Comparison between Interaction Forces at Air/Liquid and Solid/Liquid Interfaces in the Presence of Non-Ionic Surfactants

Interactions in thin liquid foam films and between solid/liquid surfaces coated with the non-ionic surfactant hexaoxyethylene dodecylether (C$_{12}$E$_{8}$) were investigated with a TFPB (thin film pressure balance) and the MASIF (Measurement and Analysis of Surface Interaction Forces) technique, respectively. For foam films the formation of common black films (CBF) and Newton black films (NBF) was observed depending on the surfactant concentration and the applied pressure. With increasing surfactant concentration and increasing pressure the CBF is destabilized, whereas a stabilization of the NBF is observed. In addition, MASIF measurements with two different hydrophobic surfaces were made. In one case silanated glass surfaces and in the other case thiolated gold surfaces were used. Differences and similarities of the interactions between these two surfaces are shown and discussed. Furthermore, the results of the MASIF measurements are compared with the ones of the thin film pressure balance measurements and the influence of the surfactant concentration on the interactions is discussed.

Key words: Thin liquid films, TFPB, MASIF, stability of colloids, disjoining pressure, surface forces, surface charges, non ionic surfactants


Stichwörter: Thin liquid films, TFPB, MASIF, Kolloidstabilität, Spalt- druck, Grenzflächenkräfte, Grenzflächenladung, nichtionische Tenside

1 Introduction

The interaction forces between surfactant-coated surfaces are key factors in the stability of colloidal systems such as foams, emulsions and dispersions (see Fig. 1). In order to understand and thus to control the stability of colloidal systems several issues have to be considered. First, the extent of surfactant adsorption at the interface has to be known as each adsorbed molecule alters the properties of the surface and thus the respective interaction forces. Second, the nature of the surface itself has to be considered because it influences the interaction forces. This is due to the fact that the net interaction force results from contributions of the substrate (e.g. double-layer forces generated by charged surface groups) and from the structure of the adsorbed layer. For example, the adsorption of surfactants at hydrophilic and hydrophobic surfaces, respectively, results in adsorption layers of completely different structures, which in turn generate different interaction forces. Additionally, the nature of the surfactant is crucial in defining the quality and magnitude of the interaction forces. These interactions originate mainly from repulsive short-range confinement, repulsive long-range electrostatic, and short-range attractive van der Waals forces [1, 2]. In addition, the presence of an attractive long-range force, often referred to as the hydrophobic interaction, is observed between non-polar surfaces in aqueous solutions [3, 4]. For the investigation of these forces different 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-technique [5–7] are usually employed, whereas for both air/water and oil/

![Figure 1](image-url)
The non-ionic surfactant hexaoxyethylene dodecylether (C\textsubscript{12}E\textsubscript{6}) was purchased from Fluka (Germany) and used as Tenside Surf. Det. 41 (2004) 4 175.

2.1 Solution Preparation

The non-ionic surfactant hexaoxyethylene dodecylether (C\textsubscript{12}E\textsubscript{6}) was purchased from Fluka (Germany) and used as received. The purity was checked by measuring the surface tensions as a function of the concentration \( c \) at 22 °C by the DuNoüy ring method using a Krüss K10ST tensiometer (see Fig. 2).

Sodium chloride was obtained from Merck (Germany) and roasted at 500 °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 degassed using a water jet pump for 2 h immediately before use which is essential in order to minimize the formation of air bubbles in the vicinity of highly hydrophobic solid surfaces. All glassware (except the film holders of the TFPB) was cleaned with deconex® from Borer Chemie (as a replacement for chromic sulphuric acid) and rinsed thoroughly with Milli-Q® water before use. The film holders for the TFPB (see below) were boiled two times in acetone, six times in water and at least 0.5 l of hot water was sucked through each disc before use. Three different surfactant solutions at concentrations of \( 10^{-5} \text{ M} \), \( 5 \times 10^{-5} \text{ M} \), and \( 10^{-4} \text{ M} \), respectively, were prepared in \( 10^{-4} \text{ M} \) NaCl background electrolyte concentration. The concentrations were chosen such they were far below, next to, and above the cmc (see Fig. 2).

