Adsorption and Ordering of Surface Active Molecules and Particles at Solid Interfaces and in the Bulk

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Abstract

Factors that influence the process of adsorption and order of dilute and concentrated systems of molecules and particles are explored in this thesis. The results are based largely on neutron scattering techniques. Study of the adsorption from dilute solutions of a common surfactant, AOT (sodium bis (2-ethylhexyl) sulfosuccinate), at a solid/liquid interface showed that AOT molecules adsorbed to the interface in a bilayer structure, with the hydrocarbon tails at maximum packing density even at very low concentrations. At higher AOT concentrations, a stack of fluctuating layers each separated by large amounts of water next to the dense bilayer was seen. The driving force for adsorption is dominated by self-assembly of AOT. It was found that an oriented lamellar phase wets the interface below the bulk concentration for formation of this phase.

Proteins can be viewed as polymeric surfactants. The adsorption of proteins from seeds of the Moringa oleifera tree to a silicon oxide surface was studied to elucidate the mechanism of the protein as a flocculent in water treatment processes. The protein was found to adsorb at the interface as dense layers with a thickness suggestive of co-adsorption rather than single isolated molecules. The strong adsorption and tendency to associate in solution suggest mechanisms for flocculating particulate impurities in water.

As with surfactants, dispersions of colloidal particles can assemble in regular structures by self-assembly. Polystyrene latex particles were studied and could form large three-dimensional crystals of about 1×1 cm² in a 2 mm path cell. The diffraction pattern indicated a close packed structure with the 110 axis perpendicular to the container wall. The crystal was well-aligned and oriented by the direction of flow. At the solid interface large two-dimensional domains of about 20 cm² of highly oriented particles were formed. The particle-particle separation at the surface and in the bulk was determined by the charge repulsion of the particles.

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To Ella and Noah,

my wonderful children
List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.


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Publications not included

The following papers are not included in this thesis.


Comments on my participation

The following is a brief description of my contribution in the publications:

I  Responsible for designing and performing experiments, sample responsible, carried out the analysis and responsible for writing the manuscript
II Responsible for designing and performing experiments, sample responsible, carried out the analysis and responsible for writing the manuscript
III Responsible for designing and performing experiments, sample responsible, carried out the analysis and responsible for writing the manuscript
IV Responsible for designing and performing experiments, sample responsible, carried out the analysis and responsible for writing the manuscript
V  Participated in measurements, analysis, and writing the manuscript
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1 Introduction

The food that we eat, the paint we apply to walls in our homes and the soap we use to wash ourselves, are all examples of materials that are neither simple liquids, nor crystalline solids. This class of materials is called soft condensed matter. There are many different materials that fall into this category. These include polymers, emulsions and a variety of biological materials, all of which have a number of features in common:

- The important length scales, larger than atoms but typically smaller than micrometers.
- They are dynamic – the particles and assemblies of molecules are small enough for Brownian motion.
- They have a large surface area compared to bulk material.

This thesis is mainly based on the study of two types of materials that form soft condensed matter: surface active molecules and colloidal particles. In both cases, the species investigated were dispersed in pure water. This makes the system dynamic, yet consisting of well-defined structures that can be measured and modelled quantitatively at equilibrium. At low concentrations, the molecules or particles are on average separated sufficiently that their interactions are negligible. They move randomly by Brownian motion. As the concentration is increased, forces of attraction and repulsion between the molecules or particles begin to influence the system. Soft condensed matter is held together by intermolecular forces. These forces can be controlled by making changes to the system other than the concentration, for example by altering the ionic strength or the temperature. The behaviour at a solid interface may be different to that found in the bulk, where the interactions are essentially symmetric. The interface breaks this symmetry and creates an imbalance. Understanding the factors that control adsorption of molecules and particles at interfaces are relevant to many fields and can be applied in both industry and technology.

1.1 Surfactants

Surfactants are usually amphiphilic molecules that consist of a hydrophilic head and a hydrophobic hydrocarbon tail region. Surfactants can be ionic, non-ionic or zwitterionic. An ionic surfactant has an ionisable head group that can have either negative or positive charge. Hexadecyltrimethylammonio-
nium bromide \((C_{16}TAB, \text{CH}_3(\text{CH}_2)_{15}N(\text{Br})(\text{CH}_3)_3)\) is an example of a cationic surfactant where the head group consists of the positively charged quaternary ammonium cation and the bromide ion are dissociated in solution. A non-ionic surfactant has a head group that is not ionisable but still hydrophilic, for example the ethylene oxide units \((\text{EO}, \text{-OCH}_2\text{CH}_2\text{-})\) in tetraethylene glycol dodecyl ether with chemical formula \(\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_4\text{OH}\). A zwitterionic surfactant contains two different groups – one that can gain and one that can lose a charge (such as acid and base) for example trimethylammonioacetate (betaine) with chemical structure \((\text{CH}_3)_3\text{N}^+\text{CH}_2\text{CO}_2^-\). The two groups can dissociate and provide a head group with no net charge.

There are both attractive and repulsive potentials present between surfactant molecules in solutions, as for matter in general. The van der Waals potential is generally attractive, arising from fluctuating random dipole moments in the molecules. Between a pair of molecules, the van der Waals attractive potential varies as \(1/r^6\), where \(r\) is the separation distance between the molecules. When the molecules are sufficiently far apart \((r > 100 \text{ nm})\) the energy variation with distance becomes \(1/r^7\) as the time taken for the electric field from the first molecule to reach the second and return becomes comparable to the period of the fluctuating dipole itself.\(^1\) Electrostatic interactions between charged particles that are repulsive for like charges are stronger than the van der Waals potential if the colloids are stable. Electrostatic interactions are screened by the ions that are always present in aqueous solutions. The electrostatic potential \((\Psi)\) for dilute solutions decays exponentially as \(\Psi(x) \sim \exp(-\kappa x)\), where the decay length, \(\kappa^{-1}\) is the Debye screening length and \(x\) the separation of particles, and \(\kappa = [(e^2/\varepsilon_r \epsilon_0 k_B T)\Sigma_i z_i^2 n_i]^{1/2}\), where \(e\) is the elementary charge, \(\varepsilon_r\) relative permittivity, \(\epsilon_0\) the dielectric constant, \(k_B\) is the Boltzmann constant, \(T\) is absolute temperature \((k_B T\) describes the thermal energy), the sum over all types of ionic species as \(z_i\) is the number of elementary charges for every type of ion \(i\), and \(n_i\) is the average number concentration of ions of type \(i\) in the sample. This is shown schematically in Figure 1.7.\(^1,2\)

### 1.1.1 Phase behaviour of surfactants

In aqueous solution at low concentrations, surfactant molecules are freely dissolved with their head groups hydrated. The hydrophobic hydrocarbon tails however will not easily dissolve. Hydrogen bonding of water is inhibited across the surface area of the tail, and so it requires energy for the tails to be in contact with an aqueous solution.\(^3\) This chemical structure makes it particularly favourable to be located near an interface. The presence of surfactants at an interface will lower the surface tension of the medium in which they are dissolved. This is shown schematically in Figure 1.1 for an air/water interface, where the surface tension at the interface is shown as a function of surfactant concentration.
Surface tension is a measure of energy per area, which is equivalent to a force per unit length exerted by, as shown in Figure 1.1, water in contact with air. As the concentration of surfactant molecules is increased, the surface tension drops. When the concentration has reached a certain level, the curve suddenly levels out, the surface tension becoming close to constant. The point where the curve levels out is called the critical micelle concentration (cmc). Here it becomes energetically favourable for the molecules to self-assemble into (often) spherical structures called micelles, which exist in equilibrium with dissolved molecules. This is because in the micelles, the hydrophobic tails in the core of the micelle are protected from water by the hydrophilic head groups located at the surface. This is favourable despite repulsions at the surface that may occur between the head groups that are sometimes charged and come into close proximity, and despite the loss of entropy from forming a more regular structure. In the micelles the head groups are hydrated, and for ionic surfactants are also associated with counter-ions. The formation of micelles can only happen if the temperature is above the so called Krafft boundary, as below the Krafft boundary surfactant molecules cannot dissolve.\(^5\)

It is worth noting that a surfactant solution at the cmc is a system in dynamic equilibrium, where surfactant molecules can leave and rejoin micelles. For ionic surfactants where there are counter ions associated with the micelle surface, the counter-ions are not bound to a particular position, but can move freely around the micelle surface.

