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How a simple anionic surfactant adopts a lamellar arrangement.

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Summary

The basic components that largely determine the structure of a liquid laundry detergent are water, salts and a mixture of surfactants. When these are mixed in the right proportions, the surfactant aggregates in a lamellar fashion. This lamellar phase is a packing of amphiphiles in a bilayer, with the tails in the inner core of the bilayer and the headgroups pointing towards the water. Several manifestations of the lamellar phase are known. Examples include a stacking of planar bilayers, either as a single continuous phase, where the lamellae span through the whole system, or a two-phase system, where the lamellar phase coexists with another phase. In special cases the lamellae can fold around one another, like in an onion. Such so-called lamellar droplets are also the basic structural unit of some types of liquid laundry detergents. In dilute solution a lamellar aggregate can appear as a vesicle, if the bilayers repel each other.

The phase behaviour of such a practical mixture of surfactants in water/salt systems is dominated by the surfactant sodium dodecylbenzene-sulfonate (NaDoBS, see figure 1.3), a polydisperse compound that is one of the most popular surfactants for detergent products worldwide. The problem that has been addressed in this thesis is how this simple anionic surfactant can adopt a lamellar arrangement, starting from a less ordered state such as either the dilute micellar phase, or the bulk isotropic liquid phase of dodecylbenzene-sulfonic acid (HDoBS), the industrial precursor of NaDoBS. Accordingly the thesis can be split into two parts: the dilute phase, comprising the salt-induced transition of micelles into lamellar aggregates (chapters 2-4), and the part on concentrated systems, that deals with the arrangement of amphiphiles into a lamellar fashion starting from a bulk surfactant situation (chapters 5-7).

The question of how the surfactant adopts a lamellar arrangement can be answered by finding out under which environmental conditions a lamellar arrangement of NaDoBS is obtained. These depend on the type and the concentration of the salt, and on the amphiphile concentration, or in other words the water/amphiphile ratio. However, the present thesis also sheds light on the *mechanism* of the *dynamic processes* of the rearrangement of amphiphiles into the lamellar phase. Moreover, the process can be viewed as a molecular transformation, but that is only part of the analysis, because the interactions between bilayers, and between the separate aggregates play also an important role in the total aggregation behaviour.

Before the analysis of the details of the aggregation behaviour of NaDoBS in aqueous surroundings begins, an introduction into the aggregation behaviour of amphiphiles is presented (chapter 1). The background of aggregation is touched upon, and the general features that determine the type of aggregate that is formed: the molecular shape, and more importantly, the solution conditions such as amphiphile concentration, presence of salt or a change in pH and mixing of different types of amphiphiles. At low amphiphile concentrations separate aggregates are found: micelles or vesicles. At higher amphiphile concentrations lyotropic liquid-crystalline phases occur.

NaDoBS forms micelles in dilute aqueous solution. Upon the addition of NaCl the NaDoBS precipitates from the solution. The precipitate consists of

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strongly flocculated lamellar droplets. In order to study the factors that determine the formation of these particular lamellar units, the influence of other alkali metal chlorides and tetraalkylammonium chlorides on the aggregation behaviour of NaDoBS was studied (chapter 2). Depending on the type and concentration of salt, a rather stable dispersion of unilamellar vesicles was formed spontaneously, but in other cases a phase separation occurred into a surfactant-rich and a surfactant-lean phase. All alkali metal chlorides eventually induce the formation of flocculated lamellar droplets at higher salt concentrations. The chapter also contains an introduction into the physical interactions between bilayers and between aggregates. The observed phase behaviour could be traced back to the hydration characteristics of the cation of the salt: the less hydrated the ion, the better it can expel Na^+ as a counterion, leading to a higher counterion binding. This increase in counterion binding primarily induces the formation of the lamellar arrangement of DoBS by allowing the headgroups to approach one another more closely. In addition, the type of ion also strongly influences the attractions between bilayers and between aggregates.

In chapter 3 the increase in counterion binding induced by a change for a less hydrated ion is illustrated. The critical aggregation concentration (CAC) of dodecylbenzenesulfonates in different electrolyte solutions was measured by microcalorimetry and conductometry. A higher counterion binding is accompanied by a lower CAC and a higher (more negative) enthalpy of aggregation, particularly in those cases where the first aggregated state is a lamellar aggregate. In this chapter it is argued that a critical vesicle concentration (CVC) never can exceed a value of approximately 10^{-4} molar.

The addition of salt to a dilute micellar solution mixture of NaDoBS and a nonionic surfactant ($\text{C}_{13-15}\text{E}_{<7>}$) induces the spontaneous formation of a very stable dispersion of giant vesicles at moderately high salt concentrations. The large interbilayer repulsions that cause the stability of this dispersion must be due to the presence of the nonionic surfactant in a good solution condition. The well-hydrated PEO headgroup will expose a large steric repulsion and will moreover allow for a high bilayer undulation repulsion. At higher salt concentrations the nonionic can be salted out, resulting in a break-down of the repulsions. By a combination of van der Waals attraction between the bilayers and attraction between the PEO segments of the nonionic headgroups in a poor solution condition, the vesicles collapse to form flocculated lamellar droplets.

The mechanism of the salt-induced spontaneous formation of vesicles described in chapters 2 and 4, probably involves a drastic growth of micelles in two dimensions. At a certain point the growth is extremely rapid resulting in a bilayer fragment of a critical size, that bends over and closes to form a vesicle.

The formation of a lamellar phase from the bulk surfactant phase was studied with the commercial processing in mind: the basic ingredients are mixed in a specific order to finally obtain a colloiddally stable dispersion of lamellar droplets. The occurrence of the lamellar phase is largely determined by the presence of NaDoBS or its precursor HDoBS, that is neutralized during processing. To understand the interactions which HDoBS molecules experience

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is noted that a bilayer-forming amphiphile not necessarily aggregates into a vesicle. In addition, some words are devoted to the formation of a dispersion of lamellar droplets from a bulk mixture of HDoBS and $C_{13-15}E_{<7>}$, partially presented in chapter 6, but extended here as a thought experiment. The chapter closes by reviewing the formation of the lamellar arrangement seen from the viewpoint of the NaDoBS amphiphile.