Short-range interactions between non-ionic surfactant layers

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Short-range interactions between surfactant and lipid layers are of great importance in technical applications in complex fluids such as foams, dispersions and emulsions, as well as in the formulation and performance of dispersants, detergents and flocculants. It is also of utmost importance in biological systems where interactions between biomembranes influence a range of processes. The field of short-range interactions has been thoroughly investigated during the past 30 years, following the emergence of a number of techniques to measure interaction forces. Thus, our understanding has increased considerably and it is timely to summarize relevant knowledge accumulated in this area. In this review we focus on the nature of short-range interactions between non-ionic and zwitterionic surfactant and lipid layers exposing their polar groups to the surrounding medium. We discuss the complex interplay of short-range (van der Waals, hydration, steric and other) forces based on recent theoretical and experimental results.

1. Introduction

Surfactants are used in the formulation of numerous everyday products, spanning over household, laundry, personal care and food commodities. They are also used in a range of industrial processes that require control of foam, emulsion or dispersion stability. Surface-active molecules are equally important in biological processes where phospholipids and glycolipids are the main constituents in biomembranes. In many cases surfactants are adsorbed onto surfaces with their polar group exposed to the surrounding medium. The nature of the polar group has a strong influence on the short-range interactions between such surfactant-coated interfaces, and therefore greatly affects the properties of the system. Understanding these interactions is not only of scientific interest, but it also has bearing on a variety of technological and biological processes.

The past 30 years have shown a dramatic development of techniques for measuring these interactions, both for solid and fluid interfaces. Pioneering work has been carried out with the surface force apparatus, SFA, \(^1\) osmotic stress techniques, \(^2\) and the thin film pressure balance. \(^3\) More recently additional techniques such as the MASIF, \(^4\) AFM colloidal probe \(^5\) and optical tweezers \(^6,7\) have increased the battery of techniques that can be used to directly measure surface forces. In addition to this, a number of techniques, including NMR, \(^8\) calorimetry, \(^9,10\) ultrasound \(^11\) and vibrational sum frequency generation spectroscopy \(^12\) are available to investigate the extent and state of hydration water. Thus, experiments combined with advanced simulations \(^13,14\) have the potential to advance our understanding further and unravel the complex interplay between hydration and molecular motion that determines the short-range interactions between surfactant and lipid layers.

This review deals mainly with short-range interactions between surfactant layers adsorbed to solid-liquid or air-liquid interfaces, even though some results about interactions in liquid crystalline phases are also discussed. We will first consider the nature of short-range attractions and discuss the relative importance of van der Waals forces and hydrogen bonding. This will lead us to a discussion on hydration of various polar groups before considering aspects of short-range repulsive interactions due to hydration, steric constraints, and molecular mobility at interfaces.

2. van der Waals forces

Electrons moving around the nuclei as well as the rotation of permanent and induced dipoles generate fluctuating electromagnetic fields that extend beyond the surface of macroscopic bodies. Correlations between the fluctuating electromagnetic fields emanating from two objects close together result in a force that is known as the van der Waals force. One way of calculating the van der Waals interaction energy between macroscopic bodies is to add all pair potentials between the atoms in the interacting bodies. This method, called the Hamaker summation method, \(^15\) assumes pair wise additivity of the pair potentials. The forces between two macroscopic bodies interacting across vacuum can then be calculated by making the proper integration over the volume of the bodies. \(^16\)

For example, it holds for the interaction energy \(W\) between two crossed cylinders \(W(D) = -A\sqrt{R_1R_2}/6D\) and between two spheres \(W(D) = -AR_1R_2/6(D(R_1 + R_2)\), respectively, with \(D\) being the distance between the two interfaces and \(R_1\) and \(R_2\) the radii of the two cylinders or spheres. The constant \(A\) is known as the Hamaker constant and its value depends on the
chemical composition of the two interacting bodies but not on their geometry.

However, the van der Waals interaction between two atoms is affected by the presence of a third atom, and consequently the assumed additivity is not correct. This problem is avoided in the Lifshitz theory,\textsuperscript{17} where the interacting bodies are treated as continuous media. In this approach the Hamaker constant is calculated from the frequency-dependent bulk dielectric properties of the materials. Approximate equations using the refractive indices and dielectric constants are often rather accurate. The non-retarded Hamaker constant for two macroscopic phases 1 and 2 in a medium 3 is approximately given by:\textsuperscript{16}

\[
A = \frac{3}{4} kT \frac{\epsilon_1 - \epsilon_2 - \epsilon_3}{\epsilon_1 + \epsilon_2 + \epsilon_3} + \frac{3\hbar\nu_e}{8\sqrt{2}} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \left( \frac{1}{n_3^2} - \frac{1}{n_2^2} \right)
\]

\[
= \frac{3\hbar\nu_e}{8\sqrt{2}} \left( \frac{1}{n_1^2} + \frac{1}{n_2^2} + \frac{1}{n_3^2} \right)
\]

(1)

where
\[
\epsilon_i = \text{the static dielectric constant for medium } i
\]
\[
\nu_e = \text{the main electronic absorption frequency in the UV region assumed to be the same for all three media. A typical value is } 3 \times 10^{15} \text{ Hz}
\]
\[
n_i = \text{the refractive index of medium } i \text{ in the visible region}
\]
\[
k = \text{the Boltzmann constant}
\]
\[
h = \text{Planck’s constant}
\]
\[
T = \text{the absolute temperature}
\]

At large separations retardation effects, which emanate from the finite speed of propagation of electromagnetic radiation, have to be taken into account as they lower the Hamaker constant below the value calculated from eqn (1). Such effects typically become important at separations larger than \(\sim 10 \text{ nm}\). We note that the expressions for the interaction energies between bodies of given shapes are the same in both the Hamaker and the Lifshitz theories. The only difference is the evaluation of the Hamaker constant. Advantages of the Lifshitz theory, besides avoiding the problem of non-additivity, are that it is applicable to interactions in a medium and that it takes into account the effect of temperature. The reader interested in knowing more about van der Waals forces is recommended the recent book by Parsegian.\textsuperscript{18}

Van der Waals forces between two bodies interacting across a medium can be either repulsive or attractive depending on the dielectric properties of the three media. From eqn (1) it is seen that between two identical bodies the Hamaker constant is positive, \textit{i.e.} the force is attractive. Further, the magnitude of the van der Waals attraction increases as the difference between the dielectric properties of the medium and those of the interacting bodies increases.