2.2 Thin Film Pressure Balance

The most prominent method for investigating the interactions between two surfactant films at the air/water interface, i.e., the interactions acting in foam films, is the thin film pressure balance (TFPB) [7–11] and its modified versions [reviewed in 11]. In brief, a film is formed in a film holder F consisting of a porous glass disc that is connected to a glass tube. A hole is drilled in the disc in which the film is formed. This film holder is fixed in a gas-tight cell C, a pressure is applied to the cell via a syringe S, and the film thickness \( h \) at this particular pressure is determined interferometrically. By calculating the disjoining pressure \( \Pi \) from the applied pressure \( P_g \) one obtains the characteristic \( \Pi-h \) curves (see Fig. 5, top). The main parts of the TFPB are shown in Fig. 3.

2.3 MASIF

The MASIF technique was used to investigate the interactions between surfactant-coated solid surfaces. MASIF is an acronym for “measurement and analysis of surface interaction forces” [6, 7, 13] which basically employs a bimorph sensor.
Comparison of three techniques that can be used to measure interaction forces in thin films. For the investigation of forces acting in foam films the film pressure balance (TFPB) is commonly used. Interactions between solid surfaces can be quantified with the surface force apparatus (SFA), while in the TFPB only repulsive pressures are accessible. Second, with the TFPB the interactions are measured as pressures, whereas with the SFA it is a force that is obtained. As the disjoining pressure is proportional to the mathematical deviation of the force, high disjoining pressures (TFPB) do not necessarily correspond to high forces (SFA), which can make it difficult to compare the results obtained by the different methods. For instance, small forces correspond to high pressures in case the slope of the force curve is steep. In this particular case, the small forces are hard to detect, while the high pressures are easily measurable, which could lead to the erroneous assumption that one method is more sensitive than the other. A comparison between the results obtained by the TFPB with those obtained by the SFA is made in [7, 15].

The MASIF technique is another experimental approach to measure surface forces acting between solid surfaces. Although the MASIF is much easier to operate (and less time-consuming) than the SFA, studies with MASIF are rare in the literature [12, 16–20]. In the MASIF the measured distance $D$ between the surfaces is not an absolute value but refers to a distance relative to the “hard wall” contact between the surfaces. This “hard wall” contact is attained when the two “bare” surfaces or when two firmly attached surfactant layers coating the respective surfaces make contact. This means that any movement of one of the surfaces is directly transmitted to the other one without, presumably, any “distortion”. This is generally the case for thin surfactant layers. However, for soft adsorbed layers (e.g., thick layers of adsorbed polymers) a compression of the non-rigid adsorbed layers was observed [16].

In the case of contact between surfaces with two surfactant monolayers as intervening medium, the value of $D = 0$ means that the two layers are in direct contact. This has to be taken into account when the MASIF results are evaluated and compared with results of other techniques. A similar situation takes place for force profiles obtained with the thin film pressure balance (TFPB) commonly used. Interactions between solid surfaces can be quantified with the surface force apparatus (SFA) and the MASIF technique, respectively.
“Atomic Force Microscope” (AFM). Finally, it is worth noting
that in the MASIF (and also in the AFM) the interactions are
measured under dynamic conditions, i.e. the data is automatic-
ically acquired while the surfaces are moving with re-
spect to each other (approaching or separating) whereas in
the SFA it is possible to determine “equilibrium” forces as
the measurement is usually performed manually and en-
ough time can be allowed for the surfaces to reach equili-
brium at a given distance \( D \). In any case, hydrodynamic cor-
rections \( [21, 22] \) can be made to correct for effects related to
the movement of the liquid medium as the surfaces are driven
at any given rate of approach or separation. In this way
it is possible to calculate the net surface force, which, in
turn, can be compared with data from the SFA. Table 1 pres-
ts the most important features of the TFPB, the SFA, and
the MASIF techniques.

The origins of the disjoining pressure \( \Pi \) in the foam
film and of the surface force \( F \) between two solid surfaces
are the same, namely short-range repulsive confinement,
long-range repulsive electrostatic, and short-range attractive
van der Waals interactions \( [1, 2] \). The two latter interac-
tions are accounted for in the classical DLVO theory \( [23, 24] \).
Structural forces \( [1, 11, 25] \) as well as attractive long-range
forces, often referred to as the hydrophobic interactions
\( [3, 4] \), may also be present. The measured pressure and force
are usually considered to be the sum of the above-men-
tioned interactions. For the repulsive short-range com-
ponent no simple mathematical description is known yet
\( [2, 26] \). However, in the case of adsorbed surfactants with
large non-ionic headgroups the interaction force is domi-
nated by elastic and osmotic contributions arising from the
overlap of these headgroups which can be modelled by the-
tories used for polymer brushes, for example by the theory of
de Gennes \( [27] \). To obtain the electrostatic component of the
net interaction force the nonlinear Poisson-Boltzmann equa-
tion has to be solved using appropriate boundary conditions.
In the present work this was done with the algorithm of
Chan et al. \( [28] \), using either constant charge or constant po-
tential boundary conditions and the theoretical Debye length
\( \kappa^{-1} \) (see \( [12] \) for details). The van der Waals component can
be calculated according to \( [1] \)

