The use and science of laundry detergents

1.1 Detergents: from saponin to LAS

In ancient societies, and even today, people clean their clothes by beating the wet textiles on rocks near a stream. This is good practice, because the mechanical agitation facilitates the removal of solid soil, and the water dissolves the hydrophilic (‘water-loving’) stains composed of, for example, sugar, salt, and certain dyes. However, oily soil is hard to remove in this way, since fatty substances do not dissolve in pure water and remain attached to the fabric. Nature has allowed man to solve this problem by providing saponins, soap-like substances which are found in chestnuts, in leaves and seeds of Saponaria Officinalis (soapwort), in the bark of Quillaja saponaria Molina (South American soaptree), and in the fruits of Acacia Auriculiformis (Figure 1.1.).1,2,3 These compounds produce a rich lather when dispersed in water.

While these natural detergents were probably the first cleaning agents ever used in fabric washing, the oldest substance manufactured for removal of oily stains is soap, the sodium salt of a long-chain carboxylic acid. A soap-like material found in clay cylinders during the excavation of ancient Babylon provides evidence that soapmaking was known as early as 2800 B.C.4 Inscriptions on the cylinders state that fats were boiled with ashes. By the 15th century, soap was produced in Venice and Savone by treating animal or vegetable fats with aqueous

Figure 1.1 Chemical structure of a saponin from Acacia Auriculiformis.3
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Figure 1.2 The soap boiling process. For beef tallow as a starting material, \( R_1 \), \( R_2 \), and \( R_3 \) = 6:5:8 mixture of \( C_{15}H_{31} \), \( C_{17}H_{35} \), \( C_{17}H_{33} \) (not necessarily \( n \)-alkyl chains).
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sodium hydroxide. By the 18th century, soap manufacture was widespread throughout Europe and North America, and by the 19th century ‘soap-boiling’ had become a major industry (Figure 1.2). As a matter of fact, soap became a detergent in the modern sense of the word when ‘Persil’ was launched on the Western European market in 1907.

From an ecological point of view, soaps stand up to modern demands: they are made from renewable sources and are readily biodegraded, not polluting rivers. One may ask why soap, having such benefits, has been replaced synthetic detergents made from petrochemicals. Two main answers to this question relate to performance and price:

1) Alkyl carboxylates are insoluble in ‘hard water’ due to strong complexation with Ca\(^{2+}\) and Mg\(^{2+}\) ions. Hence, the wash performance is significantly decreased. Moreover, a curd-like precipitate forms and settles on the fabric being washed. These residues gradually build up and cause both bad odour and deterioration of the fabric. In contrast, synthetic detergents such as alkyl sulfonates are much more calcium-tolerant, although some precipitation of these compounds in hard water occurs, leading to reduced detergency.

2) The price argument is double edged. At the end of the 19th century, margarine had become a food-of-the-people. The technology of transforming animal and vegetable fats into edible alternatives to butter opened the possibility of feeding the rapidly growing population using raw materials which are much cheaper and available in much larger quantities than milk. The price of these fats increased with demand, and the manufacture of soap, using the same raw materials, became less and less economical. At that time, the petroleum industry was growing and had a waste product, propylene, which was burnt off. However, by acid-catalyzed oligomerization, this waste product could be converted into a branched, long-chain 2-alkene, which was subsequently reacted with benzene and sulfuric acid; the product from this combined Friedel-Crafts alkylation/sulfonation was neutralized with NaOH to yield a mixture of long-chain branched sodium alkylbenzene sulfonates, abbreviated as ABS; the synthesis of one isomer containing 4 propylene units is shown in Figure 1.3. By the 1960s the amount of ABS used for household laundry washing had grown to the point that significant buildup in the environment occurred and caused foam blankets on bodies of water. At the same time, commercialization of the Ziegler process for ethylene oligomerization provided a relatively economic route to straight-chain hydrophobes that could be converted into linear alkylbenzene sulfonates (LAS). Up to present, LAS (more specifically sodium dodecylbenzene sulfonate, NaDoBS, Figure 1.4) has been the ‘work horse’ of nearly all detergent

![Markovnikov regioselectivity](image)

![Synthesis of ABS](image)

**Figure 1.3** Synthesis of ABS
formulations.

We note the striking similarity of the chemical structure of ABS and LAS to that of an ordinary soap; in fact, all detergent molecules, or surfactants, are characterized by the presence of a water-loving (hydrophilic) headgroup (sulfonate or carboxylate) and a water-hating (hydrophobic) alkyl chain. In the following sections we will show that these properties are essential for the removal of fatty substances from garments.

