements. Supporting Glass Surfaces. The hydrophobic surfaces on which the adsorption of C12E6 was studied were obtained by silanization and thiolization, respectively, of hydrophilic glass surfaces. The supporting glass surfaces were prepared from rods of borosilicate glass (Pyrex) with 2-mm diameter that were cut into pieces of 25-30 mm in length, rinsed with ethanol, and melted at one end with a butane-oxygen burner. The treatment was conducted until a surface of spherical shape with a radius of approximately 2 mm was obtained. It has been shown that flame-polished glass surfaces are smooth enough to enable accurate measurements of surface forces down to molecular separations.19

Silanated Glass. Flame-polished glass surfaces were hydrophobized through a vapor-phase silanization with (3,3-dimethyl) dimethyloxypropyltrimethoxysilane (Petrich). For the silanization procedure, the flame-polished glass surfaces were used immediately after they had been prepared and then secured on a holder. This holder was placed in a silanization glass chamber containing a few milliliters of silane solution. The chamber was blown with nitrogen and tightly closed for at least 18 h to allow a complete (vapor) deposition. After silanization, the surfaces were thoroughly rinsed with ethanol and then blown dry with nitrogen for 2 h immediately before use.
a gentle stream of nitrogen. This vapor-phase silanization procedure was chosen because it was shown to give good quality surfaces with satisfactory reproducibility.20-22

Thiolated Glass. In this study, thin gold films were prepared on the above-mentioned glass surfaces to provide substrates suitable for self-assembly of alkanethiolate monolayers. The gold substrates onto which the thiol is adsorbed are polycrystalline, with typical peak-to-valley roughness of about 1.5 nm and rms roughness in the 0.15–0.20 nm range (as measured over 1 × 1 mm²).19 The roughness of the gold layer is low enough to make them suitable for direct measurements of surface forces. Since the wetting of silica by gold is poor (which might lead to patchy layers of this metal), we promoted the adhesion between gold and the glass substrate during evaporation by adding an “adhesion” layer of titanium. This was accomplished by vapor deposition of a thin (1 nm) layer, preceding the gold evaporation step rarely exceeded 7 × 10⁻⁵ N m⁻¹. All forces were normalized with the harmonic radius of the spheres (R = 2R₂(R₁ + R₃)). The radii of the spherical surfaces were measured using a micrometer screw after each experiment. The resulting normalized force F/R is related to the interaction free energy per unit area G between parallel plates of unit area through the Derjaguin approximation25 F/R = −G. F/R versus distance D curves are presented without any averaging, if not otherwise stated. The point of zero separation corresponds to the location of the “hard wall”, as selected in the analysis. In some cases, hydrodynamic effects are considered as explained below.

The procedures for assembling the measuring chamber and preparing the solutions were carried out inside a laminar flow cabinet. At the beginning of each set of experiments, the interaction profiles were determined in air as well as in Milli-Q water to ensure that the system (i.e., the surfaces and the measuring chamber) was free of contamination. Concentrated stock surfactant solution was then introduced into the water-filled measuring chamber until the desired concentration was attained. The surfactant concentration in the chamber was varied consecutively by replacing a fraction of the total volume in the chamber with a surfactant solution of appropriate composition. Thus, in these measurements, each new solution comes in contact with a surface prequillibrated with the previous solution.

2.5 DLVO Calculations. We compared the measured [1(h) and F/R(D) curves with interaction curves calculated within the framework of DLVO theory, by considering the repulsive double-layer forces and attractive van der Waals forces. To obtain the electrostatic component, the nonlinear Poisson–Boltzmann equation was solved. The calculations were done with the algorithm of Chan et al.,28 using either constant charge or constant potential boundary conditions and the theoretical Debye length λ. The van der Waals component of the interaction should ideally be calculated using (at least) a five-layer model (e.g., air–surfactant–water–surfactant–solid or surfactant–solid–water–surfactant–solid). However, for our purpose it is sufficient to use a simple nonretarded Hamaker constant (A) which for the foam films was set to A = 3.7 × 10⁻²⁰ J, and for the silanated glass surfaces A = 1.10 × 10⁻²⁰ J. The Hamaker constant for the thiolated gold surfaces was estimated from the measurements leading to a value of A = 2.5 × 10⁻²⁰ J (see discussion in connection with Figure 10).

The parameters extracted from these calculations are the apparent surface potential φapp from which the corresponding surface charge density q can be calculated using the Grahame equation.21 The parameters extracted from the DLVO calculations are summarized in Table 1.

Hydrodynamic Effects. For the MASIF measurements, we considered the effect of hydrodynamic forces in the interaction profile. Since this can become an important issue, especially in cases where the electrostatic repulsion is minimal. The hydrodynamic interactions result in an extra repulsion when the surfaces approach each other and in an extra attraction when they are separated. To eliminate this effect, we used low enough driving rates, both on approach and on separation. In some cases (which will be indicated), the hydrodynamic forces were considered by subtracting the calculated hydrodynamic force Fh from the measured total interaction force F. The hydrodynamic forces between two approaching surfaces are given by

\[ F_h = \frac{3\eta R}{2D} \frac{d(D - 2D)}{dt} \]  

where \( \eta \) is the viscosity of the solution (assumed to be identical to water).
known using the Gibbs equation (eq 4):

\[ \sigma = \sigma_0 - RT \Gamma_\infty \ln \left(1 + \frac{C}{a} \right) \]  

(3)

where \( \sigma_0 = 72.2 \text{ mN m}^{-1} \) is the surface tension of pure water, \( \Gamma_\infty \) is the maximum surface concentration of surfactant, and \( a \) represents the concentration at which 50% of \( \Gamma_\infty \) has been reached. The best fitting parameters are \( \Gamma_\infty = 3.18 \times 10^{-6} \text{ mol m}^{-2} \) and \( a = 4.67 \times 10^{-7} \text{ M} \). With this set of data, the surface excess \( \Gamma \) of C12E6 was calculated using the Gibbs equation (eq 4):

\[ \Gamma = -\frac{C}{RT \partial \sigma / \partial C} \]  

(4)

Knowing \( \Gamma \), one can calculate the area per molecule at the interface according to \( A = (N_A \Gamma)^{-1} \). In Figure 2, the surface excess \( \Gamma \) is plotted as a function of the surfactant concentration \( C \). In addition, the dependence of the surface pressure \( \pi = \sigma_0 - \sigma \) on the area per molecule \( A \) is shown in the inset.

