Summary

This thesis describes a study of the interactions between surfactants and water-soluble polymers carrying hydrophobic end groups, with a focus on liquid laundry detergents. The research topics can be subdivided in two main themes. Interactions between hydrophobically-modified polymers and surfactant monomers, micelles and vesicles in *dilute* aqueous solutions are described in Chapters 2 and 3. The surfactant concentrations studied were in the range of 0 to 10 mM, which is quite typical for wash conditions. The second main theme comprises the microstructure and rheology of *concentrated* structured liquid laundry detergents with added hydrophobically-single-end-capped poly(sodium acrylate)s; Chapters 4 and 5.

Commercial ‘concentrated’ liquid laundry detergents contain approximately 30 wt% of surfactants. The anionic and nonionic amphiphiles aggregate in aqueous solutions, driven by hydrophobic interactions, into a variety of colloidal structures. Micelles are well-known examples of such morphologies. However, at the high detergent levels present in liquid detergents, repulsive forces between surfactant aggregates come into play. These forces can be of electrostatic, osmotic or steric nature. In order to minimize interaggregate repulsions, various ordered mesophases are formed. Because domains with liquid-crystalline structure have a large propensity to grow, phase separation soon occurs. This process is highly unwanted, because consumers find a phase-separated product visually unattractive. Moreover, it appears that most people don’t like to ‘shake before use’.

The formation of liquid-crystalline phases can be prevented by the addition of hydrotropes, such as sodium-p-xylenesulfonate. These compounds intercalate between the surfactant molecules, disturbing their close-packing and dissolving the liquid crystals.

Phase-separation is *induced* in the formulation of structured liquids. The addition of 15 wt% of sodium citrate breaks down the hydration layers of the poly(oxyethylene) headgroups of the nonionic surfactants due to ‘salting-out’. Dehydration occurs to such an extent that the headgroups cannot be kept in solution. Moreover, the reduction of the optimal cross-sectional headgroup area results in an increase of the geometric packing parameter, which explains the transition to bilayer structures. The bilayers are arranged in a lamellar fashion due to strong osmotic attractions between salted-out nonionic headgroups. Importantly, lamellar *droplets* are formed instead of a continuous lamellar liquid crystalline phase, because a surfactant *mixture* is used. This factor allows a non-zero spontaneous curvature of the bilayer, favoring the formation of vesicles of finite size. The multimellar vesicles tend to aggregate, forming flocs of semi-solid material floating on top of a clear, surfactant-poor solution. The same osmotic forces which are responsible for the tight stacking of lamellae *within* droplets are operative *between* the multimellar vesicles. The mutual aggregation of the particles can be prevented by the addition of polymers which - by virtue of the presence of hydrophobic side chains - adsorb onto the periphery of the multimellar aggregates, with a water-soluble backbone protruding into the aqueous electrolyte solution. Adsorption of these ‘hairy’ polymers prevents close approach of the droplets through a mechanism called *steric stabilization*. A prerequisite is that the aqueous electrolyte solution is a ‘good’ solvent for the polymer, *i.e.* the polymer coil is not collapsed, and repulsive (volume restriction and osmotic) interactions overcome the attractive forces. Provided that the polymers do not penetrate into the droplets, only the interaction potential between lamellar droplets changes, whereas the forces between lamellae within droplets remain essentially unchanged. Thus, interlamellar forces are decoupled from intralamellar forces. Hence these polymers are called *decoupling polymers*.

It is the fate of all liquid laundry detergents to be diluted *ca.* 200 fold with water, to form the wash
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suds. The concentration of surfactants is then reduced to below 10 mM. The aqueous solution now contains surfactant monomers in equilibrium with micelles. Oily soil can be removed from fabrics by adsorption of surfactant molecules followed by emulsification (‘roll-up’), or by solubilization in the apolar core of micelles. However, the solution also contains decoupling polymers, which can interact with either the surfactant monomers or the micelles, complicating a clear understanding of the process of oily soil removal. A study of these interactions in dilute aqueous solution is described in Chapter 2. Decoupling polymers are able to self-associate in aqueous solution, through hydrophobic association of their n-alkyl side chains, forming hydrophobic microdomains. Experimental evidence for the formation of domains was obtained for aqueous solutions containing 1.5 wt% of copolymers of sodium acrylate and n-alkyl methacrylate, in a ratio of 25:1, provided that the alkyl chain is n-dodecyl or n-octadecyl. Surfactant monomers adsorb to these domains from solution, driven by hydrophobic interactions, instead of associating amongst themselves to form micelles. Consequently, the concentration of ‘free’ surfactant micelles is reduced.