1.2 Modern household laundry detergent formulations

Since the introduction of synthetic surfactants, laundry detergent formulations have become more and more complex. The first commercial detergent formulations already contained alkalies (sodium carbonate, sodium silicate) to enhance removal of acidic and fatty ester soils. Moreover, sodium sulfate has been added in up to 50 wt% to add bulk to the formulation, and to form a free flowing powder. Soon, nonionic surfactants were incorporated for enhanced oily soil removal. \( \text{C}_{13-15} \text{EO}_7 \) is a common example of such a surfactant, bearing the name of Synperonic A7: a long-chain alcohol coupled with on average 7 ethylene oxide units (Figure 1.5). With time, additional functional additives have been introduced by manufacturers of detergents with the purpose of improving the ‘cleaning action’.

1.2.1 Builders. Builders are substances that augment the detersive effects of surfactants. Most important is their ability to remove Ca\(^{2+}\) and Mg\(^{2+}\) ions from the wash liquor, thus preventing these ions
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\[
\begin{align*}
\text{Na}^+\text{O}^–\text{P}–\text{O}–\text{P}–\text{O}–\text{P}–\text{O}^–\text{Na}^+ \\
\text{OH} \\
\text{Na}^+\text{O}_2\text{C}–\text{CH}_2–\text{CH}_2–\text{CO}_2^–\text{Na}^+ \\
\text{CO}_2^–\text{Na}^+
\end{align*}
\]

\[(\text{STP})\quad (\text{NaCit})\]

**Figure 1.6** Chemical structures of two important organic builders.

from interacting with the surfactant. Hardness ions can even ‘bind’ dirt onto (cotton) fabric by interacting with the negative charges present on both soil and cloth.

Ions responsible for hardness can be sequestered by chelating agents, so that a strongly associated but soluble complex is formed. Sodium triphosphate, STP, is particularly effective (pK\text{eq} = 6) and has been the most widely used inorganic builder until its use became restricted after the 1960s in the US and later in Europe. The presence of large amounts of phosphate in rivers, canals and lakes led to excessive growth of algae due to eutrophication. The water became depleted with oxygen, causing starvation of marine life. As an alternative to phosphate, trisodium nitrilotriacetate (NTA) has been recommended. However, NTA was withdrawn almost immediately in 1970 because adverse laboratory reports identified possible teratogenic effects. Currently, trisodium citrate (NaCit) has found widespread use as a biologically degradable sequestrant (Figure 1.6).

Zeolites constitute another class of builders. Type A zeolites are water-insoluble particles with a size of ca. 10 µm. The empirical chemical composition is Na\text{2}O.Al\text{2}O\text{3}.4.5H\text{2}O. The mechanism of action involves ion exchange: sodium ions released from the zeolite crystals are replaced by calcium ions in hard water.

### 1.2.2 Additives for secondary benefits

These compounds are usually costly and are added in low percentages. Sodium carboxymethyl cellulose (SCMC) is a cellulose derivative of which 0.4 - 1.5 hydroxyl groups are linked to -CH\text{2}.CO\text{2}.Na moieties; its molecular weight ranges between 20,000 and 500,000. This polymer prevents redeposition of soil on cotton.
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Figure 1.7  Chemical structure of an anti-redeposition agent, sodium carboxymethyl cellulose.