As expected, the surface excess increases with increasing bulk concentration and comes closest to the saturation value at concentrations around 1/2 cmc (Figure 2). The area per molecule at the surface extracted from this plateau equals 0.52 nm², which is in perfect agreement with results derived from neutron reflectivity measurements. A consequence of the increasing surface coverage is an increasing surface pressure \( \pi \), which can be considered as a measure for the interactions in the surface layer. The higher the surface pressure the stronger the repulsive forces between surfactant molecules, which results in a strong resistance against further adsorption of surfactant molecules at the surface. At concentrations around the cmc, a sharp increase in the surface pressure is observed (see Figure 2, inset), demonstrating strong repulsive short-range interactions in densely packed monolayers.

#### 3.2 Interactions between Air/Water Interfaces

To investigate the interactions between the surfactant-loaden air/water interfaces, the disjoining pressure \( \Pi \) has been measured as a function of the film thickness \( h \). More precisely, the \( \Pi(h) \) curves have been examined for the effect of the C12E6 concentration at a fixed electrolyte concentration of 10⁻⁴ M NaCl. Film thicknesses range from more than 80 nm to less than 5 nm, depending on the composition of the sample and the applied pressure, which ranges from 200 to 9000 Pa. The model DLVO calculations using constant charge boundary conditions and the theoretical DLVO calculations are summarized in Table 1.

In Figure 3, the \( \Pi(h) \) curves for three different C12E6 concentrations are shown, two of which were below and one above the cmc (cmc = 7.3 × 10⁻⁵ M).

Two different kinds of films were observed: thick common black films (CBF), stabilized by electrostatic repulsion, and thin Newton black films (NBF), stabilized by short-range repulsion. The thicknesses of the CBFs decrease monotonically as the disjoining pressure increases. While the slope \( \partial \log \Pi / \partial h \) is independent of the surfactant concentration, a significant shift of the curves toward lower disjoining pressures is observed by increasing the surfactant concentration from 10⁻⁵ M to 5 × 10⁻⁵ M. Apart from this shift, a CBF → NBF transition takes place for the film stabilized by the 5 × 10⁻⁵ M solution, an observation which was not made for the lower concentration. The increasing tendency to form an NBF with increasing surfactant concentration is demonstrated by the fact that for the highest surfactant concentration investigated (10⁻⁴ M), the transition pressure is so low that under the experimental conditions only an NBF was seen.

#### Common Black Film (CBF)

The present study provides additional supporting evidence for the general

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**Table 1. Surfactant Concentration c and Corresponding Surface Concentration \( \Gamma \) at the Air/Water Interface**

<table>
<thead>
<tr>
<th>c(C₁₂Em) M</th>
<th>( \Gamma ) 10⁻⁶ mol m⁻²</th>
<th>( \psi_{0,1} ) mV</th>
<th>( q_{b,1} ) mC m⁻²</th>
<th>area/charge₁ nm²</th>
<th>( \psi_{0,2} ) mV</th>
<th>( q_{b,2} ) mC m⁻²</th>
<th>area/charge₂ nm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>10⁻⁵</td>
<td>3.0</td>
<td>60</td>
<td>1.70</td>
<td>95</td>
<td>100</td>
<td>4.03</td>
<td>40</td>
</tr>
<tr>
<td>5 × 10⁻⁵</td>
<td>3.2</td>
<td>24</td>
<td>0.57</td>
<td>280</td>
<td>30</td>
<td>0.72</td>
<td>220</td>
</tr>
<tr>
<td>10⁻⁴</td>
<td>3.2</td>
<td>b</td>
<td>b</td>
<td>b</td>
<td>b</td>
<td>b</td>
<td>b</td>
</tr>
</tbody>
</table>

\( \psi_{0} \) is the surface tension isotherm according to eq 3. Surface potentials \( \psi_{0} \), surface charges \( q_{b} \), and area/charge are from DLVO calculations for the foam films (index 1) and the silanated surfaces (index 2) as described in section 2.5. The calculated Debye length is \( \kappa^{-1} = 30 \text{ nm} \) at the given electrolyte concentration of 10⁻⁴ M NaCl. No measurable electrostatic repulsion under the given experimental conditions.

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The stabilizing mechanism is clearly seen in Figure 3 for repulsion and higher monolayer cohesion. This change of stabilization of a NBF because of increased short-range forces across the 5 × 10⁻³ M C₁₂E₅ solution is less convincing. Further work to clarify this is under way. The fit between calculated and measured forces across the 5 × 10⁻³ M C₁₂E₅ solution is less convincing. However, noting the difficulty of measuring weak forces accurately, we propose that indeed also in this case the force observed at long distances is a double-layer force. Newton Black Films (NBF). As has already been mentioned, the tendency of the NBF to form increases with increasing surfactant concentration, that is, the magnitude of the applied pressure needed to induce the CBF—NBF transition decreases. In fact, for the highest surfactant concentration (10⁻⁴ M), an equilibrium CBF was not formed and only an NBF was seen under the given experimental conditions. The NBFs are very thin with an aqueous core of 1–2 nm and the surfactant film consists of two surfactant monolayers with only small amounts of water separating the headgroups (mainly hydration water).