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**Figure 1.1.** Schematic representation of surface tension at the air/water interface as a function of surfactant concentration. Re-drawn from reference 4.
On increasing the concentration above the cmc, new micelles may form, or the additional molecules may assemble into already formed micelles resulting in micelles that are growing in size. There is a maximum number of molecules that can be associated with any size and shape of micelle, which depends on the structure of the individual molecules. Normally the so-called aggregation number falls in the region of 50-100 molecules per micelle. As there can be no void in the centre of the micelle, and also the whole of the surfactant molecules need to fit inside the micelle, the diameter of the micelle is determined by the lengths of two tails, plus the thickness of two head groups including the space taken up by water and counter-ions in the head group region. When the micellar system is saturated, more elaborate structures can be formed through self-assembly, such as cylinders and bilayers as in the lamellar phase and vesicles, shown in Figure 1.2. The type of structure that is formed is determined by the shape of the individual surfactant molecules. Overall, surfactants with a single tail and a large head group are overall cone-shaped and they will form spherical micelles, while if the head group is small cylinder shapes will instead be formed. Surfactants with two tails are overall cylinder-shaped, and will, as a consequence, readily form bilayer structures, lamellar phases, which are more curved if the head group is large. Also reverse micelles can be formed in apolar solvents.

Figure 1.2. Schematic diagram of some possible surfactant structures above cmc.
One surfactant investigated in this thesis is sodium bis (2-ethylhexyl) sulfo-succinate, called aerosol-OT or AOT for short. The family of aerosols are salts of diesters of succinic acid that contain a sulfonate substituent group in the succinate moiety. The chemical structure of AOT is shown in Figure 1.3. It is a small molecule with a hydrophilic anionic head group through dissociation of the sodium ion in solution, with two branched tails. The Krafft temperature for AOT is below 0°C, and the cmc is 2.5 mM or 0.1% by weight at room temperature in pure water. The hydrophobic and hydrophilic regions of AOT have approximately equal cross-sectional areas, which makes AOT pack efficiently into planar bilayer structures found in the lamellar phase at concentrations above the cmc. The bilayers found in the lamellar phase are still dynamic equilibrium systems, where molecules can move between the layers, exist in between the layers and also the layers themselves fluctuate due to Brownian motion. The phase diagram for AOT was published by Rogers and Winsor in 1969. A part of this phase diagram is shown in Figure 1.4.
The two black dots in the diagram in Figure 1.4 indicate measured data from which, along with data at higher concentrations and temperatures not shown in Figure 1.4, the phase boundaries (lines) have been extrapolated. For concentrations below 2.5 % wt AOT is expected to be in a micellar phase at room temperature. At concentrations higher than 2.5 % wt AOT will begin to form lamellar structures in equilibrium with micelles and freely dissolved molecules. At concentrations above approximately 10 % wt there is a true lamellar phase at room temperature. Apart from changing the concentration and temperature, the phase that is formed is dependent on the ionic strength and may also depend on the pH of the solution. AOT can be forced into a more structured phase, that is, one where the hydrophobic tails are protected, at a lower surfactant concentration by the addition of salt that will increase the ionic strength of the solution. The effect of changing the pH is described in Paper I.
1.1.2 Surfactants at an interface

Even at concentrations below the cmc, surfactants can form ordered structures such as bilayers at the presence of an interface, in equilibrium with freely dissolved molecules in the bulk of the solution. This is shown in Figure 1.5. The amount of material at the interface is called surface excess, and values are often given in units of mg m$^{-2}$. As the concentration is raised the surface layer becomes saturated, and will eventually exist in equilibrium with more complex near surface and bulk structures. Understanding the factors that control adsorption of molecules at interfaces is important for example in industrial applications and the optimisation of formulations for detergents and personal care products.

1.1.3 Proteins

Molecules made up of many small units linked together are called polymers. Proteins can be viewed as being polymeric surfactants. They occur in abundance naturally. Proteins generally consist of one or more polypeptide chains that are typically folded into complex three-dimensional structures. A polypeptide is a linear polymer chain made up of a sequence of amino acids held together by peptide bonds between the carboxyl and amino groups.

1.1.3.1 Protein adsorption at the solid/liquid interface

The molecular structures of proteins make them good stabilizers. In milk, for example, the protein casein stabilizes fat droplets. When proteins adsorb to a surface, only parts of the molecule are attached, the rest of the molecule remain solvated so that they very efficiently keeps particles apart. Proteins are charged and this adds to the efficiency as stabilizers. Proteins often adsorb to a solid interface irreversibly, a property that is used in many areas. Paper V in this thesis describes the molecular interaction/adsorption of a
naturally occurring protein extracted from the seeds of the *Moringa oleifera* tree at the silicon oxide/water interface. There is no concern with the biological function of the proteins in the work described in this thesis, rather the use as natural occurring materials in a process application is considered.

These seeds have long been known to purify water. There has been extensive research into the extraction, purification and efficiency of the seeds, as well as evaluation of the quality of the treated water.\(^8,9,10,11,12,13,14,15\) The protein amino acid composition has been reported.\(^16,17,18\) The protein purifies water by forming large aggregates incorporating impurity particles that can be readily removed by filtration. The understanding of the molecular interactions in the adsorption process as studied in Paper V can be used to optimise the amounts of protein used in water purification process.

### 1.2 Colloidal particles

Particles in colloidal systems have dimensions larger than individual atoms or molecules and typically smaller than about 10 \(\mu\)m. Their interactions are as a consequence of their size dominated by their relatively large surface area compared to that of the bulk within the particle. The colloidal system described in this thesis is of spherical particles, and the following arguments will be focused on spherical particles. The stability of colloidal dispersions is a delicate balance of forces. Just like for surfactants, there are attractive van der Waals forces between the particles, in balance with repulsive forces. The particles are small enough to be able to move by Brownian motion. This motion may cause the particles to collide with each other, resulting in the particles sticking together irreversibly. With time larger and larger aggregates would form.

One way of overcoming the particles coming into contact with each other and sticking, flocculating, is by steric stabilization where the particle interface is modified by attaching polymer chains to the surface so that the particles are hindered from coming into contact with each other, or by introducing surfactants in the system. Another way of keeping the particles dispersed is by charge stabilization, where the particles carry a net charge on their surface in solution, repelling other particles of like charge. Charged particles in dispersions are similarly to surfactants associated with counterions of opposite charge surrounding their surface that will screen the repulsive electrostatic potential, while the overall dispersion remains neutral. This is shown schematically in Figure 1.6.
Figure 1.6. Schematic illustration of charge stabilized particles that carry a net negative charge on their surface, and their associated counter-ions. The dispersion is over-all neutral.

The DLVO theory is named after two independent groups; Deryagin and Landau, and Verwey and Overbeek, who separately developed the theory. It is a theory that describes the interactions between charged particles as the sum of the van der Waals attractive and the screened electrostatic repulsive potential. According to this theory the lowest energy state, the primary minima, is obtained when the particles are very close together, the attractive potential being dominant. Colloids that are separated from each other in stable equilibrium dispersion, reside in a secondary local energy minima (metastable), if the energy barrier of attractive and repulsive potentials is large enough to prevent them from entering the primary minima. This is shown in Figure 1.7. Charge stabilized colloids are therefore very sensitive to changes of the ionic strength of the dispersion medium that will alter the energy barrier between the primary and secondary energy minima. Increasing the ionic strength by the addition of salt decreases the energy barrier as the particle-particle repulsion potential is reduced through screening. At sufficiently high salt concentration, the particles will flocculate. This is called the critical coagulation concentration.
Gravity can be also an issue in stability of colloidal dispersions. Particularly for larger particles, where if the particles are less dense than the dispersing medium the particles may raise to the surface, cream. Particles more dense than the medium can sediment. Brownian motion will oppose creaming and sedimentation, and for smaller particles the effect of gravity is less important.