This water-soluble cotton look-alike competes for soil particles in the wash liquor. Stilbene disulfonates and coumarin derivatives are examples of fluorescent whiteners.\(^\text{16}\) These additives confer enhanced whiteness to the appearance of washed fabric. Whiteners deposit on the cloth, and when exposed to ultraviolet light (present in sunlight), they emit some of the radiation energy in the blue part of the spectrum. Enzymes are widely used in premium products, degrading proteinaceous stains (proteases), starches (amylases) and fatty acids (lipases). Bleaches remove ‘chemical’ stains produced for example by fruit and wine. Sodium perborate, NaBO\(_3\)\(\cdot\)3H\(_2\)O, is often used in combination with tetraacetyldihylenediamine (TAED) as a bleach activator, which is necessary for effective bleaching at low washing temperatures of 30 or 40 °C. Fragrances mask odors of other ingredients and provide brand identity. Sodium silicate (Na\(_2\)O\(\cdot\)\(x\)SiO\(_2\); \(x\) = 3-5) is a corrosion inhibitor,\(^\text{17}\) which protects metal parts of

('traditional' di-n-alkyldimethylammonium chloride softener)

Figure 1.8  Chemical structures of fabric softeners.
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The washing machine. Ordinary soap is added in small quantities to suppress foaming, which is undesirable in washing machines.

Fabric softeners constitute another class of compounds for secondary washing benefits. Although they may be present as a wash cycle additive (i.e., in the main detergent formulation), fabric softeners are often added separately to the rinse water at the last rinse cycle after the main wash. The active ingredients are cationic surfactants, e.g. di-n-alkyldimethylammonium chloride (n-alkyl = n-C₁₄, n-C₁₆, n-C₁₈), or the more readily biodegradable esterquats. These compounds adsorb on cotton; the cationic headgroups couple to the carboxylate anions on the surface of the cloth, while the alkyl chains form a fatty monolayer which lubricates the cotton fibers. The lubrication prevents friction damage to the fibers, leading to a more pleasant feel of the fabric. Moreover, reduced surface friction accounts for the ease of fabric ironing and the reduced tendency for static electricity generation from the rubbing together of dissimilar materials when fabrics are tumbled in an automatic dryer.¹⁸

Typical compositions of universal powdered detergent formulations are given in Table 1.1. ‘Compact’ formulations are filler-free (see below).¹⁹

Table 1.1 Composition of powdered laundry detergent formulations in Western Europe (1997).

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>weight % (traditional)</th>
<th>weight % (compact)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surfactants</td>
<td>10-15</td>
<td>10-25</td>
</tr>
<tr>
<td>Builders</td>
<td>28-55</td>
<td>28-48</td>
</tr>
<tr>
<td>Bleach</td>
<td>10-25</td>
<td>10-20</td>
</tr>
<tr>
<td>Bleach activator</td>
<td>1-3</td>
<td>3-8</td>
</tr>
<tr>
<td>Fillers</td>
<td>5-30</td>
<td>none</td>
</tr>
<tr>
<td>Corrosion inhibitors</td>
<td>2-6</td>
<td>2-6</td>
</tr>
<tr>
<td>Enzymes</td>
<td>0.3-0.8</td>
<td>0.5-2.0</td>
</tr>
<tr>
<td>Optical whitening agents</td>
<td>0.1-0.3</td>
<td>0.1-0.3</td>
</tr>
<tr>
<td>Anti-foaming agents</td>
<td>0.1-4.0</td>
<td>0.1-2.0</td>
</tr>
<tr>
<td>Water</td>
<td>to 100%</td>
<td>to 100%</td>
</tr>
</tbody>
</table>

1.3 The detergents market: Europe and the United States

The detergent ingredients market is huge. In 1996, US demand was 3 billion kg; sales were $7 billion. Although large in volume - see Table 1.1 - the sales value of builders (22%) is dwarfed by surfactants (45%) and additives for secondary benefits (33%).

1.3.1 Sales of powders and liquids. With reference to commercial formulations, two developments can be discerned. In the US, liquid laundry detergent sales soared at the expense of powders. Procter & Gamble liquid detergent sales grew 39% from 1993 to 1997, whereas powders
increased only 4%. US-wide, the two product types have reached a 50/50 market split. Consumers find liquids more convenient to use, with a measuring cap as opposed to a cup which has to be dug out of a box of dusty powder. Moreover, liquids dissolve more rapidly, especially in cold water, and this property is becoming more and more important with the advent of high-efficiency, low temperature, low water consumption washing machines. In Europe, however, liquids still have only 13% of the laundry detergent market, and powder formulations are expected to dominate the market for some years to come. Better enzyme stability and/or building properties (especially in hard water areas) may account for this pattern. In Europe, the trend is towards concentration of active ingredients, completely eliminating fillers from formulations. These sodium sulfate-free powders are called ‘(super) compact’ laundry detergents. Compact powders have conquered mainly the Western European market, where they are responsible for 60% of total sales (1996). The Netherlands are the compact-champion: 90% of the laundry detergent market is occupied by filler-free washing powders. Environmental advantages of compact formulations accompany economic benefits when transportation and packaging costs are considered. For example, the amount of material required to package 1 kg of powder detergent has dropped from 90 to 60 g in the years 1991-1995.