The thickness of the NBF decreases from around 7 to 5 nm with increasing pressure, which indicates large flexible headgroups that can change their conformation or packing in the NBF. This is consistent with previous surface force data using C₁₂E₅ adsorbed to nonpolar solid surfaces. It is important to realize that for a stable NBF to form not only short-range repulsive interactions normal to the surfaces are required but also a densely packed adsorption layer (see chapter 3.4.3 and 3.4.4 in ref 8c). The packing density increases with increasing alkyl chain length. In the alkyl polyglycolethers C_iE_j, for example, at least 10 carbon atoms in the nonpolar tail are needed to stabilize an NBF. Thus, stable C₁₂E₅ NBFs are not surprising. However, looking at Figure 3, a CBF—NBF transition can clearly be seen for c < 5 × 10⁻⁵ M at pressures around 1000 Pa, whereas for the lowest concentration only a CBF was observed. To check if this is because the surface coverage at c < 10⁻⁵ M is too low to stabilize an NBF, we performed a series of measurements at an electrolyte concentration of 10⁻¹ M to screen electrostatic forces (the results are not shown). In the absence of electrostatic forces, only NBFs were formed at all three concentrations (10⁻⁵, 5 × 10⁻⁵, and 10⁻⁴ M). However, the NBF formed at the lowest concentration ruptured immediately after its formation, verifying the assumption that the surface coverage is too low to stabilize an NBF (see ref 41 for further details with regard to the rupture of NBFs). Thus, at concentrations far below the cmc only CBF films stabilized by repulsive electrostatic forces are formed. However, at concentrations close to the cmc the surface coverage is high enough to stabilize NBFs, whereas the lower surface charge reduces the stability of the CBF. Above the cmc, the charge at the surface is too small to support a CBF under the given experimental conditions and only the NBF is sufficiently stable to be seen.

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**Figure 3.** Disjoining pressure Π as a function of the film thickness h for three concentrations of C₁₂E₅ in 10⁻⁴ M NaCl solution, namely, 1 × 10⁻⁵ M (C), 5 × 10⁻⁵ M (○), and 1 × 10⁻⁴ M (□). The two lower concentrations are below, the highest is above the cmc (7.3 × 10⁻⁵ M). The solid lines are calculated according to the DLVO theory assuming interactions at constant charge. The upper one corresponds to a surface potential of Φ₀ = 60 mV and the lower one to Φ₀ = 24 mV.

| (34) In a Scheludko–Exerowa cell (Scheludko, A.; Exerowa, D. Comm. Department Chem. Bulg. Acad. Sci. 1959, 7, 123), where the pressure does not exceed values around 40 Pa, CBFs of the nonionic surfactant n-dodecyl-β-D-maltoside (β-C₇G₇) and the shorter homologue tetraoxyethylene decyl ether (C₁₀E₄). Several suggestions to explain these findings have been reported in the literature, for example, changes in the adsorption density with film thickness or effects due to an inhomogeneous charge distribution. To this we would like to add the suggestion that fluctuations within the film may result in an extra repulsion when the adsorption density is high (in contrast to film rupture that occurs because of these fluctuations at low surfactant adsorption densities). Further work to clarify this is under way. The fit between calculated and measured forces across the 5 × 10⁻³ M C₁₂E₅ solution is less convincing. However, noting the difficulty of measuring weak forces accurately, we propose that indeed also in this case the force observed at long distances is a double-layer force. Newton Black Films (NBF). As has already been mentioned, the tendency of the NBF to form increases with increasing surfactant concentration, that is, the magnitude of the applied pressure needed to induce the CBF—NBF transition decreases. In fact, for the highest surfactant concentration (10⁻⁴ M), an equilibrium CBF was not formed and only an NBF was seen under the given experimental conditions. The NBFs are very thin with an aqueous core of 1–2 nm and the surfactant film consists of two surfactant monolayers with only small amounts of water separating the headgroups (mainly hydration water). The thickness of the NBF decreases from around 7 to 5 nm with increasing pressure, which indicates large flexible headgroups that can change their conformation or packing in the NBF. This is consistent with previous surface force data using C₁₂E₅ adsorbed to nonpolar solid surfaces. It is important to realize that for a stable NBF to form not only short-range repulsive interactions normal to the surfaces are required but also a densely packed adsorption layer (see chapter 3.4.3 and 3.4.4 in ref 8c). The packing density increases with increasing alkyl chain length. In the alkyl polyglycolethers C_iE_j, for example, at least 10 carbon atoms in the nonpolar tail are needed to stabilize an NBF. Thus, stable C₁₂E₅ NBFs are not surprising. However, looking at Figure 3, a CBF—NBF transition can clearly be seen for c < 5 × 10⁻⁵ M at pressures around 1000 Pa, whereas for the lowest concentration only a CBF was observed. To check if this is because the surface coverage at c < 10⁻⁵ M is too low to stabilize an NBF, we performed a series of measurements at an electrolyte concentration of 10⁻¹ M to screen electrostatic forces (the results are not shown). In the absence of electrostatic forces, only NBFs were formed at all three concentrations (10⁻⁵, 5 × 10⁻⁵, and 10⁻⁴ M). However, the NBF formed at the lowest concentration ruptured immediately after its formation, verifying the assumption that the surface coverage is too low to stabilize an NBF (see ref 41 for further details with regard to the rupture of NBFs). Thus, at concentrations far below the cmc only CBF films stabilized by repulsive electrostatic forces are formed. However, at concentrations close to the cmc the surface coverage is high enough to stabilize NBFs, whereas the lower surface charge reduces the stability of the CBF. Above the cmc, the charge at the surface is too small to support a CBF under the given experimental conditions and only the NBF is sufficiently stable to be seen. |
Figure 4. Force F normalized by the harmonic radius R as a function of surface separation D. The forces were measured between silanated glass surfaces across aqueous solutions containing $10^{-4}$ M NaCl in the absence (■) and in the presence of $1 \times 10^{-5}$ M C$_{12}$E$_6$ (□). The lines are calculated according to the DLVO theory for a surface potential of $\Psi_0 = 100$ mV assuming interactions at constant charge (full line) and at constant potential (dashed line), respectively.