1.2.1 Colloidal phase behaviour

As with surfactants, colloidal particles in dispersions show interesting phase behaviour by self-assembly. They can exist as disordered liquids, in crystalline packing, and many intermediate structures. At very low concentrations, the particles in dispersions are distributed throughout the dispersion medium without regular structure, at maximum entropy of the system, moving by Brownian motion. Charge stabilized particles dispersed in de-ionised water that reside in the secondary local energy minima as shown in Figure 1.7, can form regular structures at rather low particle concentrations. As the concentration is increased, colloidal crystals can form. One condition for this to happen is that the particles have to be sufficiently mono-disperse. The Lindeman criterion for melting states that this phase transition occurs when a solid expands by 10%. If there are local distortions of that magnitude,
one might expect the structure to become amorphous. When spherical colloidal dispersions crystallize by self-assembly, they form close packed structures, often with many stacking faults, see for example references 2,22,23,24. Less dense crystal structures such as the body centred cubic (bcc) are found for lower colloidal particle concentrations. Colloidal crystals with order in three dimensions can be described in crystallographic terms, and higher concentration dispersions often assemble in face centred cubic (fcc) and hexagonal close packed (hcp) structures. The only difference between these two structures of close packed hexagonal layers is the position of subsequent layers. This is indicated in Figure 1.8. For fcc the packing sequence is abcabc… and for hcp the packing sequence is ababab…

![Figure 1.8](image)

Order and crystallization can be induced in colloidal dispersions by external fields, even if the concentration is not high enough for the particles to self-assemble into regular structures as described above. Flow is an efficient means to align colloidal particles that promotes close packed structures. Exposing colloidal dispersions to flow can also destroy order formed by self-assembly. It may also transform a structure of close packed layers from for example predominantly (fcc) to predominantly (hcp) structures. Order can also be induced if the particles sediment by gravity, forming a more concentrated phase at the bottom of a container. For sterically stabilized systems, other crystal structures are observed, particularly in mixed particle-size systems (see for example reference 30).

The colloidal dispersions investigated in this work were charge stabilized monodisperse spherical polystyrene latex particles dispersed in pure water. The particles provide a good model system as they are perfect spheres and can be prepared very monodisperse. From the emulsion polymerization process using potassium persulfate initiator, the particles carry a negative charge on the surface that repels other particles, keeping the dispersion stable and the particles uniformly distributed.
1.2.2 Colloids at an interface

The way particles assemble at an interface may be different from that found in the bulk. At an air/liquid or liquid/liquid interface for example, there can be a favoured position that will optimise the contact angle between the two different phases so as to minimise the energy, or balance forces. Pickering emulsions are an example where solid particles act as surfactants, residing at liquid/liquid interface stabilizing two partially or immiscible liquids. At a solid/liquid interface there might be specific interactions such as charge or molecular binding that are the driving force, and this is rather similar to molecular surfactants. Hydrophilic particles like polystyrene latex would for example readily assemble at a hydrophilic interface.

Just as colloidal dispersions can form three-dimensional crystals in the bulk, structures with two-dimensional crystal order can be found at interfaces. The first report of an observation of a two-dimensional colloidal crystal was in 1980, and it involved a polystyrene latex at the air/water interface. Since then there has been extensive work on ways to produce large areas of highly ordered two-dimensional structures. This is partly due to technological requirements in fields such as photonics, where knowledge derived from colloidal science is valuable.

The order of colloidal bulk dispersions can be induced by for example flow, and the same argument holds at an interface. At the solid/air interface methods such as spin-coating and drop-deposition can be used to achieve two-dimensional crystallization.
2 Sample preparation and characterization

The work in this thesis is based on samples of surface active molecules and colloidal particles. It is vital that well-characterized high purity samples are used in order to interpret correctly the effects from exposing the materials to various factors in highly controlled environments.

The anionic surfactant AOT was used in studies of adsorption at the hydrophilic sapphire interface. This work relates to other studies of AOT at interfaces such as the hydrophobic and hydrophilic silica surfaces. The role of the net negative charge on the bilayer along with associated oppositely charged counter-ions, as well as molecular structure could be investigated in the adsorption study, and compared to the adsorption of the non-ionic surfactant Brij-30 at the sapphire interface.

The choice of investigating the protein Moringa oleifera, a small, globular and charged polymer, was primarily to deduce its adsorption behaviour and hence mechanism as a flocculent in water purification treatment.

Self-assembly of colloidal dispersions was investigated with charge stabilized polystyrene latex, where again the balance of forces involved in structure formation could be investigated both at the interface and in bulk.

The results from the two main types of systems – molecular and particle – makes for interesting comparisons, as the molecular structures are very small and separated by large amounts of water, whereas the particles are, relative to molecules, large and separated by small amounts of water.

2.1 Surface active molecular samples

2.1.1 AOT

The surfactant AOT, sodium bis (2-ethylhexyl) sulfosuccinate, C₂₀H₄₇O₇SNa, was obtained from Sigma-Aldrich (98% purity). It was prior to measurements purified by liquid-liquid extraction following the procedure described by Li et al. as follows; AOT (2.5 g) was dissolved in pure H₂O (50 ml), whereby heptane (5 ml) was added. Organic impurities would more readily dissolve in heptane, and after mixing the heptane layer was separated off, leaving pure AOT aqueous solution. The AOT aqueous solution was freeze-dried for approximately 72 hours after rapid cooling in liquid nitrogen in order to remove all water leaving dry AOT powder. The measurements in
Paper I and II were made up from dilutions of stock solutions of purified AOT dissolved in $\text{D}_2\text{O}$ (Deuterium oxide, heavy water) or mixtures of $\text{D}_2\text{O}$ and pure water, in Paper I sometimes with addition of different salts, as well as the base NaOH and the acid HCl.

2.1.2 Other surface active molecular samples

Brij-30 was purchased from Sigma-Aldrich and used as received. Brij-30 contains a mixture of tetraethylene glycol dodecyl ether; $\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_4\text{OH}$ and pentaethylene glycol dodecyl ether; $\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_5\text{OH}$, predominantly tetraethylene glycol dodecyl ether.

SDS, sodium dodecyl sulfate, $\text{C}_{12}\text{H}_{25}\text{OSO}_3\text{Na}$, was purchased from Sigma-Aldrich ($\geq 99\%$ purity), used without further purification.

In Paper V the adsorption of proteins extracted from seeds from the tree *Moringa oleifera* were used. The sample was prepared by the group of Dr H. M. Kwaambwa in Botswana, following the method of Ndabigengesere and Narasiah.  \cite{note39}

2.2 Polystyrene latex

The polystyrene latices reported in paper III and IV were synthesized by emulsion polymerization, as previously described by Goodwin et al. \cite{note40}

Firstly styrene (Merck $\geq 99\%$ purity) was distilled at low pressure to remove any inhibitor. The emulsion polymerisation was made in deionised water under nitrogen gas flow with added sodium dodecyl sulfate (Sigma-Aldrich $\geq 99\%$ purity). Re-crystallized potassium persulfate was used as initiator (Fluka $\geq 98\%$ purity) and the reaction was allowed to continue for 24 hours with heat and constant stirring. Details of the reactions are provided in Table 2.1. By changing reaction parameters, different size latices were obtained. The latex was dialysed extensively after the reaction (pre-washed dialysis membrane obtained from Spectra/Por 7; 3.7 ml cm$^{-1}$, molecular weight cut-off 50000 formula weight) in deionised water (resistivity 18 MΩ cm) to remove ionic and surfactant residues that remained from the polymerisation process. The use of potassium persulfate in the emulsion polymerisation process leaves sulfate groups on the particle surface and the latices carry a net negative charge.

To obtain higher particle concentrations of the latices than the concentration obtained at the polymerisation process, the technique of pervaporation was used. Pervaporation was performed by putting the latex in dialysis tubing (described above; Spectra/Por 7) which was allowed to hang in air in a refrigerator until the desired amount of water was lost. To give some time
estimate for the process, increasing the concentration of 50 ml latex from 7 to 10% by volume would take approximately 3 days.