1.3.2 Developments in household laundry cleaning in Western Europe. The trend towards compact detergent formulations is accompanied by a steady decrease per-head in the consumption of washing powder; for example, 8.7 kg/year in 1991 to 7.5 kg/year in 1996 (Germany). At the same time, washing machines are becoming more and more efficient. Whereas in 1980, 120-140 l of water were used per wash load, water consumption has been reduced to 50 l per 4.5 kg of dry fabric. Electric power consumption has dropped by a factor of two over the same period, to 1.5 kWh per wash.

1.4 Oily soil removal by detergents: how it works

Having summarized the (history of) consumer use and production of surfactants, we now consider the reason why they are needed in laundry detergency. The special properties of water are at the heart of the problem to remove oily soil from garments. In general, the apolar compounds present in the soil are virtually insoluble in water due to their hydrophobicity. At sufficiently high concentrations, detergents form micelles in aqueous solution due to the same hydrophobic effect; these dynamic entities solubilize the fatty stains.

1.4.1 Hydrophobic hydration. Water can be regarded as a macroscopic network of molecules connected by hydrogen bonds. This description implies that the dissolution of an apolar molecule in water necessitates the formation of a cavity in the three-dimensional hydrogen bonded network. The thermodynamics of such a process are quite characteristic. At room temperature, the Gibbs energy for the transfer of n-butane molecules from the vapor phase at 0.101325 MPa to the hypothetical solution phase of unit mole fraction is unfavorable by 25 kJ mol$^{-1}$. The process is accompanied by a large entropy decrease ($\Delta S = 50$ kJ mol$^{-1}$), hence, the hydration of n-butane (and of other apolar gases) is exothermic. It might be speculated that the orientation of the water molecules in the (first) hydration layer gives rise to a bulk polarization phenomenon, leading to favorable London dispersion forces between water and the hydrophobic solute.

The entropic penalty for the solvation of alkanes by water is an important fingerprint of hydrophobic hydration. However, its molecular origin has been interpreted quite differently over the past fifty years. In 1945, Frank and Evans published their classical study where the ‘iceberg model’
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was invoked to explain the negative entropy of hydration: the water molecules were proposed to be quasi-soliddly structured around a nonpolar solute (increased hydrogen bonding in the hydration shell). Indeed, the partial molar volumes at infinite dilution of nonpolar solutes in water ($V^\text{M}$) are larger than their ‘molecular’ volumes ($V^\text{M}$) as calculated from Van der Waals radii. Although these observations are consistent with the notion that the density of hypothetical ‘solid’ water of dense ice-III structure is lower than the density of bulk ‘normal’ water, one should take into account that the difference ($V^\text{M} - V^\text{M}$) is an average value, offering no direct information about the properties of water molecules in the vicinity of individual solutes.

Theories on hydrophobic hydration have continued to change. Spectroscopic techniques have been refined and developed, allowing a structural interpretation at a molecular level. Good indications for the absence of hydration cages was obtained by NMR relaxation measurements. Additional evidence for the absence of iceberg-like water structuring has been recently obtained from neutron scattering studies and computer simulations. It was found that, at room temperature, the number and strength of the hydrogen bond interactions in the hydration shell are similar to those in bulk water. Thus, (hydrogen bond) enthalpy losses are kept at a minimum. This condition is achieved by a certain preferred orientation of the water molecules. One OH-bond points to the bulk water, the other is oriented tangentially with respect to the surface of the apolar solute. Of course, water molecules in the hydration shell have less translational and rotational degrees of freedom as compared with their bulk counterparts, and this accounts for the strongly negative entropy of solvation.