\[
\Pi_{vdW}(h) = -\frac{A}{6\varepsilon h^3}
\]

or

\[
\frac{F_{vdW}(D)}{R} = -\frac{A}{6D^2},
\]

where \( A \) is the Hamaker constant. What is difficult about
calculating the van der Waals component is the estimation
of the Hamaker constant \( A \) since the systems usually consist
of several layers \( [1, 29] \). Ideally, \( A \) should be calculated using
(at least) a five-layer model (e.g. air-surfactant-water-surfac-
tant-air or solid-surfactant-water-surfactant-solid). However,
if the thickness of the film core is large compared to that of
the stabilizing monolayers, approximations are often suf-
cient. The reader is referred to \( [30] \) for a simple explana-
tion of these issues. In the case of foam films the Hamaker con-
stant for the air-water-air system, i.e. \( A = 3.7 \times 10^{-20} \) J,
is usually used. Finally, by adding the various interactions it
is possible to compare experimental profiles such as \( \Pi-h \)
(from the TFPB) and \( F/R-D \) (from the MASIF or SFA). The
parameter extracted from these calculations is the apparent
surface potential \( \psi_0 \), from which the corresponding surface
charge density \( \rho_0 \) can be calculated using the Grahame equa-
tion \( [1] \).

4 Results and Discussion

As already mentioned, the TFPB and the MASIF measure-
ments were carried out with the same \( \text{C}_{12}\text{E}_6 \) solutions in or-
der to compare the results obtained by these two different
methods. All solutions contained \( 10^{-4} \) M NaCl to produce a
well-defined electrostatic Debye decay length for the fits that
were done on the basis of the DLVO theory. The results for
the three different kinds of non-polar surfaces, namely air/
water, silanated glass, and thiolated gold surfaces, are shown
in Fig. 5 and Table 2 for three surfactant concentrations

![Figure 5](image-url)
The thickness of the CBFs decreases monotonically as the concentration of surfactant increases for the origin of the charges in thin foam films stabilized by non-ionic surfactants is the presence of excess OH– ions at the air/water interface. At present, the widely accepted explanation of the origin of the electrostatic repulsion, which are of relevance for the following comparison, can be summarized as follows. Two different kinds of films were observed, namely electrostatically-stabilized Newton black films (NBF) and thin Newton black films (NBF). The latter are known to be stabilized by short-range repulsive forces. The thickness of the CBFs decreases monotonically as the disjoining pressure increases. The curves shift towards lower disjoining pressures when the surfactant concentration is increased. This shift is accompanied by an increasing tendency to form an NBF which is demonstrated by the fact that the transition from a CBF to an NBF does not appear for the lowest concentrations, whereas it is observed at intermediate concentrations via “black spot” formation in the CBF. Moreover, at the highest concentrations investigated no CBF is formed at all, which means that only an NBF, with constant thickness, is observed. Once formed, the NBFs are stable over the whole pressure range investigated. As the thickness and the stability of the NBF do not change significantly within the reported pressure range, the NBF is represented as a dashed line. 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 (see below) – which prevents the film from rupturing. 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 [10]).

Both the Π-h curves shown in Fig. 5 and the fact that the surfactants dealt with are non-ionic raise the question of the origin of the electrostatic repulsion, i.e. the charges at the air/water surface. At present, the widely accepted explanation for the origin of the charges in thin foam films stabilized by non-ionic surfactants is the presence of excess OH– ions at the air/water interface [10, 11, 31–33]. However, it has not been clarified yet whether the OH– ions are specifically adsorbed [32,33] or if other mechanisms such as surface reactions [12] are responsible for the excess of OH– ions at the air/water surface. Moreover, the accumulation of halide ions at the air/water interface was discussed only recently [34].

This has to be mentioned as our C12E6 solutions were prepared with an electrolyte concentration of 10–4 M NaCl (see 2.1). However, according to Garrett [34] the amount of chloride ions at the air/water interface is expected to be negligible due to their low polarizability.