<table>
<thead>
<tr>
<th></th>
<th>PS3</th>
<th>PS4</th>
<th>PS11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene / g</td>
<td>73.42</td>
<td>73.12</td>
<td>73.04</td>
</tr>
<tr>
<td>Potassium persulfate / g</td>
<td>0.50</td>
<td>0.62</td>
<td>0.60</td>
</tr>
<tr>
<td>Sodium dodecyl sulfate / g</td>
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<td>1.11</td>
<td>2.10</td>
</tr>
<tr>
<td>H₂O / g</td>
<td>718</td>
<td>718</td>
<td>718</td>
</tr>
<tr>
<td>Temperature / °C</td>
<td>60</td>
<td>70</td>
<td>70</td>
</tr>
</tbody>
</table>

Table 2.1.

In the preparation of PS3, by doing the emulsion polymerisation at a lower temperature of 60 °C, larger particles were obtained. The radius was found to be 724 ± 10 Å, with a Gaussian distribution polydispersity of 4 % obtained from model fits to neutron data as shown in Figure 2.1. The particles were also characterized by scanning electron microscopy (see Paper III), dynamic light scattering (ALV-5000 multiple digital autocorrelator, HeNe laser and diode detector, measurements at 25°C and scattering angle 90 degrees) and atomic force microscopy (Nanosurf Mobile S, measurements performed in contact mode). The number average radius from these measurements was 720 Å with a polydispersity of about 2 %. The particle concentration was determined by dry weight to be 8.7 % by volume.

![Figure 2.1](image)

Figure 2.1. PS3, PS4 and PS11 form factor P(Q) and model fit. For clarity, PS4 data and fit were multiplied by 0.1, and PS11 data and fit were multiplied by 0.001. The error bars are very small, and most lie within the data point symbol.

The PS4 latex was polymerised at 70°C, and the increase in reaction temperature of 10°C compared to PS3 resulted in particles with a smaller radius of 483 ± 18 Å, with a polydispersity of about 4 % (values obtained from
model fits to small angle scattering data shown in Figure 2.1). The particles were also characterized by scanning electron microscopy (Figure 2.2), atomic force microscopy and dynamic light scattering. The number average radius from these measurements was determined to be 490 Å. The particle concentration was 7.8 % by volume, determined by dry weight.

For PS11 the amount of surfactant in the polymerization reaction was doubled compared to PS4 and PS3, in order to achieve even smaller size particles. PS11 was found to have a particle radius of 370 ± 30 Å with a polydispersity of 8% (neutron scattering, Figure 2.1). The particles were also characterized with dynamic light scattering, radius 440 Å. The particle concentration was 7.0 % by volume (by dry weight).

Figure 2.2. SEM image of a dried dilute sample of PS4 (electron beam 5kV).

In Figure 2.1 the form factor $P(Q)$ is shown for the three latices PS3, PS4 and PS11 mentioned above, all dispersed in D$_2$O, the solid line though the data points is the model fit. The form factor depends on the particle size and shape, and is measured with small angle neutron scattering (described in section 3.3 in this thesis). The sample is diluted to a known concentration, often about 0.5% vol. and 1 mM salt is added in order to screen out any inter-particle interactions (known as $S(Q)$ in small angle scattering terminology). The particle size and shape can be determined well from the positions of the first $P(Q)$ minima. Figure 2.1 shows that as PS3 has the largest size particles, the first $P(Q)$ minimum arise at the lowest $Q$ value; $Q = 0.006$ Å$^{-1}$, followed by medium sized particles PS4 with $Q = 0.009$ Å$^{-1}$ for the first minimum, and finally PS11, the latex with smallest size particles; first minimum at $Q = 0.013$ Å$^{-1}$. The visibility of the minima in $P(Q)$ is an indication as to how monodisperse is the latex, as a distribution of size will smear the minima out. It can be seen that PS3 has a very low polydispersity (4%) while PS11 has higher (8%).

For studies of mixtures of different size latices, it is useful to have one deuterated and one hydrogenous, so that the relative positions of each can be determined in a neutron scattering measurement. For this purpose, PSD1
and PS10 were synthesised by the same procedure as described above. The reaction parameters are shown in Table 2.2. PSD1 is a deuterated latex where the hydrogen atoms have been exchanged for deuterium atoms. PS10 was prepared in a large excess of sodium dodecyl sulfate, in order to produce latex with a very small particle radius.

**Table 2.2**

<table>
<thead>
<tr>
<th></th>
<th>PSD1</th>
<th>PS10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene / g</td>
<td>3.65</td>
<td></td>
</tr>
<tr>
<td>d-Styrene / g</td>
<td>3.66</td>
<td></td>
</tr>
<tr>
<td>Potassium persulfate / g</td>
<td>0.032</td>
<td>0.034</td>
</tr>
<tr>
<td>Sodium dodecyl sulfate / g</td>
<td>0.11</td>
<td>1.00</td>
</tr>
<tr>
<td>H₂O</td>
<td>40.3</td>
<td>40.3</td>
</tr>
<tr>
<td>Temperature / °C</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>Radius / Å</td>
<td>410</td>
<td>180</td>
</tr>
</tbody>
</table>

2.3 Surfaces and cleaning

For neutron reflection measurements of adsorption of molecules or particles at a solid/liquid interface, the smoothness and cleanliness of the substrate for adsorption is of crucial importance. Sapphire single crystals were obtained from PI-KEM Ltd and cut on the (0001) plane. Silicon crystals (111) face covered with an oxide layer were obtained from Crystran. The crystals obtained were polished to a roughness of less than 10 Å. Before the measurements, the crystals were cleaned with ‘dilute piranha’ at a temperature of 80°C for 15 minutes. ‘Dilute piranha’ consists of concentrated sulphuric acid (H₂SO₄), hydrogen peroxide (H₂O₂) and pure water in ratios 4:1:5. This mixture removes effectively inorganic impurities. It should be handled with immense care. There are also ideas that the cleaning procedure may affect the substrate surface chemistry, and hence all substrates used in measurements included in this thesis were cleaned the same way.
3 Techniques and data interpretation

3.1 Neutron scattering

In this thesis, studies on solid/liquid interfaces were carried out with neutron reflection and grazing incidence neutron scattering. Bulk structures were probed with small angle neutron scattering. The following section will briefly describe aspects of scattering related to work presented in this thesis. For a more thorough introduction to neutron (and X-ray) scattering, reference 41 is recommended.

Neutron scattering is a technique well suited for studying materials at buried interfaces as well as bulk structures, as neutrons interact weakly with matter. The technique can in a straightforward manner measure structures on the length scale molecular up to sub-micron size. Neutron scattering is a nuclear interaction, and isotopic substitution, or ‘contrast matching’, is widely used to highlight specific components in complex systems. In scattering, information is derived from scattering length densities ($\rho$) of the measured material as $\rho = \Sigma n_i b_i$ where $n_i$ is the number density of the element and $b_i$ is the coherent neutron scattering length.

The scattering length density ($\rho$) determines the neutron refractive index (n), which is approximately given by the equation $n = 1 - (\lambda^2 \rho / 2\pi)$, where $\lambda$ is the neutron wavelength. Different molecules and isotopes have different values for $b_i$. Hydrogen and deuterium for example have very different scattering lengths, where for hydrogen $b_i = -1.68$ fm and for deuterium $b_i = 19.05$ fm. It is therefore possible to identify different components in a complex system by contrast matching for example solvent to substrate by using mixtures of H$_2$O/D$_2$O, or by using deuterated molecules or particles dispersed in H$_2$O. The principle of contrast matching is shown schematically in Figure 3.1 for a reflection measurement, where a bilayer structure is adsorbed at a sapphire interface, the sapphire having a scattering length density almost equal to that of D$_2$O. Hydrogen containing molecules such as most surfactants will therefore show up very clearly if dispersed in D$_2$O, but are almost invisible to neutrons if instead dispersed in H$_2$O. The same principles are naturally also valid for bulk studies.
3.2 Neutron reflection

Neutron reflection is a technique that probes structures perpendicular to an interface. The scattering geometry is shown schematically in Figure 3.2, for the sample in horizontal (Figure 3.2a) or vertical (Figure 3.2b) geometry. For specular neutron reflection, the angle of the incoming neutron beam ($\theta_I$) is the same as the angle of the reflected beam ($\theta_R$). The reflectivity is the ratio of the intensity of the reflected beam ($I_R$) to that of the incoming neutron beam ($I_I$); $R(Q_z) = I_R/I_I$ where $Q_z$ is the wave vector transfer perpendicular to the interface $Q_z = (4\pi/\lambda) \sin \theta$ and $\lambda$ is the wavelength of neutrons. Measurements can be done in monochromatic mode by varying the angle, or at a fixed angle in time-of-flight mode where the wavelength of neutrons is determined from a polychromatic pulsed source, and most commonly a combination of both.