Another characteristic of hydrophobic hydration is the temperature dependence of the enthalpy of solvation. The partial molar isobaric heat capacity of the nonpolar solute in aqueous solution is large and positive. In other words, the solvation process becomes less and less exothermic with increasing temperature. Interestingly, the Gibbs energy of transfer of a nonpolar molecule from the gas phase to water only slightly increases. Hence, changes in enthalpic and entropic contributions to the hydration process largely compensate each other. Fast and accurate computer simulation techniques have recently shed some light on this compensation phenomenon. Increased thermal motions hinder the tangential orientations of water molecules in the first hydration shells surrounding the apolar solute. The number of hydrogen bonds in bulk water also decreases with increasing temperature, but to a lesser extent. Hence, at higher temperatures, hydration of hydrophobic molecules is accompanied by a greater loss of hydrogen-bond interactions, so that more enthalpy has to be paid. At the same time, the preferred orientation of water molecules in the hydration shell is disturbed, so that the entropic penalty for hydrophobic hydration becomes smaller.

In conclusion, it is clear that the term ‘hydrophobic hydration’ is in fact misplaced. Alkanes do not hate water, but it is the water which is ‘alkanophobic’. Hydration effects result from a subtle balance of enthalpy and entropy. Both thermodynamic quantities are large, and oppose each other. Water is special mainly because it is such a small molecule: each solute in solution is surrounded by a large number of water molecules.

1.4.2 Hydrophobic interactions. The tendency of nonpolar molecules to associate in aqueous solutions is called the hydrophobic effect. What is so characteristic of hydrophobic interactions is the narrow concentration range over which aggregation of apolar molecules in water occurs. At present, there is no satisfactory explanation for the occurrence of such a ‘critical aggregation concentration’ in terms of a physical mechanism.
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The state-of-the-art is based on the results of computer simulations, which are, however, contradictory. The idea is that aggregation of nonpolar molecules at low concentrations is hampered by the special orientation of water molecules in the first hydration shell. At a certain concentration of solute, the number of water molecules available to form a complete hydrophobic hydration shell is insufficient, leading to interference and mutual obstruction of hydration shells and the inevitable sacrifice of hydrogen bonds. The result is demixing. This model accounts qualitatively for the sudden aggregation of hydrophobic solutes in water, at well-defined concentrations. However, the model implies an extended hydrophobic hydration shell (as has been often assumed). For example, the solubility of hexanol in water at room temperature is only $10^{-4}$ (expressed as a mole fraction), suggesting that the hydration shell of one alcohol molecule is composed of, on average, 1000 water molecules. This conclusion seems unacceptable. Indeed, neutron scattering studies indicate that hydrophobic hydration shells are relatively small. A methane molecule is surrounded by a shell containing ‘only’ 19 ± 2 waters. Of course, the hydration characteristics of methane and hexanol are different - the latter molecule having both a hydrophilic and a hydrophobic hydration sphere. Intuitively, however, the experimentally determined hydration number for methane is much too small as compared with the number of 1000 waters surrounding one hexanol molecule, as implied by the model.

From a thermodynamic point of view, bulk hydrophobic interactions and phase separation can be in treated in terms of a solubility limit, which results from a balance between the positive mixing entropy of the solute and the negative entropy of the water molecules entering the hydration shell from the bulk (vide supra). Thus, as more and more nonpolar molecules are dissolved in water, their mixing entropy degressively increases. The entropy of the water molecules decreases linearly with solute concentration. Therefore, the total entropy change of the system will become positive at a certain solute concentration, and neglecting enthalpy, this will be the point where phase separation occurs. We contend, however, that this thermodynamic view is just a description of trends in bulk properties of water; it does not explain hydrophobic hydration in molecular terms. On the other hand, the model that appears to fail quantitatively in predicting the number of water molecules present in the hydrophobic hydration shell is in qualitative agreement with the thermodynamic description.