Another interesting result of the present study is the fact that the NBF is formed via a stepwise CBF–NBF transition. In an extensive disjoining pressure study, it has been shown that the CBF–NBF transition is discrete for C$_{10}$E$_4$ and continuous for C$_{12}$E$_6$ because in the latter case the film is stabilized by short-range repulsive forces before attractive van der Waals forces dominate the interactions. In other words, it is between E$_4$ and E$_6$ that a crossover from a discrete to a continuous NBF formation is expected. With the results obtained in the present work, we can define the range for this crossover more precisely, namely, between E$_4$ and E$_6$.

3.3 Interactions between Solid/Liquid Interfaces.

The interactions between nonpolar surfaces across aqueous solutions in the presence of C$_{12}$E$_6$ were determined with the MASIF surface force apparatus, using two different substrate surfaces. The first substrate chosen was silanated glass that, despite being hydrophobic, carries a significant net negative charge. This charge comes from the dissociation of unreacted silanol groups. The other substrate chosen was a gold surface modified by hexadecanethiol. This surface is uncharged in aqueous solutions.

Silanated Surfaces. The forces acting between a pair of silanated glass surfaces immersed in a $10^{-4}$ M aqueous NaCl solution are shown in Figure 4 (filled squares).

The long-range forces are dominated by an electrostatic double-layer force having the expected decay length (30 nm) for the given ionic strength. The apparent surface potential according to DLVO calculations is 100 mV, corresponding to an area per charge of 40 nm$^2$. The force measured at separations below ~20 nm is less repulsive than predicted by theory assuming either interactions at constant charge (full line) or at constant potential (dashed line). In fact, this is not surprising but in line with a multitude of measurements demonstrating the presence of a long-range attractive force, significantly larger than the van der Waals force, between nonpolar surfaces in aqueous solutions. For robust hydrophobic surfaces, that is, surfaces that are intrinsically nonpolar or where a strongly anchored film generates the surface hydrophobicity, there is growing evidence that this force is due to capillary evaporation and bridging because of microbubbles adsorbed to the surfaces. Both silanated glass and thiolated gold surfaces fall within this category. For such robust hydrophobic surfaces, it has been clearly demonstrated that a hydrophobic force due to capillary evaporation and bridging is present even when the (advancing) contact angle is above 90°. This has been proved by modifying the wetting properties both by tuning the chemical composition of the surface layer and by varying the solvent composition. Thus, it is natural that a reduction in contact angle because of surfactant adsorption also reduces the long-range attraction. Our observation is consistent with other studies that have demonstrated the reduction and subsequent removal of the "hydrophobic interaction" because of surfactant adsorption.

Addition of C$_{12}$E$_6$ to a concentration of $10^{-5}$ M has a rather limited effect on the long-range interactions (see Figure 4, unfilled squares). The double-layer force is virtually unchanged. However, the strong non-DLVO attraction is significantly reduced, which is mirrored in a clear inward shift of the force maximum. However, the experimental maximum is still located at a larger separation than predicted by DLVO theory. The decrease in the attractive force component indicates that the hydrophobicity of the surface has decreased as a result of the adsorption of some surfactant. However, the adhesion force remains too strong to be measurable.

The forces between the silanated surfaces change significantly when the C$_{12}$E$_6$ concentration is increased to $10^{-4}$ M. In Figure 5a, the force curves measured 30 min and 18 h after increasing the surfactant concentration are shown. For comparison, the equilibrium force curve for the 10$^{-5}$ M solution is shown once again. In addition, the time development of the interaction forces acting across the 5 $10^{-5}$ M solution is shown in Figure 5b on a linear scale.

It is seen in Figure 5a that the forces measured after 30 min are well described by the DLVO theory down to a separation of 3 nm. The double-layer force falls between that predicted for constant surface charge and constant surface potential, respectively, as is expected for charge-regulating surfaces.

The magnitude of the double-layer force is the same after 30 and 50 min (see Figure 5b), respectively, and it is similar to the double-layer force measured at $10^{-5}$ M (see Figure 5a). (We attribute the difference in force observed between the two surfactant concentrations at distances above 40 nm to experimental uncertainties, and this difference does not persist when

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an area per charge of 220 nm². Clearly, adsorption of the but the magnitude of the apparent double-layer potential decay length of the double-layer force remains the same, the force barrier is present at small separations which is associated with the removal of surfactants from the contact zone. (The solution was not stirred since stirring affects the force measurements. Thus, the adsorption occurs significantly slower than, e.g., in an ellipsometric measurement.) It is seen in Figure 5b that at 30 min a small force barrier is present at small separations which is overcame at a compressive force \( F/R \) of 1.8 mN m⁻¹. The extra repulsion is due to the work needed to remove the adsorbed surfactants from between the approaching surfaces. This force barrier increases from 1.8 mN m⁻¹ after 30 min to 2.5 mN m⁻¹ after 50 min. In the equilibrium state, that is, after 18 h, the surfactant layer can no longer be displaced even under a high compressive force \( F/R \approx 30-40 \) mN m⁻¹. In other words, it is no longer possible to reach contact between the hydrophobic surfaces. The adhesion is the third parameter that is changed as a function of time. With increasing time the adhesion is reduced, for example, from 17 mN m⁻¹ after 30 min to 6 mN m⁻¹ after 50 min (data are not shown). After equilibrium adsorption had been established, only a weak adhesion of 0.7 mN m⁻¹ was observed on retraction (see Figure 6).