Off-specular scattering can arise when there is lateral structure across the interface in the x- and/or y-directions, of length scales smaller or comparable to the coherence length of the neutron beam (typically in the order of micrometer). For off-specular scattering, the angle of the incoming beam is not the same as the angle of the reflected beam.
3.2.1 Data interpretation

The scattering length density ($\rho$) determines the neutron refractive index, and reflectivity can be calculated from the profile of refractive index as a function of the thickness of an adsorbed layer. By matching $\rho$ of the solvent with that of the substrate, one can obtain a signal that depends only on the interfacial layer. By making additional measurements with different isotopic composition of the solvent, one can verify the composition of the surface layer(s). $\rho$ is related to the volume fraction of each component in the layer as $\rho_{\text{layer}} = \sum \phi_i \rho_i$ where $\phi_i$ is volume fraction of component $i$ and $\rho_i$ is its scattering length density. Tables with parameters relevant to the systems described in this thesis can be found in the respective publications.

If a molecule in the adsorbed layer has a total scattering length $b_L$ (that is the sum of all components in the molecule) then the area per molecule $A$, in the interfacial layer of thickness $t_L$ is $A = b_L / (t_L \phi_L \rho_L)$ which is an average area per molecule over the entire surface that is being measured. The optical matrix method of Abelès$^{43}$ can be used to calculate reflectivity $R(Q)$. For a bilayer structure there are two molecules involved in the layer thickness $t_L$, and for surfactants it is often useful to identify the area per head- and tail region separately$^{44,45}$ rather than the molecule as one unit. The relevant parameters are shown schematically in Figure 3.3 for a multilayer structure. As the molecular volume is constant; $t_L = 2t_h + t_t$ where there are two head group regions $t_h$ in the layer, and one tail region $t_t$ which contains the tails from two molecules, which may or may not be intermixed.

*Figure 3.2. Neutron scattering geometries in a) horizontal b) vertical measurement set-up.*
The material adsorbed at an interface is called the surface excess (\(\Gamma\)) and is defined as follows: \(\Gamma = M / (A N_A)\) where \(M\) is the molecular mass of the material, \(A\) is the area per molecule as described above and \(N_A\) is Avogadro’s constant.

A repeating stack of bilayers such as in for example the lamellar phase of surfactants (Figure 3.3) or a colloidal crystal, will give rise to equally spaced Bragg diffraction peaks corresponding to the lamellar or particle separation \(d\) from midpoint to midpoint of the repeating structure. The condition for constructive interference is met when the path difference \(d\) is such that scattered waves from different planes add in-phase according to Bragg’s law for diffraction: \(n\lambda = 2d \sin \theta\). The momentum transfer \(Q\) at the first order Bragg peak gives the spacing \(d\) from: \(Q = 2\pi / d\) where \(d\) is the thickness taken up by the repeating structure and any separating water layer (\(t_{sol}\) in Figure 3.3).

The relative intensity of Bragg peaks from a repeating structure is reduced by disorder such as that caused by thermal fluctuations which are expected for bilayers in aqueous solutions. This reduction in intensity can be included in refined models describing the data by introducing a Debye-Waller factor of \(e^{-2W}\) where \(2W = Q^2 \xi^2 / 3\) and \(\xi\) is the root-mean-square displacement amplitude of the repeating structures. A full description of modelling the data in this way is given in Paper II. Determination of fluctuations also gives information of the elasticity of the bilayer.

Computer programs used to model data described in this thesis have been described by Adrian R. Rennie.\(^{46}\)

### 3.2.2 Grazing incidence and off specular scattering

Scattering around the specular position provides information about the lateral structure in the plane of the interface, and grazing incidence scattering (GiSANS) is the technique used for studying such structures. Off-specular scattering arises when there is structure in the plane of the interface in the x-

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*Figure 3.3.* Schematic representation of structural parameters used to define molecular assembly, here shown in a repeating lamellar structure.
and y-directions, with length scales smaller or comparable to the coherence length of the neutron beam, and the angle of the incoming beam is not the same as the angle of the reflected beam. If the incident angle or $Q_z$ is below a critical value, $\theta_c$ or $Q_c$, there is total reflection. For GiSANS measurements the angle of the incident beam is less than the critical angle, an evanescent wave penetrates the sample and scattering is restricted to come only from lateral structure at the interface. The measurements are performed easily on small-angle scattering instruments that have point-collimated beams giving high-resolution measurements and can decouple information of $Q_y$ and $Q_x$ components. As soon as the beam is over the critical angle there is increasing scattering contributions from the sample below the surface.

![Figure 3.4](image)

Figure 3.4. Detector response from a measurement of polystyrene latex dominated by off-specular scattering (SURF, slit collimated beam). The specular reflection indicated with a dotted line at $\theta = 0.35$ degrees.

Figure 3.4 is showing a detector response from a measurement with slit collimated beam of polystyrene latex PS11 (measured at SURF$^4$ time-of-flight reflectometer, ISIS, U.K.) dominated by off-specular scattering. The angle of the reflected beam ($\theta$) is shown on the vertical axis, with the angle of the incoming beam in this measurement $\theta_I = 0.35^\circ$. The wavelength of neutrons ($\lambda$) is shown on the horizontal axis. Off-specular Bragg scattering appears as lines of constant $Q_z$ above and below the specular reflection (as indicated in Figure 3.4), where $Q_z$ carries information of structures perpendicular to the interface (Figure 3.2). For an incoming angle of $\theta_I = 0.35^\circ$, these lines will
cross the vertical axis at $\theta = -0.35^\circ$ as is shown in Figure 3.4. If the sample had instead been measured at an instrument with a point collimated beam, such as a small angle neutron scattering instrument, the lines of intensity would instead be spots of intensity, carrying information in $Q_y$ and $Q_x$ in the plane of the surface (as described in Paper IV).

Measurements in grazing incidence are very useful when studying complex systems. By varying parameters such as wavelength or angle, the measurement can give information from the reflectivity describing structures perpendicular to the interface, or information from scattering about the in-plane structures at the interface. Point or slit collimation can be chosen and the information combined to extract complementary information about the extension of the perpendicular structure deep into the bulk ($Q_z$ direction), as well as resolving in-plane lateral surface structures ($Q_y$ and $Q_x$).

### 3.3 Small angle neutron scattering

Small angle neutron scattering (SANS) probes the bulk of a sample (Figure 3.5). The measured absolute intensity for non-interacting particles can be expressed as

$$I(Q) = N V^2 (\rho_p - \rho_s)^2 P(Q)$$

where $N$ is the number density of particles, $V$ is the volume of the particle, $\rho_p$ and $\rho_s$ are the scattering length densities of particles and dispersion medium respectively. $P(Q)$ is the form factor and describes the size and shape of the particles, much like parameters in reflectivity are used to describe for example structures within a bilayer. The expression is also valid for other non-interacting systems. For systems where there are particle interactions, the absolute intensity can be expressed as

$$I(Q) = N V^2 (\rho_p - \rho_s)^2 P(Q) S(Q)$$

where $S(Q)$ is the structure factor and describes inter molecular or particle correlations, such as repeating structures in a lamellar phase or colloidal crystal structure. Again, the same principles are found in reflectivity. Just as in reflectivity measurements, contrast matching can be used to highlight different parts of a system.

![Figure 3.5. Scattering geometry for a SANS measurement. The beam goes through the bulk of the sample, and the sample can be rotated to probe different angles of the sample.](image-url)
In this thesis small angle scattering data were collected for measurements of surfactant bulk structures, as well as colloidal dispersions. Just as repeating structures at an interface give rise to Bragg scattering, so do repeating structures in a bulk measurement. In small angle scattering (2D-detector), Bragg scattering maxima will appear as intensity modulations on rings of constant $Q$. The relative position of these scattering maxima can be used to determine structure of the sample, $S(Q)$. For a sample with order in only two dimensions, such as lamellar phase AOT shown in Figure 3.6, which has well defined uniform layers equally separated, rings of intensity will appear at constant $Q$, but without modulations around the ring.