1.4.3 Formation of micelles. Amphiphiles are bifunctional molecules consisting of two moieties: one polar, the other apolar. Soap and ABS are examples of amphiphilic compounds. In analogy with the solution behavior of alkanes in water, when dissolved in water at low concentrations, the entropy of mixing causes the molecules to become individually dispersed in the solvent. When the amphiphile concentration exceeds the critical micelle concentration, the mixing entropy term is overridden by the entropy loss of solvating water molecules, and analogously to bulk hydrophobic interactions, phase separation occurs. The only difference is that pseudophase separation takes place instead of macroscopic phase separation. This is due to the amphipolar binding properties of the bifunctional molecules: one end strongly interacts with the solvent, whereas the apolar end prefers the vicinity of a nearby hydrophobic moiety. Thus, amphiphiles cannot pack into large droplets. Instead they form a variety of structures such as micelles (vide infra), where the size of the interfacial region between the dispersed amphiphile-rich phase and bulk solvent-rich phase is considerably enhanced.

In line with the above-mentioned model of bulk hydrophobic interactions, the notion of micellization as pseudophase separation due to the presence of an ‘entropic’ solubility limit might be somewhat more realistic than the idea that micellization occurs as soon as complete hydrophobic
hydration shells cannot be independently formed. The latter notion is hard to reconcile with the observation that the CMC does not decrease linearly with increasing alkyl chain length, but exponentially. Thus, whereas the number of water molecules needed to form the hydrophobic hydration shells around the surfactant monomers is expected to depend linearly on the alkyl chain length, in practice, a tenfold reduction of the CMC upon chain elongation by two methylene units is observed. Moreover, with regard to thermodynamics, the temperature dependence of micellization is akin to the dissolution/aggregation behavior of ordinary hydrocarbons in water, providing additional evidence that micellization of amphiphiles is just an extension of phase separation of apolar solutes - in the colloidal domain.

1.4.4 Properties of spherical micelles. Laundry detergent formulations contain single-tailed amphiphiles carrying anionic or nonionic headgroups, such as NaDoBS and C_{13-15}EO_{n},. Fabric softeners are composed of single-chain cationic amphiphiles; we mention n-dodecyl trimethylammonium bromide (DTAB) as an example. As was recognized by McBain already in 1913, these compounds form micelles when dissolved in water at concentrations exceeding the CMC. According to the ‘standard’ model proposed by Gruen, ‘decently behaving’ amphiphiles, such as NaDoBS and DTAB, form spherical micelles in aqueous solution. Almost all the methylene groups comprising the hydrocarbon chain of the amphiphile are held within the micellar core. However, terminal methyl groups occasionally reach the micellar surface. Water molecules are almost completely excluded from the inner part of the micelle; only two methylene groups (closest to the headgroup) are in contact with water. Finally, the alkyl tails fill the core, which has the properties of a liquid n-alkane, the semi-flexible chains showing a high degree of conformational disorder. Critical micelle concentrations for ionic amphiphiles are usually of the order $10^{-4}$ to $10^{-2}$ M, and increase by a factor of 10 when the alkyl chain is extended by two methylene groups. Aggregation numbers are often between 40 and 100; the size of an ‘ordinary’ micelle is approximately 5 nm so that a micellar solution is transparent to the eye. Micelles ($A_n$) are in dynamic equilibrium with their monomers (A):

\[
A_n \rightleftharpoons A_{n-1} + A
\]

where $N$ is the mean aggregation number. The association rate constant $k_a$ is found to be between $2.10^8$ and $3.10^9$ M$^{-1}$ s$^{-1}$, close to diffusion controlled, and only slightly dependent on the nature of the surfactant. The residence time $T_R$ of one amphiphile in the micellar assembly is related to the ‘exit’ rate constant $k_e$ by $T_R = N/k_e$. The residence time depends on the length of the alkyl chain. For example, $T_R$ decreases from $2.7\times10^{-7}$ to $6.1\times10^{-6}$ s on going from sodium n-octyl to n-dodecyl sulfate; the aggregation number increases from ca. 30 to ca. 60, while the exit rate constant decreases by a factor of 10.

1.4.5 The cleaning action of detergents. Oily soil, by its apolar nature, can be dissolved in the hydrocarbon-like micellar interior. This is one of the mechanisms of detergency, called solubilization, and corresponds to the formation of ‘swollen’ micelles. Their size is somewhat larger than that of the original micelles, but still far below the wavelength of visible light. Swollen-micelle systems can be considered as oil-in-water microemulsions, since as opposed to grease droplets dispersed in water, the swollen micelles are physically (and colloidally) stable.