In a surface force experiment a common situation is that two mica sheets are covered with a thin layer of adsorbed molecules. The effective Hamaker constant, \(A_{\text{eff}}(D)\), also called the Hamaker function since its value depends on the surface separation, can in such a case be evaluated with the following equation:\textsuperscript{19,20}

\[
\frac{F(D)}{R} = \frac{1}{6(D - 2T)^2} \left[ \frac{A_{322}}{(D - T)^2} - \frac{2A_{123}}{D^2} + \frac{A_{121}}{D^2} \right]
\]

(2)

where
\[
F(D)/R = \text{the force, } F, \text{ at distance } D, \text{ normalized by the radius, } R
\]
\[
A_{322} = \text{the Hamaker constant for layer-solution-layer}
\]
\[
A_{123} = \text{the Hamaker constant for mica-layer-solution}
\]
\[
A_{121} = \text{the Hamaker constant for mica-layer-mica}
\]
\[
T = \text{the thickness of the layer}
\]
\[
D = \text{the distance between the surfaces}
\]

The Hamaker constants in eqn (2) can be calculated using the combining rules of Hamaker constants.\textsuperscript{16} Expressions similar to eqn (2) can be derived for any number of discrete layers.\textsuperscript{19,21}

The Hamaker function across water for two mica surfaces carrying a 2 nm thick hydrocarbon layer is shown in Fig. 1. The Hamaker constant for hydrocarbon interacting across water is about \(5 \times 10^{-21} \text{ J}\), and for mica interacting across water it is \(2.2 \times 10^{-20} \text{ J}\).\textsuperscript{1,16} The adsorbed layers come into direct contact at a surface separation of 4 nm. Clearly, at short separations the Hamaker function is identical to that of hydrocarbon interacting across water. At larger separations the Hamaker function increases and will reach that of mica interacting across water.

At short separations the van der Waals force is dominated by the properties of the outer layer. Thus, it is clear that the nature of the polar group in a surfactant layer influences this force at short separations. Let us consider the Hamaker function for non-ionic surfactants adsorbed on a hydrocarbon surface and compare the case of ethylene oxide and glucose as the surfactant’s polar head group. In order to do so we need to know the dielectric properties of hydrocarbon, the head groups, and the solvent. These data are provided in Table 1. The Hamaker functions for the two cases, setting the thickness of the polar group regions to 1 nm, are shown in Fig. 2. Due to the different dielectric constants, at short separations the Hamaker function is larger by about a factor of 2 when a glucoside head group is present instead of an ethylene oxide

![Fig. 1](image-url) The Hamaker function for two mica surfaces each coated with a 2 nm thick hydrocarbon layer interacting across water. The hydrocarbon layers are in direct contact at a surface separation of 4 nm.
head group. In this model calculation we have assumed that no water penetrates into the head group region of the adsorbed surfactant layer. This is clearly incorrect, but the calculation serves to illustrate that the nature of the surfactant head group has a large impact on the short-range van der Waals force between adsorbed layers.

Another model can be built by allowing water penetration into the head group region. We will make the assumption that the dielectric properties of this region depend linearly on the composition. Within this model the Hamaker constant across water between the head group layers as a function of the water content in these layers can be calculated, and the results are shown in Fig. 3.

We note that for any given water content the Hamaker constant, and thus the van der Waals force, is larger for the surfactant with the glucoside head group than for that with ethylene oxide as polar part. Further, the Hamaker constant decreases with increasing water content as the dielectric properties of the head group region become more similar to those of water. Clearly, in order to estimate the Hamaker constant and the van der Waals force between adsorbed surfactant layers one needs to know the water content within the adsorbed surfactant layer, which requires measurements of the layer thickness and the adsorbed amount and a calculation of the volume per surfactant (that can be estimated from the molecular weight and density). In very few cases all these data are available. However, we will illustrate the effect of water penetration into the head group region with two examples using the layer properties presented in Table 2.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Refractive index</th>
<th>Dielectric constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>1.333</td>
<td>80</td>
</tr>
<tr>
<td>Glucopyranose</td>
<td>1.51</td>
<td>6</td>
</tr>
<tr>
<td>Ethylene oxide</td>
<td>1.456</td>
<td>3.5</td>
</tr>
<tr>
<td>Hydrocarbon (dodecane)</td>
<td>1.411</td>
<td>2.01</td>
</tr>
</tbody>
</table>

Fig. 2 The Hamaker function for hydrocarbon surfaces coated with a 1 nm thick layer of glucose (filled upper line) interacting across water. The corresponding function for hydrocarbon coated with a 1 nm thick layer of ethylene oxide interacting across water is shown as the broken lower line.

Fig. 3 The Hamaker constant between two layers of glucose interacting across water as a function of the volume percentage of water within the layer (filled upper line). The corresponding curve for layers of ethylene oxide is shown as the broken lower line.

In Table 2 the layer thickness at the location of the force minimum was determined from surface force measurements, whereas the area per molecule in the layer was calculated from ellipsometry (C12E5) or from a combination of surface tension and wetting experiments (β-C8G1). The thickness of the polar region was calculated under the assumption that no water penetrates into the region occupied by the surfactant tails. The reported values clearly show that the amount of water present in the head group region of the large and flexible ethylene oxide chain is significantly larger than in the region occupied by the small and stiff glucoside unit. The Hamaker functions as a function of surface separation for the cases discussed above are shown in Fig. 4.

The minimum in the Hamaker function arises due to the fact that the second term in eqn (2) is negative. Clearly, incorporation of water in the surfactant head group region has dramatic consequences for the van der Waals force, and the ratio of the Hamaker constants (at short separations) \( A_{\text{EO}}/A_{\text{Glu}} \) is 0.07. This value is roughly consistent with the ratio of the depth of the force minimum observed for these two surfactants that is about 0.1. Thus, we conclude that van der Waals forces between adsorbed surfactant layers are of great importance for the attraction between such layers. It can also be concluded that a smaller attraction is expected when the dielectric properties of the surfactant head group region and bulk water become more similar, i.e. the more water the head group region includes. This leads us to the next question that concerns how the type of head group influences the water content within the polar part of the adsorbed layer. Before discussing this point we would, however, like to stress that the calculations made above rely on some assumptions. First, it was assumed that the composition of the head group region is homogeneous, whereas, particularly for long head groups, the water content increases as one moves outwards in the head group region. Second, at short separations the molecular nature of matter is expected to influence the van der Waals attraction and the approach used here is expected to break down. Thus, the fact that we observe a very close agreement between experimental results and calculations should be used with care. Nevertheless, the qualitative agreement, as well as the conclusions that can be drawn from this, are certainly valid.
3. Hydrogen bonds

Hydrogen atoms covalently attached to a strongly electronegative atom (e.g., oxygen, nitrogen, chlorine, fluorine) can mediate hydrogen bonds to neighbouring electronegative atoms.27 The hydrogen bond distance is larger than the covalent bond distance, and its strength depends crucially on the distance between the two electronegative atoms as well as on the angle between the three atoms, e.g. O–H–O. The hydrogen bond interaction is thus highly directional and distance-dependent, and as such it is an important element for promoting specific structures as observed in nature, including cellulose, DNA strands and globular proteins. Hydrogen bonds are also thought to play an important role in biochemical recognition.28 The hydrogen bond energy is, to a large degree, due to electrostatic interactions and partially due to some, minor, covalency:29 when a hydrogen bond is formed it gives rise to a change in the electron density around the participating nuclei and this gives the hydrogen bond the covalent character.