![Figure 3.6. SANS measurement of 2% AOT (D22, ILL, France).](image)

![Figure 3.7. The sample holder. (Modified from M. S. Hellsing et al (2010) Progress in Colloid and Polymer Science, 138, 139-142)](image)
3.4 Sample holder

In order to optimize the neutron scattering measurements, a sample holder was developed that can be used for surface reflection measurements both in horizontal and vertical geometry, as well as for bulk measurements where it would be rotated around a vertical axis by 90 degrees. The sample holder was made with the aim of being compact so that it can easily fit at any neutron scattering instrument. A small sample holder can be rotated and tilted when mounted on the sample stage, without restrictions from geometric factors such as collimation pieces or walls. The sample holder is shown in Figure 3.7.

The sample holder consists of an aluminium frame holding two 5 × 5 cm blocks together, separated by a PTFE gasket holding the liquid sample in place, with two sample injection ports located at the top and bottom diagonally opposite each other, enabling uniform filling of the sample. The thickness of the PTFE gasket is approximately 2 mm, which is a suitable thickness for SANS measurements. The inset in Figure 3.7 shows schematically surfactants adsorbed at the interface and how the neutron beam would probe the sample in different measurements. The material of the two 5 × 5 cm blocks sandwiching the sample is chosen to suit each experiment. For example in surface measurements the front reflection surface may be chosen to be a smoothly polished single crystal, while the back surface can be a ‘rough’ polycarbonate piece, in order to minimize any reflections from the back surface. The cell can be temperature controlled by water flow through the aluminium framework, and can be fitted with a Pt100 to monitor the sample temperature.

For measurements of non-viscous liquid solution samples, a HPLC pump (Knauer Smartline 1000 HPLC pump with Smartline Manager 5000 degasser unit) was bought in order to optimise experiments. The pump can be run from the neutron instrument control computer and can be programmed to make injections of mixtures into the sample holder from four different solutions at various flow rates. This enables sample changes without any interference with the sample holder, which risks causing misalignment when the sample is changed manually by injection with syringe. Having the pump also frees up time to inspect and analyse data as it is being measured, rather than spending that time in the laboratory making up solutions. In Figure 3.8 the sample holder is shown mounted on D22 small angle scattering instrument (Institut Laue Langevin, Grenoble, France), connected to the pump and water flow for temperature control.
Figure 3.8. The sample holder mounted at D22, ILL, France.
4 Results

The results of the work in this thesis describes physicochemical factors that influence the process of adsorption and order of both dilute and concentrated systems of surface active molecules and particles in solution. The knowledge derived from dilute systems can be applied to more challenging investigations of complex concentrated systems. The results are based largely on models to neutron scattering data, where one has to be able to distinguish different components of the measured signal in order to correctly interpret the results. This poses a number of technical questions: what is true reflectivity? Is there structural information in the background? What is background? How big is the reflected signal arising from surface structures compared to the signal from the background? Where is the boundary between near surface structures and true bulk solution, if there is one? By optimising measurements, systems of complex structures can be understood.

4.1 Surfactants

The adsorption of different surface active molecules was investigated at solid/liquid interfaces. Dilute solutions of AOT and the adsorption to the solid sapphire interface (single crystal 0001 face) were done at room temperature. An extensive literature on AOT exists, and the adsorption to various surfaces has been described.\cite{35,36,38,40,48,49,50} The investigation reported in this thesis filled in missing gap of the adsorption to a hydrophilic sapphire interface, which may be neutral or carry a slight positive charge at neutral pH.\cite{51,52,53}

AOT molecules were found to adsorb to the hydrophilic interface in a bilayer structure even at as low concentrations as 0.2 mM AOT, which is ten times below the critical micelle concentration\textsuperscript{6} (0.1 × cmc) where the AOT molecules are freely dispersed in bulk solution. The amount of surfactants at the interface at this low concentration was found to be, described as a surface excess, 1.1 ± 0.2 mg m\textsuperscript{-2}. Through model fits of the data, the molecules at the interface bilayer had a thickness of tails of 15 Å, which is the maximum packing density for the tails. The area per two molecules in the bilayer was 138 ± 25 Å\textsuperscript{2}. As the concentration was successively increased to 7.4 mM (3 × cmc), the surfactant layer became denser laterally with the area per two molecules in the bilayer just 51 ± 9 Å\textsuperscript{2}, while the bilayer thickness
remained at a constant $33 \pm 2$ Å. The surface excess for a concentration of 7.4 mM was $2.9 \pm 0.2$ mg m$^{-2}$. These results are very similar to those that has been found previously for the hydrophobic silica surface, $^{35}$ and indicates that the presence of an interface is important, but not the interface chemistry. The tendency of AOT to associate in planar structures is the dominant factor in driving AOT to the interface from an aqueous solution. Adding salt to dilute surfactant solutions is known to change the critical micelle concentration, and this was also observed for AOT at the sapphire interface. The addition of 0.5 mM NaCl and other monovalent salts to 0.5 mM AOT doubled the adsorbed amount at the interface. The effect of pH was found not to be significant in the range of 3 to 9, as changing pH through addition of NaOH or HCl of the same concentration as the salts had about the same effect as the addition of salt at the same ionic strength. This is different to what has been seen for example for the non-ionic surfactant pentaerythritol glycol monododecyl ether, which showed significantly enhanced adsorption at the sapphire interface as the pH = 3 was reached.$^{54}$ Sodium dodecyl sulfate is an anionic surfactant that also shows enhanced adsorption at the sapphire interface at lower pH.$^{55}$

When the adsorption from low concentration AOT solutions was established, studies of higher concentration AOT solutions were performed. An oriented lamellar phase wetting the interface was observed at a concentration of just 25 mM, or 1% wt, at the sapphire interface. The formation of a lamellar phase at 1% wt is markedly lower than what has been reported previously for bulk concentrations.$^{7,56,57}$

Measurements from 2% wt AOT aqueous solutions at the sapphire interface gave rise to Bragg scattering maxima of decreasing relative intensity. A model to fit the data included the change of the intensity of Bragg scattering maxima as fluctuations in the bilayers, described by a Debye-Waller factor. The system consisted of a stack of 20 ± 10 fluctuating bilayers, each separated by large amounts of water, next to a very dense bilayer closest to the interface, shown schematically in Figure 4.1.
The scattering length density profile in Paper II derived from the model fit shows that the amount of surfactant in the fluctuating bilayers is significantly less than in the very near surface layer. Also, the amount of surfactant in subsequent layers decreases away from the interface. The AOT phase that wets the surface was found to be different to the bulk, with a composition of 10% wt near the interface for a 2% wt bulk solution.

Careful consideration of the background scattering from bulk solution is required when interpreting surface adsorption data at angles high enough for the beam to penetrate into the sample. In concentrated systems, the bulk solution may also have significant structure. For this reason, measurements of 2% wt AOT were done in grazing incidence geometry of structures at the interface, as well as probing deeper into the sample. The scattering pattern shown in Figure 4.2 is one of a series of measurements at different angles for fixed a wavelength (6 Å fixed wavelength, varying incident angle and detector distance fixed at 10 m) to cover a wider $Q$-space.
From this measurement, it is clear that the Bragg scattering peaks as observed in reflectivity measurements lie on rings of constant $Q$ arising from bulk scattering. Hence, the interlayer separation of the aligned lamellar phase found at the interface and that found in the bulk are approximately the same. However, the bulk structures lack the alignment induced by the surface, as there is no intensity modulations around the ring.