![Table 2](image)

**Table 2** Surfactant concentration c, surface potentials Ψw, surface charges qw, and area per charge A\text{charge} calculated from DLVO calculations for the foam films (index 1) and the silanated surfaces (index 2) as described in [12]. The calculated Debye length is k−1 = 3 nm at the given electrolyte concentration of 10−4 M NaCl. In addition, the area per molecule A\text{C12E6} at the air/water surface is given (index 1). A\text{C12E6} was obtained from fitting the surface tension isotherms to the Langmuir-Szyskowski equation.

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Despite the fact that the origin of the OH– ions is not clear yet, the experimental Π-h curves can be fitted with the DLVO theory to obtain the surface charge density qw (see Tab. 2). Looking at Fig. 5 and Table 2, one sees that the value of qw decreases with increasing surfactant concentration until it is so low that a CBF can no longer be stabilized and an NBF is directly formed under the chosen experimental conditions. These results are in absolute agreement with those published by other authors [reviewed in Ref. 11]. Experimentally it has been observed repeatedly that the surface charge is constant at low surfactant concentrations and decreases significantly above a certain concentration, which is proposed to be connected with the total number of ethylene oxide units [35]. What is important to realize is 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 (see Tab. 2). Although this observation is not understood yet, the typical explanation of a competitive adsorption between surfactant and hydroxide can be excluded.

**Silanated glass surface:** The silanated surface is negatively charged due to the dissociation of unreacted silanol groups in the glass substrate. Although the origin of the charge is different, the interaction forces between two silanated surfaces and two air/water surfaces are very similar (see Fig. 5 and Tab. 2). At the lowest surfactant concentration investigated the interaction forces are dominated by long-range electrostatic double-layer forces. By analogy with the air/water surface further adsorption of C12E6 reduces the net charge until long-range forces are negligible. Moreover, it is seen in Fig. 5 that the NBF formation corresponds to the appearance of a force barrier between the silanated surfaces. This barrier is a measure of the force that is needed to remove surfactant from between the two surfaces. As this barrier is located at a distance that corresponds to the thickness of a surfactant bilayer (from the contribution of one monolayer from each of the two interacting surfaces) the analogy with the NBF formation is obvious. Thus, in both cases, the adsorption of C12E6 leads to a decrease of the surface charge resulting in the formation of a densely packed bilayer which generates a force barrier. Note that a “removal” of this bilayer results in film rupturing in the case of foam films, whereas in the case of surfactant-coated water/solid surfaces it leads to a direct contact between the two solid surfaces.

**Thiolated gold surface:** As seen in Fig. 5 the situation is different for the interaction forces between thiolated gold surfaces coated with C12E6. The substrate, i.e. the thiolated gold surface, is uncharged so that double-layer forces do not play any role either in the absence or in the presence of C12E6. However, the adsorption of C12E6 influences significantly the short-range interaction forces. In contrast to the...
silanated glass surfaces, at the lowest surfactant concentration of \(1.0 \times 10^{-5}\) M a force barrier is already observed. This force barrier can be overcome experimentally and the surfactant monolayers are squeezed out from between the surfaces (see the step-shape profile in the force curve). The increase of the surfactant concentration leads to an increase of the force barrier so that eventually the densely packed bilayer can no longer be removed. Comparing these results with those for the silanated surfaces, one clearly sees that the \(F/R-D\) curves obtained for surfactant concentrations of \(5.0 \times 10^{-3}\) M and \(1.0 \times 10^{-4}\) M, respectively, are hardly distinguishable. In both cases 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.

5 Final Remarks

It was shown that for low surface coversages the nature of the surfaces onto which the surfactant adsorption takes place significantly influences the interaction force profiles. 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 \(\Gamma\), the area per molecule A and the conformation of \(C_{12}E_6\) at the different surfaces. For the air/water surface \(\Gamma\) and \(A\) can be obtained from the surface tension isotherms. With a detailed neutron reflectivity study not only the surface excess but also the monolayer thickness and its roughness were obtained [36]. Moreover, by using sum-frequency spectroscopy and ellipsometry the conformation of the \(C_{12}E_6\) molecules at the air/water surface is known [37]. What is still missing, however, is the corresponding data for the adsorption (adsorption isotherms) of \(C_{12}E_6\) at a silanated glass and a thiolated gold surfaces, respectively.

The fact that we did not observe any double-layer forces between the \(C_{12}E_6\)-coated thiolated surfaces provides evidence for the fact 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 surface. Work in progress deals with interaction forces between non-polar surfaces coated with the non-ionic sugar surfactant \(\alpha\)-dodecyl-D-maltoside (\(\beta\)-C\(_{12}\)G\(_3\)). These measurements are intended to clarify the influence of the headgroup on the interaction forces.

References


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