Water molecules are able to form very strong hydrogen bonds with each other. The hydrogen bond in water was first suggested by Latimer and Rodebush in 1920.30 It is now accepted that each water molecule can participate in four strong hydrogen bonds (average energy \(10^{-11}\) kJ mol\(^{-1}\) \(\approx -8\) kT bond\(^{-1}\), two serving as acceptors and two as donors. This makes water the densest hydrogen bonding liquid of any solvent with almost as many hydrogen bonds as there are covalent bonds. This is the reason for the strong positional and orientational order in liquid water, which, in turn, results in a small number of nearest neighbours where a preferential tetrahedral coordination is observed (we note, however, that this structural model of liquid water has recently been questioned.31) It is clear that hydrogen bonds are the key to many peculiar features of water, and despite being the most important liquid on earth there is still quite a lack of insight into water as a liquid and solvent.31–35

Water molecules rearrange in response to the presence of solutes, which changes the local hydrogen-bonding pattern. As a result water forms strong hydrogen bonds with polar solutes, like carbohydrates.36–38 Typical water–carbohydrate bond energies are in the range \(-6–11\) kT, and cooperative effects can lower this energy by an additional \(2\) kT.38 This seems to support a claim made already in 1955 that the water–carbohydrate hydrogen bond can be stronger than the water–water hydrogen bond.39 It has been demonstrated that the spatial arrangement of carbohydrate’s hydroxyl groups strongly influences their interaction with water, and most favourable interactions are observed for carbohydrates that fit into the dynamic structure of liquid water.30,41 Non-polar solutes in water also induce changes in the liquid water structure. In this case the water molecules rearrange in the vicinity of the solute to maximize the number of water–water hydrogen bonds, and this typically results in the formation of a dynamic cage, or clathrate, around the solute.32,42 This change in water structure is the basis for the hydrophobic effect43 that drives self-assembly of non-polar entities in liquid water. Overall, it can be stated that hydrogen bonding is an important factor in aqueous systems carrying solutes and surfaces and a long range molecular correlation has been confirmed using hyper-Rayleigh light scattering.44

It is very difficult to obtain experimental information on the structure of water adjacent to solutes. The main reason for this is that in most cases the spectroscopic signal from the hydration shell is swamped by that of bulk water. However, recently some progress has been made where an inherently surface sensitive spectroscopic technique, vibrational sum frequency spectroscopy (VSFS), has been employed to investigate the hydration of sugar groups and oligo(ethylene oxide) chains anchored to the air–water interface. It was found that some very strong hydrogen bonds are formed between sugar and water, whereas the hydration of the oligo(ethylene oxide) chain is dominated by a clathrate-like structure.12

Hydrogen bond formation between solutes capable of forming such bonds with each other is very important in liquids that by themselves cannot form hydrogen bonds. In water the hydrogen bond formation between solutes is of less importance simply because water molecules can also form strong hydrogen bonds with the solute, and the situation becomes

Table 2 Layer properties of \(n\)-octyl-\(\beta\)-glucoside, \(\beta\)-C\(_8\)G\(_1\), and penta(ethylene oxide) dodecyl ether, C\(_{12}\)E\(_5\)

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Layer thickness/nm</th>
<th>Thickness of polar region/nm</th>
<th>Molecular area/nm(^2)</th>
<th>Water molecules per surfactant</th>
<th>Volume% water</th>
<th>Hamaker constant (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\beta)-C(_8)G(_1)</td>
<td>1.5(^{23})</td>
<td>0.8</td>
<td>0.38(^{24})</td>
<td>4</td>
<td>36</td>
<td>4.0 (\times) 10(^{-21})</td>
</tr>
<tr>
<td>C(_{12})E(_5)</td>
<td>3.45(^{25})</td>
<td>2.7</td>
<td>0.52(^{26})</td>
<td>37</td>
<td>77</td>
<td>0.27 (\times) 10(^{-21})</td>
</tr>
</tbody>
</table>

![Fig. 4](image-url) The Hamaker function for hydrocarbon surfaces coated with a 0.8 nm thick glucose layer containing 36% water interacting across water (solid upper line), and for hydrocarbon surfaces coated with a 2.7 nm thick ethylene oxide layer containing 77% water interacting across water (broken lower line). This corresponds to the situations described in Table 2.
rather complex. For instance, when two sugar units dispersed in water come into contact, it results in the disruption of hydrogen bonds between water and sugar and the creation of new water–water and sugar-sugar hydrogen bonds. The energy and entropy changes accompanying this process have to be considered to determine whether or not the association process is favourable. We note that the formation of solute–solute (or solute–surface) hydrogen bonds is not a sufficient condition for association (or adsorption). This is because the free energy change associated with the disruption of solute–water (surface–water) hydrogen bonds and the formation of new water–water hydrogen bonds also has to be considered. It does, however, seem plausible that if hydrogen bonds are able to form between solutes (solute–surface) the association (adsorption) process in water will be more favourable than if no such bonds could be developed.

Similar arguments can be used when considering short-range interactions between surfactant layers. The fact that hydrogen bonds can form between the polar head groups of, for example, sugar-based surfactants does not directly lead to the conclusion that the short-range interaction across water should be attractive due to hydrogen bond formation. It is thus of some interest to compile available data on the depth of the interaction force minimum (related to the adhesion energy) measured between adsorbed non-ionic surfactant layers. This will allow us to learn if the possibility of forming hydrogen bonds between two head groups has a bearing on the short-range attraction observed in these systems (see Table 3).

The data in Table 3 correspond to systems with aqueous surfactant solution at or above the respective cmc, when the surfactant layers are saturated. SFA = surface force apparatus,\(^1\) MASIF = measurement and analysis of surface interaction forces.\(^4\)

We note that no direct hydrogen bonds can be formed between DDAO molecules in uncharged form, DDPO, or surfactants with ethylene oxide head groups. However, such interactions are possible for surfactants with polyhydroxyl head groups and also C12 amine molecules. By comparing the data compiled in Table 3 we note that the trend is that head groups that are able to form interlayer hydrogen bonds display a somewhat larger attractive short-range force component than layers that are unable to form such bonds. This could indicate that there is a contribution from interlayer hydrogen bond formation, but the extension of this effect is difficult to determine since the nature of the head group also influences other short-range interactions, e.g. the van der Waals force as discussed in the previous section. The data obtained with the two techniques, SFA and MASIF, largely agree with each other. However, comparison of the force data should be made with caution since in some of the experiments with the MASIF it was necessary to correct for the hydrodynamic contribution to the total force. The depth of the attractive minimum is affected by this correction, which results in less accurate values. Moreover, the non-polar substrates used in MASIF and SFA are different, which in turn, might lead to slightly different structures of the adsorbed layers and thus differences in interaction forces.

Interactions between chemical groups covalently attached to surfaces are somewhat easier to understand than interactions between physically adsorbed surfactant layers. The main reason is that the surface density of covalently attached groups does not vary with surface separation, whereas such changes are expected for adsorbed surfactant layers in thermodynamic equilibrium with the bulk solution.\(^5\) The ω-functionalised thiols attached to gold surfaces provide good model surfaces for elucidating the effect of surface anchored groups on short-
range interactions. This has recently been utilized by Blomberg et al.\textsuperscript{56} who investigated interactions between self-assembled monolayers anchored to gold with terminal groups of the ethylene oxide type and with globotriose groups (an uncharged trisaccharide). They found no attraction between the surfaces exposing ethylene oxide head groups whereas the attraction between surfaces exposing globotriose was found to depend strongly on the packing density of the large sugar group, and in some cases also on the contact time. Some data are shown in Fig. 5 and 6.