However, poly(sodium acrylate) containing 4 mol% of n-nonyl side chains forms hydrophobic domains rather less efficiently. Added surfactant aggregates cooperatively to form micelles at a critical micelle concentration (CMC) which is slightly lower than that in the absence of the polymer. This result is interpreted in terms of stabilization of the micelle by the polymer, analogously to the interactions between surfactant micelles and water-soluble homopolymers such as poly(ethylene oxide).

Studies of the interactions between decoupling polymers and unilamellar bilayer vesicles are described in Chapter 3. The concentration of ‘free’ (double-tailed) surfactant molecules is negligible, hence, adsorption of surfactant monomers to hydrophobic microdomains is unimportant. The interactions are best rationalized in terms of anchoring of hydrophobic side chains into the bilayer. Using differential scanning calorimetry (DSC), it was shown that anchoring lowers the phase transition temperature of the bilayer vesicles ($T_m$), and the enthalpy of melting ($\Delta_m H$) accompanying the transition from the gel-like to the liquid crystalline state. From these results we conclude that the packing of surfactant molecules in the bilayer is disturbed by anchoring of the side chains. However, $T_m$ and $\Delta_m H$ are only slightly affected in the presence of poly(sodium acrylate)s bearing n-dodecyl side chains, indicating that the bilayer is least disturbed if the n-alkyl chain length of the anchor matches that of the surfactant forming the bilayer.

In order to obtain more quantitative information regarding the affinity of hydrophobically-modified poly(sodium acrylate)s for bilayer vesicles, isothermal titration calorimetry was used to study the binding process. Anchoring of n-dodecyl chains into bilayers composed of a sodium di-n-dodecyl phosphate analog is indeed stronger than binding of n-octadecyl anchors, despite the greater hydrophobicity of the latter side chains. Thus, hydrophobic match/mismatch plays an important role in the interactions between decoupling polymers and bilayer vesicles.

It is not only the length of the hydrophobic anchor, but also the distribution of the anchors over the main chain of the polymer that determines the properties of the decoupling polymer in a liquid detergent. The commercial decoupling polymer is synthesized by copolymerization of acrylic acid and n-dodecyl methacrylate, in a ratio of 25:1. The acidic groups are neutralized by addition of sodium hydroxide. Due to the copolymerization technique, the $C_{12}H_{25}$ anchors are randomly distributed among the polymer backbone and $ca$. 30% of the polymers do not contain a hydrophobic side chain. For this reason, we developed a synthetic route to specifically hydrophobically-single-endcapped poly(sodium acrylate)s. Radical polymerization of acrylic acid in the presence of dilauroyl peroxide as an initiator and
n-dodecanethiol as a chain transfer agent followed by neutralization of the acidic groups and precipitation yielded the desired polymer in more than 70% isolated yield. This method allows a variation of the molecular weight of the polymer, independent of the number of anchors per polymer, which is useful for fundamental studies of steric stabilization. We obtained a series of hydrophobically-end-capped decoupling polymers having molecular weights ranging between 750 and 34,000 g/mol.

The lamellar dispersions under study are based on a 40/60/20 model system, comprising 28 wt parts of sodium dodecylbenzenesulfonate, 12 wt parts of Synperonic A7 (a nonionic surfactant), 60 wt parts of water and 20 wt parts of sodium citrate. Flocculated dispersions of lamellar droplets are turned into colloidally stable, milky-white dispersions upon addition of (typically less than) 1 wt% of hydrophobically-end-capped poly(sodium acrylate)s having a molecular weight between 3000 and 9000. Using confocal scanning laser microscopy it was shown that the mechanism behind the observed deflocculation is indeed steric stabilization; a layer of a fluorescently-labeled hydrophobically-end-capped decoupling polymer is observed at the rim of the droplets.

It is of scientific and practical importance to address the relation between (the extent of) polymer adsorption and droplet size (distribution); Chapter 4. In particular, we wished to answer the following questions: (i) Are the polymers irreversibly grafted to the bilayer membranes, or involved in an adsorption equilibrium? (ii) Do anchored polymers affect the size and/or shape of the (multilamellar) vesicles? And if so, what is the role of the molecular weight of the polymer? (iii) Can we understand and predict relations between the average droplet size and the amount of adsorbed polymer? Laser diffraction and refractive index measurements were used to determine average particle sizes of the colloidal particles, and it was established that increasing the molecular weight of the hydrophilic (pendant) backbone at constant (hydrophobic) anchor density, or increasing the concentration of polymer in the dispersion at constant molecular weight, results in a decrease of the average droplet size. This pattern agrees with theoretical predictions that an increased lateral pressure in the adsorbed layer, due to a higher polymer-segment density near the surface, is relieved by increasing the curvature of the lamellar droplets. Interestingly, the decrease of the average particle size with increasing polymer concentration becomes less pronounced as the polymer concentration in the model system is increased beyond 1 wt%. A likely explanation involves the finding that the amount of polymer adsorbed onto the lamellar droplets degressively increases with polymer concentration. This result is consistent with the notion that increasing the graft density at the surface results in an increased lateral tension within the polymer layer - the same factor that is held responsible for the concomitant reduction of the average particle size.