However, unlike the situation at lower surfactant concentrations and prior to equilibrium, the attractive minimum is located outside the position where the surfactant layers come into direct contact. This reflects the short-range interaction between the surfactant layers. We note a weak trend of a slightly larger adhesion force between the surfactant layers with increasing compressive load prior to separation.

As can be seen in Figure 7, a further increase of the C₁₂E₆ concentration to \( 10^{-4} \) M has only a small effect on the interactions. For the sake of clarity, the same F/R data are shown on a logarithmic scale (Figure 7a) as well as on a linear scale (Figure 7b).

The differences in the short-range interactions across the \( 10^{-4} \) M and the \( 5 \times 10^{-5} \) M surfactant solution, respectively, are within the scattering of the experimental data (see Figure 7b). However, the magnitude of the double-layer force is further reduced at the higher surfactant concentration (see Figure 7a). This result indicates a small increase in the adsorption density when the C₁₂E₆ concentration is increased from \( 5 \times 10^{-5} \) M to \( 10^{-4} \) M. Looking at Table 1, one sees that the situation at the air/water interface is similar—the surface concentration \( \Gamma \) increases slightly from \( 5 \times 10^{-5} \) M to \( 10^{-4} \) M. Moreover, as was discussed in connection with Figure 3, it is in this concentration range where NBFs are formed, whereas the stability of the CBF decreases significantly. We will come back to this comparison in the discussion.

Thiolated Surfaces. There are some differences between the thiolated gold surfaces and the silanated glass surfaces...
that should be kept in mind. First, the hexadecanethiol layer is in a crystalline state whereas the silane layer is disordered. Second, the hydrophobicity of the thiolated layer is larger than that of the silanated glass surfaces. The advancing and receding contact angles of the thiolated gold surface are 110° and 104°, respectively, whereas the corresponding values for the silanated surfaces are 100° and 70°. Third, the silanated surfaces are, as shown in Figure 4, strongly charged whereas the thiolated gold surfaces are uncharged, which will be demonstrated in the following.

It can be seen in Figure 8 that no long-range repulsive forces act between the hexadecanethiol coated gold surfaces but that the forces are attractive below separations of about 30 nm. This attraction has a similar origin as the one seen for the silanated glass surfaces and thus is due to capillary evaporation and bridging bubbles.\(^{19,44}\) Like the silanated surfaces, the adhesion force between the thiolated surfaces is too high to be measurable \((F/R > 80 \text{ mN m}^{-1})\). Addition of \(\text{C}_{12}\text{E}_6\) to a concentration of \(10^{-5} \text{ M}\) removes the long-range attraction completely. Instead, a weak repulsive force dominates at large separations. This force is of hydrodynamic origin (see Figure 10 below). After a short equilibration time of 1 h, a weak repulsive barrier can just be distinguished at separations below 5 nm. Similar to the results presented in Figure 5, the magnitude of this barrier increases with time and reaches about 0.8 mN m\(^{-1}\) after 24 h. The force barrier can clearly be attributed to the removal of surfactants from between the two surfaces approaching each other. The adhesion force decreases from about 16 mN m\(^{-1}\) after 1 h to 2–3 mN m\(^{-1}\) after 24 h.

It is demonstrated in Figure 9 that the magnitude of the force barrier present at 4–5 nm separation shows some variability, typically between 0.7 and 1.2 mN m\(^{-1}\). We see no clear effect of the driving rate of approach, but the magnitude of the barrier is on average somewhat larger when the surfaces are left undisturbed for longer times (more than 2 min). However, this correlation is also weak. The most plausible explanation for the variation in the magnitude of the force barrier is that the adsorbed layers are not homogeneous. Inspecting the structure of the thin evaporated gold surface with AFM one sees that it is polycrystalline, despite being very smooth.
The attractive interaction is well described by a van der Waals force with an effective Hamaker constant of $2.5 \times 10^{-20}$ J for two spheres of hydrocarbon interacting in water\(^1\). The high value of $A$ (compared to $1 \times 10^{-20}$ J for two spheres of hydrocarbon interacting in water\(^1\)) is due to the presence of the gold layer.\(^{48}\) In fact, the deduced effective Hamaker constant is lower than that calculated by Ederth for SAM-coated gold surfaces\(^{48}\) but identical to that found by Persson and Kumpulainen for thiolated gold surfaces coated with n-decyl-$\beta$-D-glucoside,\(^{49}\) which can be rationalized by the presence of the adsorbed surfactant layer. The value of the Hamaker constant for a multilayer system depends on the separation. However, this refinement of the calculation was not considered in the present case. Also, the subtraction of the hydrodynamic force from the measured force is a subtle exercise since the magnitude of the hydrodynamic force is relatively large compared to the other force contributions. This means that measured force curves prior to calculations of the local speed and the hydrodynamic force must be smoothened (by a running average) to remove noise. Nevertheless, artifacts may occur. One such artifact is illustrated in Figure 10 by the local maximum observed in the static forces for one of the curves at a separation of 7–8 nm. It is due to the small noise seen in the corresponding measured curve of the total force.