Remarkably, as illustrated in Fig. 5, for surfaces exposing globotriose head groups it was found that the largest attraction occurred at intermediate packing densities. This observation can hardly be rationalised by a variation in the van der Waals force, but it rather points towards another mechanism. It is suggested that the increased conformational freedom of the globotriose head group with decreasing packing density is the key. At high packing densities the globotriose head groups are locked into specific conformations and orientations with strongly restricted possibilities to adapt to changes in the environment. As the packing density is decreased this restriction is relaxed and the head groups become more able to adopt orientations and conformations that allow favourable interlayer head group interactions to develop. This will lower the free energy of the system, which is measured as an increased attractive force component (note: the force between curved surfaces is proportional to the free energy between flat surfaces). At even lower packing densities of the globotriose head group, the conformational freedom is even higher, but now the probability of developing favourable globotriose–globotriose interactions is decreased simply due to the low density of such surface groups. Thus, we conclude that there are favourable interactions between globotriose head groups and that a certain conformational freedom of the sugar head group is necessary for these interactions to develop. This means that the head group interaction depends on the mutual position of two neighbouring head groups, and it seems natural to assign this directionality to the possibility of hydrogen bond formation, either directly or via water bridges.

Another remarkable feature of the interactions between globotriose-terminated SAMs is that under some conditions an attractive force contribution that depends on the contact time is observed (see Fig. 6), which is explained by the dynamics of the interfacial region. A time-dependence of the depth of the force minimum was observed only in situations where a relatively large number of exposed globotriose groups were present on the surface. However, this was not observed in cases when a tightly packed layer was formed.\textsuperscript{56} It was suggested that the orientation of the sugar unit changes with increasing contact time in order to minimise the free energy of the system and that these changes favour the formation of hydrogen bonds, possibly mediated by water molecules. Similar slow changes within glycolipid monolayers at the air–water interface have been reported and explained by attractive head group interactions.\textsuperscript{57,58} We note again that hydrogen bonds are highly directional and thus require highly specific orientations to reach their optimal strength. The relevant time scale is thus not that for the formation of a hydrogen bond, but that related to achieving optimal head group orientations for the formation of hydrogen bonds. The time scale for this process will depend on the packing density of the sugar head group anchored to the surface. At too high packing densities, this time is larger than the experimental time scale (seconds) and no time-dependent adhesion is observed. At moderate packing densities the time scales of the measurement and the reorientation process are similar and an attractive force component that depends on the contact time is observed. For freely moving head groups the conformational changes are expected to occur much more rapidly than the time scale of these measurements and again no time dependence of the attractive force contribution is expected with the technique employed. Clearly, a stronger attraction is expected when the surface layer is flexible enough to allow conformational changes as compared to the cases when the conformation is effectively “frozen” during the measurement.

The data obtained for $\omega$-functionalised thiols suggest that hydrogen bond interactions occur between layers exposing sugar groups provided the head group is able to adopt suitable conformations. However, the magnitude of the attractive forces observed for these systems is smaller than between physically adsorbed layers of sugar-based surfactants. This

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**Fig. 5** Adhesion force as a function of solution ratio of HSC$_{15}$CONH-EG$_4$/HSC$_{15}$CONH-EG$_4$-Globo during formation of mixed SAMs on gold surfaces. Modified from ref. 56.

**Fig. 6** Adhesion force as a function of contact time for (SC$_{16}$O-Globo)$_2$ (unfilled squares) and (SC$_{15}$CONH-EG$_4$-Globo)$_2$ (filled squares) coated gold surfaces. The broken line is included as a guide for the eye. Modified from ref. 56.
could be due to the higher mobility of physically adsorbed surfactants compared to covalently attached thiols, which would favour hydrogen bond formation. However, we argue (see section 2) that the main cause for the relatively high attraction observed between non-ionic sugar-based surfactants as compared to their oligo(ethylene oxide) counterparts is the difference in van der Waals interactions.

Of course, if hydrogen bond formation within a layer affects the packing density and water content in the head group region, this will affect the van der Waals attraction. We can illustrate this by comparing the attractive force between layers of N-dodecylactobionamide (LABA) with that between layers of maltose 6'-O-dodecanoate (C12-maltose ester). In LABA the inner sugar unit is open, which allows for a higher flexibility as compared to for the C12-maltose ester where both sugar units are closed. Some data for these surfactant layers are compiled in Table 4.

The layer thickness was obtained from the position of the force minimum determined from surface force measurements and the molecular area was calculated from ellipsometric data. The ratio of the Hamaker constants, and thus the van der Waals force, \( A_{\text{maltose ester}}/A_{\text{LABA}} \), is calculated to be 0.8, whereas the ratio of the attractive force measured is 0.5–0.8. Thus, again it seems that differences in van der Waals interaction is an important reason for the difference in attractive force observed between adsorbed surfactant layers. We argue that intralayer hydrogen bonds are more easily formed between the more flexible head groups of LABA, and this results in a higher packing density in the adsorbed layer. This, in turn, affects the water content in the head group region and the van der Waals force between the layers.

We have so far exclusively considered attractive interactions, but there are also short-range repulsive interactions acting between surfactant layers. They can coarsely be divided into repulsive forces due to dehydration of polar groups (hydration forces) and forces due to confinement of surfactants (steric forces). Of course, the net short-range interaction, which is the only measurable quantity, is due to a balance of these attractive and repulsive force contributions, and the range and magnitude of the repulsive force component will also affect the depth of the attractive force minimum discussed above. In the next sections we will recapitulate some findings about hydration of polar groups and relate this to the short-range interactions between surfactant layers.

4. Hydration

Water molecules can loosely be referred to as either “bound” or “free”. “Free” water has the same physical properties as water molecules in the bulk and it is not significantly affected by the presence of solute molecules or surfaces in contact with the solution. Thus, the term “bound water” does include all molecules that are affected by solutes or surfaces, and these water molecules constitute the hydration layer. From this definition it should immediately be clear that “bound water” is not a well-defined concept, and the amount of bound water detected will depend on the technique used to make the measurement. Nevertheless, the existence of bound water, and thus the hydration of molecules and surfaces are important for fundamental properties and in many technical applications such as crystallisation, chemical reactions and triggered enzymatic processes. The importance of bound and free water in various applications has recently been reviewed by Ezrahi et al., where many relevant references can be found.