Lamellar phases formed at relatively low concentrations, such as that found for AOT, are structurally quite different from higher concentrations lamellar phases where the thickness of the separating water layer may be of the same order of thickness as the surfactant layer. This was observed at the sapphire interface for the non-ionic surfactant Brij-30, Figure 4.3.
As can be seen in Figure 4.3, strong off-specular scattering was observed from 55% wt Brij-30 adsorbed at the sapphire (0001) hydrophilic interface. A model fit to the data (integrated over the specular reflection) shows a structure of repeating bilayers with thickness of 50 Å, separated by 15 Å of water (Figure 4.4). The layer adsorbed closest to the interface was found to be of the same composition as the rest of the lamellar stack, unlike what was observed for 2% wt AOT, where the bilayer at the interface had a much higher packing density relative to the rest of the layers. At least 100 repeating bilayers were needed for the model to fit Brij-30 data reasonably. The fluctuations were found to be in the order of 14 Å. 55% wt Brij-30 would form a lamellar phase also in the bulk at this concentration according to the phase diagram. The aligned structures found at the interface are similar to those that are presumably randomly oriented very deep into the bulk. This is because there is less room for random arrangements of the lamellar layers as seen for AOT (2% wt), due to the much higher surfactant concentration in the case of Brij-30 (55%wt).
4.2 Proteins

The adsorption of globular charged proteins from the seeds of the tree *Moringa oleifera* can be viewed much in the same way as molecular surfactant assemblies such as micelles or lamellae that show strong surface activity. The seeds are widely used for water purification in developing countries with dry climate and poor soil where the Moringa trees flourish. The results presented in this thesis are related to the mechanism of protein adsorption and the use of the protein as a flocculent in water treatment processes, in order to optimize the amount of protein needed in the purification process. The adsorption was investigated at the silica (silicon oxide) interface, to mimic for example clays often found in dirty water. Measurements in the presence of the surfactant sodium dodecyl sulfate (SDS) were also performed, as SDS is a good model for surfactants that may act as dispersants and are commonly found in dirty water.

The proteins were found to adsorb at the interface as dense layers with a thickness suggesting co-adsorption rather than single isolated molecules even at low protein concentrations, schematically shown in Figure 4.5. SDS which on its own does not adsorb to the silica interface, was found to co-adsorb to the protein layer, and did not displace the protein. Rinsing with water did not remove the protein from the silica surface either. The strong adsorption and tendency to associate in solution suggest a mechanism for flocculating particulate impurities in water, where the protein would be added in small amounts to dirty water, form dense flocs that would settle under gravity and could then be filtered off.
Figure 4.5. Schematic representation of *Moringa oleifera* protein adsorbing to the silica surface.

A plateau was found in the adsorption isotherm (*Figure 4.6*) which means the water purification process can scale with dirtiness of water. This enables optimisation of amount of protein needed/added. In comparison, the use of aluminium sulfate in water purification processes is based on changing the ionic strength, which reduces the charge repulsions causing impurities to flocculate. Thus even for rather clean water the same amount of salt is needed as for very dirty water.

![Graph showing surface excess vs. protein concentration](image)

*Figure 4.6. Moring oleifera, surface excess on silica surface (Paper V).*
4.3 Colloidal particles

The polystyrene latex particles described in this thesis were highly monodisperse, and this opens up very interesting opportunities when it comes to the study of self-assembly and formation of colloidal crystals, both at an interface and in the bulk.

Dispersions of polystyrene latex particles were found to form large three-dimensional crystals with a grain size of approximately $1 \times 1 \text{ cm}^2$ in the 2 mm thick sample holder, by very gentle filling of the latex into the sample holder with a shear strain rate of about $0.1 \text{ s}^{-1}$. The diffraction pattern of Bragg scattering from latex PS3, indicated a close packed structure with the 110 axis perpendicular to the container wall. The crystal was well-aligned and oriented by the direction of very gentle flow.

The formation of large three-dimensional crystal structures were also observed for latices PS11 and PS4 in a rectangular sample holder with dimensions 1 cm wide and 1 mm deep. The results of rotations around a vertical axis (referred to as the $\omega$-axis in Paper III) of a PS4 colloidal crystal is shown in Figure 4.7. The first order Bragg scattering maxima arise at $Q_p = 0.004 \pm 0.0002 \text{ Å}$, which for close packed face centred cubic structure corresponds to diffraction from 111 and 002 planes. The next maxima arise at $Q = 0.006 \pm 0.0002 \text{ Å}$, consistent with the expected diffraction from 220 planes. The scattering maxima at $Q_p = 0.004 \text{ Å}$ corresponds to a d-spacing of 1570 Å. This is close to the calculated 1620 Å for a crystal made of particles of this size and concentration, aligned with the 110 plane perpendicular to the cell wall. However, the crystal determination is incomplete, as rotations beyond 30° were not possible in this experimental set-up.

Figure 4.7. Neutron diffraction of PS4 colloidal crystal with rotation. (D11, ILL, France).

By rotating the crystal in small steps, the crystal alignment can be estimated from changes in the diffraction patterns that were observed. For PS4 as
shown in Figure 4.7, even rotations as small as 1° resulted in a big change of the diffraction pattern, indicating the crystal being well aligned.

Studies of colloidal structures at the sapphire and silica interface in comparison with structures found in the bulk were done for latex PS11, concentration 10% by volume. At both interfaces large areas of nearly 20 cm² of highly ordered structures were obtained by filling the cell gently with a shear strain rate of about 0.1 s⁻¹. Measurements with a slit collimated beam (SURF, ISIS, U.K.) of the near surface structures gave rise to at least six orders of Bragg scattering, an indication that the ordered structure extended deep into the bulk. Polystyrene latex in D₂O scatters very strongly, and there is a limit as to how deep the neutron beam can penetrate a strongly scattering concentrated sample, and still reach the detector.

This sample was also measured with a point-collimated beam (D22, ILL, France) in GiSANS geometry, in order to deduce the in-plane structure of the surface layer. The surface layer consisted of close packed structure with the 111 plane aligned at the surface. Rotating the cell by 90° around a vertical axis enabled the bulk of the sample to be probed. The particle-particle separation was the same at the surface and in the bulk, but the bulk crystallites were much smaller. The particle-particle separation at the surface and in the bulk was dominated by charge repulsions.

As an extension to the studies of latex single crystals, two latices of different size, one smaller (PS10), and one larger (PSD1), were measured separately and as mixtures, keeping the volume fractions the same in all measurements. Mixtures of different size colloidal particles of essentially two different sizes are commonly used in technological applications such as film formation on surfaces and paper coatings. Packing of mixed size hard spheres has received considerable attention both experimentally and theoretically, as they can form different two and three-dimensional structures at particular compositions. The result presented here is a preliminary observation forming part of a more extensive study of concentrated latex in low ionic strength media, which allows the particles to crystallise. PSD1 is deuterated and PS10 hydrogenous, so the signal from each latex could easily be distinguished. Both latices showed clear Bragg scattering when measured separately. The determination of the full structure, including correlations between the different types of particles, also in the regions of crystal-line samples, is very interesting. In the mixture, the smaller latex (PS10) melted the crystal structure of the larger latex (PSD1), by taking up the space in between the larger latex particles, whilst retaining the same inter-particle separation as was observed when measured separately. This is shown in Figure 4.8.
Figure 4.8. Latex PSD1 (large) and PS10 (small), measured separately and as mixtures, at constant volume fractions. For clarity, data for the mixtures were multiplied by 0.1.
5 Conclusions

The work described in this thesis has focussed on factors that influence the process of adsorption and order of both dilute and concentrated systems of surface active molecules and particles. An initial study of a common molecule (AOT) showed that the adsorption process was driven by self-assembly, in contrast to many other systems where adsorption may be dominated by for example the surface chemistry of the interface. For solutions of 2% wt AOT, a well aligned lamellar phase was observed at the interface. The aligned lamellar phase was found to have an overall concentration of 10% wt, close to that reported by others as being the lamellar phase boundary, while the overall concentration of the bulk solution was much lower. The surface aligned lamellar phase was found to be fluctuating as expected. The fluctuation amplitude could be established quantitatively, and give information of the bilayer elasticity.

Study of the adsorption mechanism of *Moringa oleifera* proteins allowed for optimisation of a natural water purification process. The existence of a plateau in the adsorption isotherm enables the added amount of protein to be adjusted according to the amount of dirt in the water. Optimisation of the purification process by adjusting the amount of protein needed is of high importance and much better than conventional water treatment processes using salts, where the particulate flocculation is driven by reducing the Debye length through ionic screening. As a consequence the same amount of ionic compound is needed regardless of the level of contamination of the water.