The influence of the surfactant concentration on the interaction forces between the surfactant-coated thiolated surfaces is shown in Figure 11. An increase of the C\(_{12}\)E\(_6\) concentration to 5 $\times$ 10\(^{-5}\) M and 10\(^{-4}\) M, respectively, has no significant effect on the interaction forces. The most striking change which is observed with increasing surfactant concentration is the fact that it is no longer possible to remove the adsorbed layer from between the surfaces even under high forces ($F/R \approx 30$ mN m\(^{-1}\)). In other words, the barrier for squeezing out the adsorbed layers increases enormously. It is important to realize that the results obtained for the two higher concentrations are very similar to those measured between silanated glass surfaces at the same surfactant concentrations (see Figure 7). However, there is one noticeable difference. The force minimum observed on separation for the silanated surfaces was around $0.5–0.7$ mN m\(^{-1}\), whereas a significantly smaller value, namely, $0.2–0.1$ mN m\(^{-1}\), was observed when the thiolated gold surfaces were separated.

4. Discussion

4.1 Attractive Forces between Adsorbed Nonionic Surfactant Layers. In most cases, a weak attractive force with a typical magnitude of 0.1–1 mN m\(^{-1}\) is observed between nonpolar surfaces coated with a monolayer of nonionic surfactant. The magnitude of this force depends on the nature of the nonpolar part.\(^{50},53\) It is determined by a subtle interplay of van der Waals forces, hydration forces, and confinement forces (e.g., protrusion forces).\(^{32}\) The attraction is larger when the adsorbed chains are in a frozen state as compared to in a fluid state,\(^{32}\) which is due to a reduction in the repulsive confinement forces. For surfactants in the fluid state, the attractive force is generally larger when the polar group consists of sugar units as compared to ethylene oxide units.\(^{23}\) One effect contributing to this is the larger refractive index of sugar compared to ethylene oxide, which increases the van der Waals force. In the particular case of ethylene oxide-based surfactants, it has been noted in one study\(^{37}\) that an increase in temperature results in a larger attraction, an
effect related to the temperature dependence of the hydration interaction. Similar temperature-dependent hydration forces have also been observed for amine oxide and phosphate oxide surfactants. Work with respect to a more detailed analysis of the attractive forces between layers of sugar-based and ethylene oxide-based surfactants is under way.

In the study at hand, we have demonstrated that the adhesion force between nonpolar surfaces coated with the same surfactant, C_{12}E_{6}, is significantly different at the two substrates used, silanated glass and thiolated gold. The adhesion is significantly larger when silanated surfaces are used. This cannot be due to the difference in van der Waals attraction since this force contribution is larger for the thiolated gold substrate (the Hamaker constants for thiolated and silanated surfaces are about 2.5 × 10^{-20} J and 1.0 × 10^{-20} J, respectively). Furthermore, it cannot be due to any difference in hydration since the same temperature was used in both experiments. Instead, it appears that differences in surface roughness and the presence of less hydrophobic patches on the silanated surface is the cause of the observed adhesion effect.

4.2 Comparison of Adsorption of Nonionic Surfactants to Different Nonpolar Surfaces. The driving force for adsorption of nonionic surfactants to nonpolar surfaces is the removal of contacts between the surface and water as well as between the nonpolar surfactant tail and water. This leads to an adsorption with the surfactant tail directed toward the hydrophobic surface and the polar group directed toward the aqueous solution. The extent of the adsorption at different nonpolar surfaces will, however, vary depending on the exact nature of the surface. In general, one would expect that the adsorption would be larger on a more nonpolar surface. Hence, in the present case one would expect that the adsorption is largest on the air/water interface, followed by that at the thiolated gold, and lowest adsorption is expected on the silanated surface. In fact, Kjellin et al. have demonstrated that the adsorbed amount of C_{12}E_{5} is larger at the air/water interface than at silanated glass surfaces. Moreover, we found a repulsive force barrier (i.e., the work needed to squeeze out the surfactant layers on both surfaces) (see Figure 8), whereas no such barrier was observed for the thiolated surfaces (see Figure 4). Indeed, this observation indicates that the adsorption is, as was assumed above, larger at the thiolated surfaces, at least at low surfactant concentrations. For the two higher surfactant concentrations investigated, no such conclusion can be drawn. It was impossible to squeeze out the adsorbed surfactant layer for both the silanated (see Figure 7) and the thiolated (see Figure 11) surfaces indicating densely packed surfactant layers on both surfaces.

4.3 The Effect of Surfactant Adsorption on the Surface Charge. As can be seen in Figure 8, the thiolated gold surface is unchanged at 10^{-4} M NaCl. This conclusion is based on the absence of any repulsive double-layer force. (We thus reject the possibility of the presence of a double-layer force exactly balanced by the presence of an attractive force with equal magnitude but opposite sign at all large surface separations.) The double-layer force is absent also when surfactant is added to concentrations of 10^{-5} M, 5 × 10^{-5} M, and 10^{-4} M (see Figure 11). Thus, the adsorption of C_{12}E_{6} does not result in any charging of the surface. Hence, we conclude that, in keeping with what is expected, the surfactant is nonionic and no charged and surface-active impurities are adsorbing to the surface. We can also draw the conclusion that neither sodium nor chloride ions associate with the surfactant layer (even though in principle we could have equal amounts of sodium and chloride associated with the surfactant, which would lead to a net zero charge). The situation for the silanated surface is different since it is inherently charged because of dissociation of silanol groups. In this case, the initial adsorption does not affect the charging of the surface. However, once a significant surfactant adsorption is reached, the surface charge is decreased to a very low value. We attribute this to the decrease in the dielectric constant of the environment close to the silanol groups, which reduces the dissociation degree and thus the charge density. Let us now turn to the situation at the air/water interface, where we have, similar to the silanated surface, a net charge. Like the silanated glass surfaces, the charge of the air/water interface is reduced when the surfactant concentration is increased. However, as the origin of the surface charge has not been established yet, the interpretation of the experimental observation is not self-evident. What is clear, however, is the fact that the decrease cannot be put down to the shielding of fixed charges anchored at the surface. We will discuss this point in the following section.