**Hydration investigated by calorimetry**

Calorimetric measurements of the hydration in binary surfactant/water systems can be performed with sorption calorimetry and differential scanning calorimetry (DSC). Sorption calorimetry determines the water activity and the enthalpy of mixing as a function of water content at constant temperature, whereas DSC gives the enthalpies of phase transitions. Measurements of the hydration behaviour of different sugar based surfactants have been reported by Kocherbitov et al.,10,60–62 The surfactants investigated were n-octyl \( \beta \)-D-glucoside (\( \beta \)-C8G1), n-octyl \( \alpha \)-D-glucoside (\( \alpha \)-C8G1), n-octyl \( \beta \)-maltoside (\( \beta \)-C8G2), and n-decyl \( \beta \)-maltoside (\( \beta \)-C10G2). Their results demonstrate that the enthalpy of mixing (i.e. mixing water with pure surfactant) is highly dependent on the state of the solid surfactant. The initial hydration of the octylglucosides is highly endothermic corresponding to a transition from a crystal to a liquid crystal (melting). On the other hand, it was found that the hydration of dry maltoside samples, \( \beta \)-C8G1 and \( \beta \)-C10G2, is exothermic.61 Thus, the dry \( \beta \)-C8G2 and \( \beta \)-C10G2 samples were found to be in a glassy state, which eliminates the endothermic transition from a crystalline to a liquid crystalline state. This conclusion was supported by the absence of a melting peak for the dry surfactant sample in the DSC scan (the enthalpy change for the transition from a glassy to a liquid crystalline state is negligible). The hydration is exothermic due to the incorporation of water molecules into surfactant lamellar structures where the water molecules interact strongly with the surfactant head groups forming the hydration shell. An important consequence for practical applications is that glassy forms of surfactants require much drier storage conditions than crystalline forms because water uptake of the former starts at a much lower relative humidity.61

The sorption calorimetry measurements of Kocherbitov et al. also revealed that the water activity of \( \beta \)-C8G1 is lower than that of \( \beta \)-C8G1 at the same water content. This means that \( \beta \)-C8G2 interacts more strongly with water and is thus more hydrophilic. The reason for this is probably that the larger head group of \( \beta \)-C8G2 provides more bonding sites for

### Table 4 Layer properties of N-dodecylactobionamide (LABA) and of maltose 6'-O-dodecanoate (C12-maltose ester)

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Layer thickness/nm</th>
<th>Molecular area/nm²</th>
<th>Water molecules per surfactant</th>
<th>Vol% water</th>
<th>Hamaker constant (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LABA</td>
<td>2.25²⁴</td>
<td>0.50²⁴</td>
<td>12</td>
<td>38</td>
<td>3.7 × 10⁻²¹</td>
</tr>
<tr>
<td>C12-maltose ester</td>
<td>3.45²⁴</td>
<td>0.55²⁴</td>
<td>16</td>
<td>45</td>
<td>2.9 × 10⁻²¹</td>
</tr>
</tbody>
</table>
water. Speculative as it might be, a consequence of the stronger interactions could be that the lamellar phase of β- C₈G₁ does not swell in one dimension as has been found for β-C₈G₂. One-dimensional swelling of a lamellar phase means that water is only incorporated between the surfactant layers during water absorption/swelling. In case of β-C₈G₂, however, water is probably also incorporated between the surfactant head groups in the lamellae that may result in an increase of the molecular area during water absorption, which is not observed for β-C₈G₁.

Another interesting finding was that β-C₈G₁ is more hydrophilic (lower water activity at a given water content) than the α isomer α-C₈G₁. This difference is due to the geometry of the molecules. Surfactant molecules are not fixed at their positions in the surfactant aggregates. They are constantly exchanged with the molecules in the bulk and also protrude in and out of the water layer surrounding the surfactant aggregate. Since the β-C₈G₁ molecule is straighter than α-C₈G₁, this movement becomes easier and the mixing with water will be favoured, (leading to lower water activity). The enhanced mixing with water could be an additional explanation for the lower Krafft point of β-C₈G₁, as compared to α-C₈G₁, apart from its lower crystal energy as previously established with DSC.

The hydration of the system C₁₈:₁E₁₀/water/dodecane/butanol has been studied with sub-zero temperature differential scanning calorimetry (SZT-DSC). Two types of bound water with melting peaks at −25 and −11 °C, respectively, were observed. From these data it could be calculated that each EO group binds 2.5 water molecules (Nw/EO = 2.5), and time domain dielectric spectroscopy showed similar amounts of bound water (Nw/EO = 2.3).

**Hydration investigated by NMR**

The self-diffusion coefficient of water D(H₂O) can be determined by NMR, and this can be used for investigating hydration of surfactants. The measured value of D(H₂O) is lower than that of neat water D₀(H₂O) for two reasons. First, for surfactant concentrations above the cmc, surfactant aggregates obstruct the mobility of the water molecules. Second, a fraction of the water molecules is bound to the surfactant (hydration shell) and hence has a lower mobility than “free” water. A detailed self-diffusion study in C₁₂E₅ and C₁₂E₈ surfactant solutions revealed that 2–6 water molecules are bound to one ethylene oxide unit. The exact number depends significantly on the surfactant concentration c and slightly on the temperature T: the larger c and the higher T the smaller the hydration number. As the highest measured hydration number was found at c = 10 wt%, which is orders of magnitude above the cmc, one expects even higher values at c ~ cmc. Moreover, the deduced hydration numbers refer to the hydration of the hydrophilic head group only as all studies were carried out in micellar solutions. Consequently, even higher hydration numbers are expected for the isolated surfactant at c < cmc where the hydrophilic tail is also surrounded by water molecules. Unfortunately, an equally extended self-diffusion study on sugar surfactants does not exist. However, Nilsson et al. determined a hydration number of 6 water molecules per glucose unit for aqueous solutions of β-C₈G₁. This number was only estimated and not directly calculated from self-diffusion data. In a follow-up paper the same authors claim that each glucose unit is hydrated by 15 water molecules without explaining the origin of this number.

**Hydration determined by measurements of speed of sound and density**

Information on hydration can also be extracted from combined measurements of density and speed of sound. For instance, Pastor et al. determined the hydration number of β-C₈G₁ in both premicellar (c < cmc) and micellar (c > cmc) solutions. At c < cmc a constant value of 16 water molecules per surfactant was found. Note that this number refers to the hydration of the total surfactant and not only of the head group. As is the case for the ethylene oxide head groups, at c > cmc the hydration number decreases with increasing β-C₈G₁ concentration down to a value of 6 at c ~ 5 cmc (3 wt%).

**Comparing hydration numbers of ethylene oxide and glucose head groups**

Due to the lack of systematic data we cannot compare quantitatively the hydration numbers obtained for ethylene oxide and glucose head groups. A qualitative evaluation, however, might shed some light on the differences of these surfactants. From extensive SANS measurements in bicontinuous microemulsions we know that the area per head group at the water/oil interface is 0.56 nm² for a glucose unit, which is comparable with that of a surfactant with four ethylene oxide units which is 0.54 nm². As mentioned earlier, the hydration number of the glucose head group, as determined by NMR, is found to be 6 at a surfactant concentration of 3 wt%, whereas NMR estimates the hydration number to be 6 per ethylene oxide unit at 10 wt%, i.e. 24 per tetra(ethylene oxide) head group. Keeping in mind that the hydration number per ethylene oxide unit is expected to be even larger at 3 wt%, one can conclude that under similar conditions and for similar head group sizes the hydration of ethylene oxide based surfactants is significantly higher than that of sugar based surfactants. This is qualitatively consistent with the data presented in Table 2, which shows that the water content within the polar region of C₁₂E₃ layers adsorbed on non-polar surfaces is higher than that within β-C₈G₁ layers.