Highly monodisperse polystyrene latex particles were synthesised which enabled investigations of forces and conditions involved in the formation of ordered and oriented structures such as colloidal crystals, both at interfaces and in the bulk. The charge stabilised particles would readily self-assemble in bulk solutions, where the formation of millimetre sized crystallites could be observed. Very gentle flow of these particle dispersions with a shear strain rate of approximately 0.1 s$^{-1}$ proved to be a reliable and reproducible procedure of forming very large highly ordered structures. The low shear strain rate allowed the particles to arrange through self-assembly where the inter-particle separation was determined by charge repulsion. Tuning the
structures obtained by self-assembly can easily be done by changing parameters such as concentration and ionic strength of the bulk solution.

In summary, concentrated molecular and colloidal dispersions are important and can be understood. Different systems were investigated over many orders of magnitude in length scale, where the repeating structure for non-ionic surfactant Brij-30 was of order 50 Å, for the anionic surfactant AOT about 200 Å, and for charge stabilized polystyrene latex about 2000 Å. The nature of the different systems is varied. The forces that dominate and determine their formation of self-assembled structures are identified and can be controlled. Through studies of both dilute and concentrated molecular and colloidal model systems, we have enhanced the knowledge of the interactions that govern these systems at interfaces and in the bulk.

Neutron scattering is a technique that can successfully be applied to investigate complex concentrated systems. The results from the studies described in this work can be applied in many various areas. The model presented for the reflectivity from fluctuating layers at interfaces can be applied to other repeating systems to gain information of fluctuation amplitude and layer elasticity. The optimisation of natural water treatment methods could be extended to involve other naturally occurring materials that may be found to have similar properties as *Moringa oleifera*. The simple and quick method to produce large two and three-dimensional structures of highly ordered colloidal dispersions could be applied to create templates for photonic materials, or, when formed at interfaces serve as lithographic masks.
Majonnäs, tandkräm, målarfärg och tvål är exempel på material som vi ofta kommer i kontakt med till vardags, och som varken kan sägas tillhöra kategorin “enkla” vätskor eller fasta material. De tillhör en kategori som kallas kondenserad mjuk materia. Det finns en mängd olika material som räknas in i denna kategori, till exempel plaster, emulsioner och olika biologiska material såsom blod. Mjölk består av finfördelade fettdroppar (aggregat) i vatten, och solskyddskräm består av nanopartiklar jämnt spridda i ett flytande medium (dispersion). Storleken på partiklarna eller aggregaten är viktig. De är större än enskilda atomer, cirka en nanometer ($10^{-9}$ m), men mindre än någon tusendels millimeter ($10^{-6}$ m), tillräckligt små för att i vätskelösningar vara i ständig slumpmässig rörelse. Den ringa storleken gör att partiklarna har relativt stor yta i jämförelse med dess inre volym, vilket ger dem andra egenskaper än om de varit större. Det kan till exempel vara stora skillnader i egenskaper mellan en järnspik i en hink med vatten, och järnnanopartiklar finfördelade i vatten.

I den här avhandlingen har faktorer som verkar mellan tensider (molekyler med tendens att samlas, eller adsorbera, vid ytor) samt nanopartiklar i vatten undersöks. Studier av utspädda lösningar samt koncentrerade dispersioner har gjorts, både vid ytor där man studerar de närmsta lagren, samt genom en stor volym av materialet.

Tensider är molekyler som består av en del som vill vara i vatten, hydrofil, och en del som inte trivs där, hydrofob. Denna egenskap gör tensider ytaktiva, de orienterar sig vid en yta så att molekylens olika delar pekar mot den fas där de trivs bäst. I stora volymer av materialet och vid låga koncentrationer existerar tensiderna fritt i vatten. När koncentrationen når den kritiska micellkoncentrationen arrangerar sig molekylerna spontant i ofta sfäriska aggregat, så att den hydrofoba delen undgår kontakt med vatten i skydd av den hydrofila delen. Fortsätter man att öka koncentrationen ytterligare kan mer komplexa aggregat formas spontant, såsom membran, vilket är illustrerat schematiskt i Figur 6.1.

Ökad förståelse för faktorer som verkar inom dessa system är viktig i sig. Resultaten kan även användas för att förbättra industriella applikationer, samt driva den teknologiska utvecklingen framåt inom elektronik och fotonic optik, för att nämna några tillämpningar.
Resultaten i den här avhandlingen bygger i stort på mätningar med neutronsspridning, där material har placerats i en neutronstråle. Neutronerna sprids från provet, och det är denna spridning som analyseras. Neutroner utgör en del av atomkärnor. Neutroner är oladdade och interagerar därför väldigt lite med materia. Detta möjliggör studier av dolda ytor och strukturer djupt inne i material.

![Schematisk illustration av AOT membran vid en yta](image)

**Figur 6.1.** Schematisk illustration av AOT membran vid en yta (bara tre membraner visas här).

AOT (Natrium bis(2-ethylhexyl) sulfosuccinat) är en tensid som är välkänd för sina ytaktiva egenskaper. AOT används bland annat inom läkemedelindustrin och även vid det stora oljeutsläppet i Mexikanska golfen 2010. Studier av AOT vid ytor visade att adsorptionsprocessen drivs av AOT-molekylens spontana membranformation, och inte av specifika kemiska egenskaper hos ytan. Vid högre koncentrationer bildades flera membraner vid ytan, vilket visas schematiskt i **Figur 6.1.** Membranen rörde sig i vågor, och storleken på vågorna kunde bestämmas kvantitativt. Koncentrationen av material i närheten av ytan visade sig vara högre än den var djupt inne i materialet.

Adsorption av naturliga proteiner extraherade ifrån trädet Moringa oleiferas från studerades vid en yta. Dessa frön används vid alternativ vattenrening i bl.a. Afrika, där rent vatten är en bristvara. Syftet med studien var att finna mekanismen bakom proteinernas höga effektivitet. Studien visade hur mycket små mängder protein binder starkt till ytor, en egenskap som vid vattenrensingsprocesser resulterar i att föroreningspartiklar klumpar ihop sig och kan filtreras bort. Att avlägsna föroreningar i form av partiklar är ett viktigt första steg i vattenreningsprocess, där annars ofta aluminiumföreningar används, som har allvarliga bieffekter hos människan.

Nanopartiklar syntetiserades med mycket liten variation i storlek. Dispersionser av dessa i avjonat vatten hölls stabila genom att de har en laddad yta, så att partiklarna repellerar varandra. Dessa partiklar valdes för studier då de på samma sätt som tensider kan självorganisera i olika strukturer. Genom att
varsamt fylla en provhållare med en dispersion innehållande partiklar i storleksordningen 150 nm i diameter, kunde en stor tredimensionell kristall med en area av 1×1 cm² i en 2 mm djup provhållare skapas. Partiklarna var tätt packade och väl linjerade med provhållarens yta. Stora kristallstrukturer kunde återskapas vid flera tillfällen, och det tog bara cirka 5 minuter att skapa dem.

En annan typ av mätningar som belyser hela provets yta (5×5 cm²) utan att tränga in djupt i provet, gjordes på lite mindre partiklar, omkring 70 nm i diameter. Även denna gång fylldes provhållaren mycket varsamt, en process som tog cirka 5 minuter. Resultaten visade att partiklarna organiserade sig i mycket välordnade tvådimensionella kristallstrukturer över hela mätytan, ca 20 cm². Lite längre ifrån ytan återfanns mindre kristallstrukturer. Detta är schematiskt illustrerat i Figur 6.2. Att kunna skapa stora välordnade ytstrukturer är mycket värdefullt för olika applikationer där dessa används, till exempel inom datalagring, vilka i dagsläget kan ta många timmar, ofta dagar, att skapa. De innehåller dessutom ofta oregelbundenheter. Vi fann en metod för att mycket lätt skapa välordnade strukturer, och dessutom med material som både är tillgängliga och billiga.

![Figur 6.2. Schematisk illustration av en välordnad kristallstruktur av nanopartiklar i vatten vid en yta, med mindre kristallstrukturer lite längre ifrån ytan.](image)
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8 Bibliography

46 Rennie A. R. http://material.fysik.uu.se/Group_members/adrian/refprog.htm
55 Li, N., Thomas, R. K. and Rennie A. R, submitted manuscript.
57 Fontell, K. J. (1973) J. Colloid Interface Sci. 44, 318-329
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