4.4 The Origin of the Charge at the Air/Water Interface. From the results presented for the solid/liquid interfaces coated with C_{12}E_{6}, we draw the conclusion that the charge at the air/water interface does not arise as a result of the presence of the surfactant or any charged surface-active impurities in the sample. This last point is difficult to prove, but it is hard to envisage an impurity with a very high affinity for the air/water interface but no affinity for the nonpolar solid/liquid interface. A possibility is, of course, a charged and surface-active impurity that is present in the frit material used in TFPB measurements. Such an impurity could give rise to the charges observed. It could then be solubilized into micelles once the cmc is reached, which would explain the decrease in charge with surfactant concentration. However, this explanation seems to be far-fetched considering the large number of results showing the same trend as reported here. This includes other TFPB measurements as well as measurements of the electrophoretic mobility of gas bubbles in aqueous solutions (references and a detailed discussion are given in ref 9).

At present, the widely accepted explanation for the origin of the charges in thin liquid films stabilized by nonionic surfactants is the presence of excess OH⁻ ions at the air/water interface. However, lately it has been shown by simulations that halide ions accumulate at the air/water interface, the amount of which increases with increasing size and polarizability of the anion. Thus, fluoride is depleted at the interface, whereas bromide and iodide concentrations are enhanced. In light of this, it is obvious that OH⁻ ions are not the only anions the concentration of which is enhanced at the air/water interface. Experimentally, it has been observed repeatedly that the surface charge is constant at low surfactant

(55) In both cases, silanated and thiolated surfaces, there is some scatter in the measured adsorption data. In the thiolated surfaces, the addition of the titanium and gold layers increases slightly the surface roughness of the glass substrate (the total thickness of both metal layers is approximately 10 nm). Generally, this roughness causes some spread in the pull off forces because the effective surface area upon contact varies over the surfaces.

concentrations and decreases significantly above a certain concentration, which is proposed to be connected with the total number of ethylene oxide units.\textsuperscript{13a} The results obtained so far are reviewed in ref 9. On the basis of these observations, Exerowa\textsuperscript{10} postulated a specific adsorption of OH\textsuperscript{−}, which was further developed by Marinova et al.\textsuperscript{56} and Karraker and Radke\textsuperscript{14} only recently. They argue that the decrease of the surface charge contrasts sharply with the adsorption of the surfactant, which changes significantly at low concentrations and stays close to constant already far below the cmc. Thus, they exclude a typical competitive adsorption between surfactant and hydroxide and propose a two-site mechanism for the adsorption.\textsuperscript{14} If such sites do exist, they should be considered as highly dynamic and being related to the specific water structure as discussed above. The magnitude of the observed surface charge density, even though it is small, is too large to be explained by negative adsorption of cations only.

Nowadays, vibrational sum frequency generation spectroscopy allows us to obtain a fairly good idea of the structure of the air/water interface.\textsuperscript{15–16} Generally speaking, the water spectrum of the surface includes features from water molecules in three different environments. There is a sharp peak due to the presence of free OH\textsuperscript{−} groups pointing out toward the air side (non-hydrogen bonding). It is the OH\textsuperscript{−}-groups from water rather than OH groups pointing out toward the air side (non-hydrogen bonding) that are seen. The other features are two broad peaks assigned to weakly hydrogen bonding water (“liquidlike”) and strongly hydrogen bonding water (“icelike”).\textsuperscript{58–60} When considering the charging behavior of the air/water interface, one must be aware that we are considering a highly dynamic interface. In fact, it has been estimated that even close to 0 °C, about 3 million monolayers of water per second are exchanged between the liquid and the vapor phase.\textsuperscript{52} It is conceivable that it is in this dynamic exchange that some OH\textsuperscript{−} ions are created. For instance, consider just two of the possible reactions that can occur at the surface:

\begin{align}
H_2O_{bi} + H_2O_{vi} &\leftrightarrow OH_{vi}^- + H_3O_{bi}^+ \\
H_2O_{bi} + H_2O_{vi} &\leftrightarrow H_3O_{bi}^+ + OH_{vi}^- 
\end{align}

(5)

where subscript “bi” stands for molecules at the interface on the bulk water side and subscript “vi” for molecules at the interface on the bulk vapor side. Provided that the equilibrium constants for these reactions (K\textsubscript{1} for the first and K\textsubscript{2} for the second reaction) were slightly different, a surface having a net charge would be created.

This is one possible mechanism that we suggest should be considered and further elaborated on. First, it avoids the difficulty of ion adsorption at specific sites. Second, it explains how surfactant adsorption can reduce the charge at the surface, namely, by switching off the reactions postulated in eq 5 when no free air/water interface is left. (However, just as with the ion adsorption model this suggestion retains the difficulty of explaining why the charge density of the air/water interface is not proportional to the area of the free air/water interface.) The pH-dependence would in this scheme be related to changes in the dynamic water structure at the interface that would influence the equilibrium constants for the exchange reactions. The model also has obvious disadvantages. It cannot explain the charging of an oil/water interface.