**Vibrational sum frequency spectroscopy, VSFS**

The effect of hydration is not only determined by the extent of hydration, for instance as estimated by the hydration number, but also by the (dynamic) molecular structure of the hydration shell. This has been realised for a long time and it is common to discuss the state of hydration layers in general terms such as “structure breaker”, “structure maker”, “hydrophobic hydration”, or “clathrate”. Nowadays the structure of the hydration shell of adsorbed surfactant layers can be measured using the inherently surface sensitive technique VSFS. The technique is described in detail in ref. 70–72. This technique essentially allows recording of vibrational spectra of the anisotropic surface region without interference from the isotropic bulk solution. Thus, detailed spectra of the water located at the
air–water interface are available, and recently spectra of the hydration layer of sugar-based and ethylene oxide-based surfactants have been probed in detail.

The spectra obtained, in all independent polarisation combinations, for n-decyl β-maltoside (β-C_{10}G_{2}) and octa(ethylene oxide) dodecyl ether (C_{12}E_{8}) are shown in Fig. 7. In these spectra water molecules involved in stronger hydrogen bonds will give rise to an absorption peak located at lower wavenumbers. For example, the strong peak centred at 3150 cm\(^{-1}\) of the β-C_{10}G_{2} spectrum arises from the strong hydrogen bonds formed between the sugar moiety and water, while the peak centred around 3590 cm\(^{-1}\) has been observed for all surfactants studied so far and is assigned to non-hydrogen bonding OH-groups located next to the hydrocarbon part of the surfactant. For comparison a part of the sps spectra for pure water is included for comparison. The data are from ref. 12. Reprinted with permission from E. Tyrode, M. C. Johnson, A. Kumpulainen, M. W. Rutland and P. M. Claesson, J. Am. Chem. Soc., 2005, 127, 16848–16859. Copyright 2005 American Chemical Society.

This peak has been suggested to be due to a clathrate-like hydration structure formed around the ethylene oxide chain. The peak observed at 3150 cm\(^{-1}\), most clearly seen in the ppp polarisation combination, is tentatively assigned to water hydrogen bonding to the ether oxygens in the surfactant head group.

Thus, to fully understand the effect of hydration of surfactant head groups one needs to consider not only the extent of hydration, but also the state of hydration. Both of these quantities can vary considerably between different classes of non-ionic surfactants, and increased knowledge in this area can help explaining their different properties, e.g. why properties of sugar-based surfactants are relatively temperature-independent whereas ethylene oxide-based surfactants become more hydrophobic at elevated temperatures.

5. Steric interactions

Steric interactions between non-ionic surfactant layers are very important for the stabilisation of foams, emulsions, and dispersions especially in the absence of surface charges. For the sake of brevity we will restrict the following discussion to foam films as the behaviour of emulsions and dispersions is expected to be similar. The main difference is that in dispersions particles generally do not fuse together, while in emulsions surfactants may be soluble in the oil phase. The stability of well-drained quasi-static foam films (thickness \(<100\) nm) is usually discussed in terms of repulsive interactions, which create an excess pressure normal to the film interfaces. With a thin film pressure balance (TFPB) the thickness \(h\) of a foam film can be measured as a function of the applied pressure from which the repulsive pressure, \(P\), can be calculated thus obtaining \(P-h\) curves, often referred to as disjoining pressure isotherms. One usually describes \(P\) as the sum of long-range repulsive electrostatic (\(P_{\text{elec}}\)), attractive van der Waals (\(P_{\text{vdW}}\)), and short-range repulsive entropic confinement interactions, which will be called steric interactions (\(P_{\text{steric}}\)) in the following. Two types of films can be distinguished, i.e. common black films (CBF) that are mainly stabilized by \(P_{\text{elec}}\) and films the stability of which is determined by \(P_{\text{steric}}\). In the latter case one further distinguishes between Newton black films (NBF) in the case of low molecular weight (LMW) surfactants and bilayer films (BF) in the case of amphiphilic block copolymers. Generally, the type of foam film formed is determined by the type of surfactant, the surfactant concentration, the electrolyte concentration, and the pH (reviewed in refs. 80–82). In the following we will focus on the description and the origin of \(P_{\text{steric}}\) in foam films stabilised by LMW surfactants and amphiphilic block copolymers.

Foam films stabilized by low molecular weight surfactants

To illustrate the steric interactions between non-ionic LMW surfactant layers in foam films we will refer to a disjoining pressure study published recently. This study deals with \(P-h\) curves of foam films stabilized by three different decyl ethylene oxide surfactants, C_{10}E_{j} with \(j = 4\), 6, and 8. For C_{10}E_{4} the typical behaviour of a non-ionic LMW surfactant was observed (reviewed in ref. 81 and 82). At concentrations below the cmc a CBF is formed. The respective \(P-h\) curve is shifted...
towards lower \( P \) with increasing surfactant concentration. This shift is accompanied by an increasing tendency to form an NBF, which takes place via black spot formation in the CBF, i.e. the transition to the thin NBF occurs initially at some local spots and with time these thinner regions merge to cover the whole film area. Once formed, the NBF is stable and its thickness does not change over the whole investigated pressure range. The \( E_6 \) head group is obviously large enough to create a significant steric repulsion that stabilizes the NBF over a wide pressure range. It is believed that \( \Pi_{\text{steric}} \) originates from undulations of the interface, peristaltic fluctuations, protrusion of surfactants at the interface, head group overlap, and of course also hydration forces and van der Waals forces are of importance at these short separations. Because of this complexity no simple and general expression for \( \Pi_{\text{steric}} \) is available.\(^{77,78} \) Thus, a common practise in the literature dealing with interactions across foam films is to describe the steric repulsion generated in an NBF as a hard-wall repulsion, i.e. the surfactant bilayer is regarded as incompressible with a film thickness that does not depend on the applied pressure. In contrast, force measurements with surfactants adsorbed on solid substrates and osmotic stress measurements in liquid crystalline phases distinguish a distance dependence of the short-range interaction.

The interactions between the surfactant layers across the foam film change significantly as the head group size is increased from \( E_4 \) to \( E_6 \) and \( E_8 \), respectively. For all three surfactants a change of the stabilizing mechanism from being electrostatic (CBF) to steric in nature (NBF) is observed with increasing surfactant concentration and the NBF is formed via black spot formation at \( c = \text{cmc} \). However, there is a striking difference between \( C_{10}E_4 \) on the one hand, and \( C_{10}E_6 \) and \( C_{10}E_8 \) on the other, at \( c < \text{cmc} \). While the CBF-NBF transition of \( C_{10}E_4 \) still takes place via black spot formation, the foam films of \( C_{10}E_6 \) and \( C_{10}E_8 \) thin continuously with increasing pressure. This observation reveals that the range of the steric repulsion between the head groups is comparable to, or even larger than, the effective range of the van der Waals attraction. Consequently, the \( \Pi-h \) curves of \( C_{10}E_6 \) and \( C_{10}E_8 \) can no longer be described adequately with the combination of the DLVO theory and an incompressible surfactant bilayer (“hard-wall”). It is argued that the main reason for this difference is a force contribution arising as a consequence of the large head groups.\(^{83} \) Thus, the NBFs of \( C_{10}E_6 \) and \( C_{10}E_8 \) cannot be regarded as incompressible bilayers as \( h \) decreases with increasing \( \Pi \). On the other hand, the compressibility of an \( E_6 \) or an \( E_8 \) head group is not large enough to apply the brush theory of de Gennes.\(^{84} \) We note that when the head group contains 20 ethylene oxide units or more, the de Gennes theory can be applied,\(^{77} \) but it is as yet not clear exactly at which head group size this theory becomes applicable. On the basis of these observations a new equation of state was derived empirically. According to Stubenrauch and Strey it holds.\(^{83} \)

\[
\Pi = \frac{K q b}{h (h - b)} + C \exp(-kh) - \frac{a}{h^2} \tag{3}
\]

with \( q = \) surface charge density, \( C = \) electrostatic prefactor, \( k^{-1} = \) Debye length, \( K = \) fundamental constant for foam films, \( a \) and \( b = \) specific constants of a particular surfactant.