Decoupling polymers with a molecular weight of ca. 750 have a particular effect on the microstructure of lamellar dispersions (Chapter 5). The polymer molecules are so small that they can penetrate into the lamellar droplets. Consequently, the water layers become thicker and the droplets swell. The increase of the volume fraction of the lamellar phase ($\phi_{\text{lam}}$) with polymer concentration, and constant surfactant concentration, provides a clear indication for the occurrence of this ‘building-in’ effect. As more and more polymer accumulates between the layers in the droplets, the difference between intra- and interlamellar interactions gradually disappears, and when $\phi_{\text{lam}}$ approaches unity, the curved droplets are transformed into continuous lamellar structures.

It is not only the microstructure, but also (its influence on) the rheology of lamellar dispersions which is of general scientific and fundamental importance. The rheology of a liquid laundry detergent is directly related to the consumer’s sensory reaction of pouring the liquid into the dosing system of the washing machine. The appearance of a nicely flowing liquid is of direct relevance to the consumer’s decision of buying the product (again). A second aspect of the rheological behavior of liquid detergents
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relates to the possibility of suspending solid particles in the liquid. To prevent sedimentation of the particles, the dispersion can be thickened, \textit{i.e.}, its viscosity can be enhanced. In one approach, ‘building-in’ polymer can be added so that $\phi_{\text{lam}}$ increases (at constant surfactant concentration); droplet-droplet interactions become stronger and more frequent, and the viscosity increases. However, this is not the best way to proceed, since a high-viscosity liquid does not pour nicely. It is much better to formulate a ‘shear-thinning’ dispersion, which has an appreciable consistency when left on the shelf, but becomes more ‘liquid’ under the influence of shearing forces, \textit{i.e.}, due to pouring. The dispersion can be endowed with enhanced shear-thinning properties by addition of equal (weight) amounts of a hydrophobically-single-endcapped decoupling polymer and a high-molecular weight copolymer of sodium acrylate and lauryl methacrylate. The latter polymer contains multiple anchors per molecule and is therefore able to link adjacent droplets. Consequently, a network of droplets is formed, which is (due to the additional presence of hydrophobically-single-endcapped decoupling polymer) broken down under the influence of shear. Hence, the liquid can be easily poured while it has the ability to suspend solid particles.

It is of scientific interest to describe the elastic component of lamellar dispersions in terms of interparticle interactions (Chapter 5). When the volume fraction of the lamellar droplets exceeds 0.8, particle-particle interactions are governed by overlap of the repulsive adsorbed polymer layers. Hence the particles are arranged in a repulsive network. A disturbance of the equilibrium positions of the particles raises the total potential energy of the system, and the particles react by exerting an opposing force. This is the reason why concentrated (lamellar) dispersions are characterized by appreciable elastic moduli ($G'$).

At constant surfactant concentration, $G'$ increases with the molecular weight of the adsorbed hydrophobically-endcapped polymer. The reason is that the adsorbed layer contributes to the \textit{effective} volume fraction of the droplets ($\phi_{\text{eff}}$). When the molecular weight of the polymer is raised, the adsorbed layer thickness ($\Delta$) increases relative to the droplet radius ($R$). Consequently, $\phi_{\text{eff}}$ increases, and the interparticle interactions in the repulsive network become stronger, explaining the increase of the elastic modulus. If the molecular weight remains below 19,000, the ratio of $R/\Delta$ exceeds 15, and the droplets behave as hard spheres. This was inferred from the observation that in the empirical relation

$$G' \propto \phi_{\text{lam}}^n$$

the exponent $n$ is \textit{ca.} 20, the same value which has been found in case of (monodisperse) latex and silica particles. Finally, the elastic modulus can be described with satisfactory accuracy in terms of the second derivative of the distance dependence of the theoretical potential energy for sterically-stabilized particles.

In conclusion, we hope to have illustrated how fascinating the physical chemistry of structured liquid laundry detergents can be, because of the challenging possibilities to influence the physical properties of \textit{end products} by rational design of \textit{molecules}.