Further, just as with the specific ion adsorption mechanism, it does not couple the OH\textsuperscript{−} concentration at the surface to the bulk water ion concentration through a simple Boltzmann distribution in the mean electrostatic potential on the waterside. It seems that further understanding can only be obtained by increasing the knowledge of the dynamic water structure at the air/water interface and how this influences ion adsorption and surface reactions.

5. Conclusions

In this study, we considered the interactions between nonpolar surfaces coated with the nonionic surfactant hexaoxyethylene dodecyl ether, C\textsubscript{12}E\textsubscript{6}. As nonpolar surfaces, the air/water interface, silanated glass, and thiolated gold surfaces were chosen. To investigate the influence of the surface on the interaction forces, three different surfactant concentrations were investigated, namely, 10\textsuperscript{−5} M, 5 \times 10\textsuperscript{−5} M, and 10\textsuperscript{−4} M (cmc = 7.3 \times 10\textsuperscript{−5} M). The most important results with respect to the comparison of different surfaces are presented in Figure 3 (air/water interface), Figure 7 (silanated glass surface), and Figure 11 (thiolated gold surface) and can be summarized as follows.

(a) Air/Water Interface. Although the mechanism for generating the surface charge is not fully clarified, the available data strongly points to that the pure air/water interface is negatively charged because of the presence of anions, particularly OH\textsuperscript{−} ions. Ion adsorption driven by the specific dynamic water structure at the interface or surface reactions are two possible mechanisms for the origin of the surface charge. The adsorption of the nonionic surfactant C\textsubscript{12}E\textsubscript{6} leads to a decrease of the surface charge. This decrease eventually results in a transition from an electrostatically stabilized common black film (CBF) to a Newton black film (NBF) that is stabilized by short-range repulsive forces (see Figure 3). In the NBF, a surfactant bilayer consisting of two densely packed monolayers creates a “force barrier”—similar to the force barriers observed in MASIF measurements—that prevents the film from rupturing. Sufficient monolayer cohesion is also a necessary criterion for the formation of a long-lived NBF.

(b) Silanated Glass Surface. The silanated surface is negatively charged because of the dissociation of unreacted silanol groups. Although the origin of the charge is different, the interaction forces between two silanated surfaces and two air/water interfaces, respectively, are very similar (see Figure 3 and Figure 7). At the lowest surfactant concentration investigated (10\textsuperscript{−5} M), the interaction forces are dominated by long-range electrostatic double-layer forces. In analogy to the air/water interface, further adsorption of C\textsubscript{12}E\textsubscript{6} reduces the net charge until long-range forces are negligible. Comparing Figure 3 and Figure 7, one sees that the NBF formation (Figure 3) corresponds to the appearance of a force barrier between the silanated surfaces (Figure 7). This barrier is a measure for the force that is needed to remove surfactant from between the two surfaces. As this barrier is located at a distance corresponding to the thickness of a surfactant bilayer, the analogy to the NBF formation is obvious. Thus, in both cases, the adsorption of C\textsubscript{12}E\textsubscript{6} leads to a decrease of the surface charge resulting in the formation of a densely packed bilayer which generates a force barrier. A “removal” of this bilayer results in film rupturing in foam films, whereas in solid/liquid interfaces it leads to a direct contact of the solid surfaces.

(c) Thiolated Gold Surface. The situation is different for the interaction forces between thiolated gold surfaces

\begin{align}
(60) \text{Richmond, G. L. Chem. Rev. 2002, 102, 2693.}
\end{align}
coated with C₁₂E₆ (see Figure 11). The substrate, that is, the thiolated surface, is uncharged and double-layer forces do not play a role either in the absence or in the presence of C₁₂E₆. However, the adsorption of C₁₂E₆ significantly influences the short-range interaction forces. In contrast to the silanated surfaces (see Figure 7), it is already at the lowest surfactant concentration of 10⁻⁵ M that a force barrier is observed. An increase in the surfactant concentration leads to an increase of this barrier. Comparing Figure 7 and Figure 11 one clearly observes the similarities between the C₁₂E₆ coated silanated and thiolated surfaces at surfactant concentrations of 5 × 10⁻⁵ M and 10⁻⁴ M, respectively. Electrostatic forces are absent (or at least negligible) and the force barrier is so high that the surfactant cannot be removed from between the surfaces under the given experimental conditions.

To conclude, one can say that the nature of the surface at which the surfactant adsorption takes place mainly influences the interaction forces at low surface coverages. Once a densely packed surfactant layer is formed, it is the surfactant itself that determines the interaction forces. It would be of interest to quantify the surface concentration Γ, the area per molecule A, and the conformation of C₁₂E₆ at the different surfaces. Detailed studies for the air/water interface have already been made. Lu et al. used neutron reflection to study the surface excess as well as the monolayer thickness and its roughness. Moreover, from sum-frequency spectroscopy and ellipsometry, the conformation of the C₁₂E₆ molecules at the air/water interface is known. What is still missing, however, are the corresponding data for the adsorption of C₁₂E₆ at silanated glass and thiolated gold surfaces, respectively. The fact that we did not observe any double-layer forces between the C₁₂E₆ coated thiolated surfaces proves that the surfactant did not contain any charged surface-active impurities. This is an important result with respect to the discussion of the charge origin at the air/water interface.

Work in progress deals with interaction forces between nonpolar surfaces coated with the nonionic sugar surfactant n-dodecyl-β-D-maltoside (β-C₁₂G₂). These measurements are aimed to clarify the influence of the headgroup on the interaction forces.

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