---

**Fig. 8** \( \Pi-h \) curves for two concentrations of \( C_{10}E_8 \) with \( c < \text{cmc} = 10.4 \times 10^{-4} \) M and an electrolyte concentration of \( 10^{-4} \) M NaCl. The solid lines are calculated according to the new equation of state (eqn (3)). Modified from ref. 83.

As was the case for the classical description (hard-wall + DLVO), eqn (3) includes two repulsive contributions and one attractive contribution, which are all explained in detail elsewhere.\(^{83} \) It is the first term that describes the short-range steric repulsion that is considered to be a hard-wall repulsion in the case of small head groups. According to eqn (3), however, the short-range repulsion is a function of both \( q \) and \( h \) and it is only for \( h \to b \) that this term approaches infinitely high values, i.e. the hard-wall limit. As argued in ref. 83, the parameter \( h \) can be interpreted as the “excluded volume of a foam film” which equals the thickness of a completely compressed film (water-free surfactant bilayer). The values for \( C_{10}E_8 \) of the thickness of the NBF (around 8 nm) and the best-fitted value of \( b \) (5.2 nm) may help to illustrate this argument. Thus, it should theoretically be possible to reduce the NBF thickness down to \( \sim 5 \) nm if very high pressures are applied. Practically, however, we do not expect to obtain such a thin NBF as it will definitely rupture before reaching the final “compressed” stage.

Fig. 8 illustrates some experimental \( \Pi-h \) curves for \( C_{10}E_j \) surfactants. They could all be described satisfactorily with eqn (3). The main breakthrough is the fact that the first term of eqn (3) allows us to quantitatively describe the steric repulsion arising from oligomeric non-ionic head groups.

**Foam films stabilized by amphiphilic block copolymers**

A continuous transition from electrostatic to steric stabilisation has also been observed for foam films stabilized by amphiphilic block copolymers\(^{12-14} \) (reviewed in ref. 82). In this case, however, the short-range repulsion can be described with the brush theory of de Gennes\(^{84} \) according to which the head group is compressible, which results in eqn (4).

\[
\Pi_{\text{steric}}(h) = kT \frac{3}{2} \left[ \left( \frac{h_{\text{head}}}{h_{\text{core}}} \right)^{9/4} - \left( \frac{h_{\text{core}}}{2h_{\text{head}}} \right)^{3/4} \right] \tag{4}
\]

for \( h_{\text{core}} < 2h_{\text{head}} \)

where \( k \) is the Boltzmann constant, \( T \) the temperature, \( \Gamma \) the surface concentration of the amphiphilic polymer, \( h_{\text{head}} \) the...
length of the head group at infinite separation, and $h_{\text{core}}$ is the thickness of the film core consisting of the head groups and water.\textsuperscript{80,85,86} Note that what is plotted here is the equivalent water layer thickness $h_w$ and not the real film thickness $h$ (see text for details). The solid lines were calculated according to the DLVO theory (assuming constant surface charge boundary conditions) and de Gennes polymer brush theory (eqn (4)), respectively. Modified from ref. 85.

In conclusion, it can be argued that repulsive steric interactions are an important stabilizing factor for foam films. The range of these interactions depends on the size of the surfactant. In the case of amphiphilic block copolymers the magnitude of the steric repulsion is much larger than that of the van der Waals attraction in the relevant distance regime, which leads to a continuous decrease of the film thickness as shown in Fig. 9. The long-range repulsion can be described within the Poisson Boltzmann model of the electrical double layer and the short-range repulsion with de Gennes’ brush theory. The behaviour of foam films stabilized by LMW surfactants with relatively large head groups such as E6 or E8 is qualitatively similar. In this case, however, the $\Pi-h$ curves can be described neither with the classical (DLVO + hard-wall) nor with the polymer (DLVO + de Gennes) approach. To overcome this problem a new equation of state was derived with which both the total $\Pi-h$ curves of these surfactants and the steric repulsion arising from large non-ionic head groups can be described satisfactorily.

6. Interactions in liquid crystalline phases

In biology, membrane–membrane and vesicle–membrane interactions underlie phenomena such as adhesion, membrane stacking, and fusion. The DLVO theory helps to explain the interactions between smooth, charged surfaces. However, it fails in describing short-range interactions between many physiologically important molecular assemblies, including phospholipid membranes. This is in part because biological membranes (a) have relatively large surface areas and are very hydrophobic; (b) are rough at the molecular level (because of protruding lipid head groups, proteins, and carbohydrate moieties); and (c) are flexible.\textsuperscript{87} These properties generally give rise to strong short-range repulsive hydration and steric forces, as discussed in the previous sections. Again water plays a key role, now in determining the interactions between membranes and in liquid crystalline phases formed by e.g. phospholipids.\textsuperscript{88}

Experiments carried out during the last 30 years have shown that strong short-range repulsive forces act between non-ionic surfactant bilayers, between zwitterionic lipid bilayers with e.g. phosphatidylcholine (PC) and phosphatidylethanolamine (PE) head groups,\textsuperscript{89} and between non-ionic bilayers of galactolipids such as monogalactosyldiglyceride (MGDG) and digalactosyldiglyceride (DGDG),\textsuperscript{90,91} and it is thus a common force encountered between adsorbed lipid and surfactant layers, as well as between bilayers in liquid crystalline phases. Experimental studies with osmotic stress techniques have demonstrated that the force acting between model membrane surfaces containing molecules such as dipalmitoylphosphatidylcholine (DPPC) can be described as an exponentially-decaying repulsion with a decay length of 0.1–0.3 nm,\textsuperscript{2,92–94} and a stronger repulsive force acts between PC as compared to between PE.\textsuperscript{2,95} The fact that the decay length is close to the size of a water molecule gave rise to the idea that interbilayer water is responsible for this effect, the “hydration force”. It was argued that the origin of the repulsive force was due to the removal of structured water between lipid bilayers, which requires work and results in an increase in free energy as the
distance between the bilayers decreases. This observation inspired the development of several theoretical and simulation approaches to explain the hydration force. However, experiments also showed that the repulsive force was larger between phospholipid layers with the hydrocarbon chains in fluid state, as compared to layers with the same polar group but with the chains in a frozen state. Furthermore, it was demonstrated that polymerization of the lipid layer strongly reduces the short-range repulsion. These findings demonstrated that the mobility of the molecules in the bilayer have an important bearing on the magnitude of the repulsion, and this led to a completely different suggestion for the molecular origin of this force. It was proposed that the motion of molecules in the bilayer, in the normal direction to the bilayer, was hindered by the proximity of a second bilayer. This reduced the entropy of the system and generated a repulsive force known as the protrusion force or the steric protrusion force. The debate on the main origin of the repulsive force between phospholipid bilayers, and between other surfactant and lipid bilayers, is still continuing, and a theoretical discussion on the nature of this repulsion, providing arguments in favour of either point of view, has been presented recently (see ref. 14 and references therein).

A detailed set of experiments was carried out by McIntosh and co-workers, who measured pressure-distance data by X-ray diffraction analysis of osmotically stressed lipid multilayers in the subgel phase. They also performed a series of experiments using substitutions in the structure of lipid molecules to study the short-range force acting between phospholipid bilayers. The results of their experiments suggest that the short-range repulsive force has three regimes. The first regime is at large distances, where the force depends on the phase of the lipid bilayer, and it is suggested that the interactions are mainly caused by undulation of the membrane surfaces. (A discussion on undulation forces can be found in e.g. 16.) In the second regime, when the distance between the membrane surfaces is in the 0.4–0.8 nm range, the force is independent of the lipid phase, and it was suggested that this force is due to dehydration of the lipid head group. In this regime there are roughly two to three layers of water that separate the membrane surfaces. Finally, in the third regime, when the distance between the bilayers is below 0.4 nm, steric interactions between head groups are proposed to play the dominant role. These observations led to the conclusion that the part of the repulsive force that is due to dehydration of the head group is rather short-ranged and that the surface influences the structure of water only one to two layers away from the surface. The interpretation of these measurements was later corroborated by simulations.

The swelling pressure between different monoglycerides has also been investigated at different temperatures. In the lamellar phase, a strong repulsive force is observed, which does not depend significantly on the type of monoglyceride or on the temperature. In the gel phase, the repulsive pressure is significantly lower. Thus, for both monoglycerides and phospholipids a decreased mobility of the molecules is found to lower the magnitude of the short-range repulsion. The measurable range of the swelling pressure is less for monoglycerides than for phospholipids (about 1 nm for monoglycerides and 2–3 nm for phospholipids), demonstrating the decisive role of the polar head-group. A comparison with the forces acting between monoglyceride layers deposited on solid surfaces, measured by a surface force apparatus, reveals a qualitative agreement between surface force and osmotic stress techniques. The most significant difference is that the repulsive force at short separations is lower between deposited layers than between free bilayers. This can be rationalized in terms of differences in the change in area per molecule with bilayer separation for the two experimental techniques mentioned above. In the SFA it is expected that the area/molecule increases as the repulsion increases with decreasing separation, whereas in an osmotic stress measurement the area/molecule is expected to decrease as the bilayer separation is decreased.

The assumption that the chemical nature of the head group is crucial for the magnitude of the short-range forces in liquid crystalline phases has also been confirmed by comparing the interactions and structural parameters of the hexagonal and lamellar phase of simple surfactant systems such as dimethyl-dodecylamine oxide (DDAO)–water and the dimethyl-dodecylphosphine oxide (DDPO)–water. It was found that the swelling pressure was considerably higher in the DDAO–water system than in DDPO–water. Furthermore, the repulsion decreased significantly with increasing temperature for the DDPO–water system and only marginally for the DDAO–water system. These results are consistent with the finding that micellar solutions of DDPO phase separates on heating, whereas micellar solutions of DDAO do not. In passing we note that water interacts exceptionally strongly with the amine oxide head group, where the hydration in the lamellar phase has been found to be both enthalpically and entropically favorable.

The hydration of surfactants with oligo(ethylene oxide) head groups have also been described in a few reports. Pfeiffer et al. concluded that the hydration pressure in the lamellar phase decays roughly exponentially, whereas a non-exponential decay was found in other liquid crystalline states, which was suggested to be related to the bending energy of non-lamellar liquid crystalline phases. The results demonstrate that the repulsion is largely unaffected by the hydrocarbon chain length, and increases substantially with the number of ethylene oxide groups present in the head group. This is qualitatively consistent with the short-range interactions determined across foam films stabilized by such surfactants. Pfeiffer et al. also found that surfactants in the solid crystalline state show almost no hydration.

7. Summary and outlook

The short-range interaction between surfactant layers exposing the polar groups towards the bulk is due to a complex interplay between van der Waals forces, hydration and steric effects. It is only the total force that can be measured, and this force displays both attractive and repulsive regimes. The interpretation of the results in terms of different force contributions relies on theoretical and simulation efforts. In our analysis of the available data we find that the van der Waals interaction is the main attractive force. Furthermore, differences in the attractive force contribution found for different
surfactant systems can also be rationalized by differences in dielectric properties and water content in the adsorbed layers. The simplicity of the van der Waals analysis impedes us from drawing far-reaching conclusions despite the fact that in some cases nearly quantitative agreement was found. The reason for this is that the van der Waals analysis is too simple. Nevertheless, we argue that hydrogen bonding between adsorbed layers play a minor role compared to van der Waals interactions. The exception to this rule is found when considering interactions between relatively large sugar groups, where the data is best interpreted in terms of hydrogen bonding interactions, directly or via water molecules. Hydrogen bonding within adsorbed layers, again directly or mediated by water molecules, increases the packing density within adsorbed surfactant layers and this increases the van der Waals force.

In order to advance our understanding further we need to gain more insight into the nature of hydration phenomena of polar groups. There is a need to elucidate the extent of hydration, where different techniques will give different answers, and the structure of the hydration layer that differs strongly between different non-ionic polar groups. To this end the VSFS technique is promising since it allows vibrational spectroscopic studies of interfacial water without interference from the bulk phase. Since both hydration and the mobility of surfactants are important for the short-range interactions it seems probable that advances in theoretical understanding will come mainly from simulation work. The steric interaction between surfactants with oligomeric head groups also deserves further attention. It has been observed that as the head group size increases the short range repulsion goes from a (close to) hard wall repulsion, via a compressible excluded volume repulsion to a steric repulsion described by polymer brush theories. The boundary between these two latter regimes deserves to be further explored. We note that so far systems containing only one surfactant have been explored nearly exclusively. On the other hand, it is well known that mixed surfactant systems may show synergism in terms of surface tension lowering and in terms of adsorption to solid surfaces. It largely remains to be shown if synergism in terms of surface sorbed layers play a minor role compared to van der Waals interactions. It largely remains to be shown if synergism in terms of surface tension lowering and in terms of adsorption to solid surfaces. Surfactant systems may show synergism in terms of surface tension lowering and in terms of adsorption to solid surfaces. On the other hand, it is well known that mixed surfactant systems may show synergism in terms of surface tension lowering and in terms of adsorption to solid surfaces. This work was supported by the Marie Curie network “Self-assembled nanostructures: from understanding to manipulation”.

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