A major contribution to the cleaning power of detergents is provided not by their aggregation
in aqueous solution, but by their surface-active properties. Thus, amphiphiles are surfactants, which tend
to concentrate at almost any water/liquid, water/gas or water/solid interface due to the tendency of the
apolar groups leave the aqueous phase while the headgroups tend to remain hydrated. Thus, when we add
a surfactant to a system comprising two immiscible phases (e.g., water and n-pentane), it will be adsorbed
at the interface between the two phases, and will orient with the hydrophilic group toward the aqueous
phase and the hydrophobic group toward n-pentane. Where the surfactant molecules replace water and/or
pentane molecules of the original interface, the interaction across the interface is between the hydrophilic
group of the surfactant and water molecules on one side, and between the hydrophobic chains of the
surfactant and pentane molecules on the other side of the interface. Since these (‘like-like’) interactions
are much stronger than the original interactions between the highly dissimilar pentane and water
molecules, the tension across the interface (or the surface Gibbs energy per unit area, \( \gamma \)) is reduced.\(^\text{54}\) In
other words: surfactants compatibilize aqueous solutions with their interface. When this theory is applied
to oily soil removal, the model only explains the emulsifying power of detergents: by the input of
mechanical energy, with the help of surfactants, layers of dirt can be dispersed as small droplets, and then
washed away. (Just as the oil droplets in mayonnaise are coated with a ‘protecting’ layer of lecithin, the
emulsified dirt is characterized by a surfactant-rich surface layer that acts as a potential energy barrier
against coalescence. More importantly, this layer prevents the dirt from coming into intimate contact with
the fabric, so that redeposition of the soil on the cloth is hampered.\(^\text{55}\) These droplets are much larger
than swollen micelles, and hence the aqueous dispersion has a turbid appearance.

To understand the mechanism of oily stain removal, we have to take account not only of the soil
(S) and the water (W), but also the fabric (F). The equilibrium contact angle \( \theta \) between water and the
other phases is related to the interfacial Gibbs energies per unit area of those phases (Figure 1.9). Imagine
that the interfacial areas fabric/water and fabric/soil are increased by a certain amount \( \Delta a \). The interfacial
area between the soil and the water is increased by \( \Delta a \cos \theta \). Thus, the resultant change of the interfacial
Gibbs energy is

\[
\Delta G_w = -\Delta a \gamma_{FW} + \Delta a \gamma_{FS} + \Delta a \cos \theta \gamma_{SW}.
\]

Since as \( \Delta a \rightarrow 0 \), \( \Delta G_w \rightarrow 0 \), we obtain \( \cos \theta \gamma_{SW} = \gamma_{FW} - \gamma_{FS} \), or

\[
\cos \theta = \frac{\gamma_{FW} - \gamma_{FS}}{\gamma_{SW}}
\]

Equation 2 is Young’s equation.\(^\text{54}\) By adding a surfactant, the interfacial tensions between water and the

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**Figure 1.9** Contact angle in water/soil/fabric system.
fabric, and between water and the soil, become exceptionally low: \( \gamma_{FW}, \gamma_{SW} \to 0 \). The interfacial tension between soil and the fabric does not change. Hence, in the presence of surfactant, \( \gamma_{FS} > \gamma_{FW} \). Thus, \( \cos \theta \) is negative, so that the contact angle is larger than 90°. As is shown in Figure 1.10, this means that the area of contact between the soil and the fabric can be reduced to zero while maintaining the contact angle at its equilibrium value. In other words: there are no thermodynamic restrictions on the removal of soil by hydraulic action, provided that surfactant is present. This mechanism of detergency is called roll-up.

In the absence of surfactant, part of the soil droplet can be withdrawn by mechanical action, but as the area of contact is reduced, a neck is formed directly above the contact region (Figure 1.11). If the contact angle is maintained, the drop must divide at this neck, leaving a small quantity of oil adhering to the substrate. This result confirms that detergents are required to remove all oily stains from the fabric if water is the solvent.

1.5 Surfactant aggregate morphology and formation of liquid crystals

Apart from spherical micelles described above, surfactant molecules can aggregate into a variety of colloidal structures, having different sizes and shapes. The morphology of these aggregates critically
depends not only on the surfactant type, but also on temperature and the presence of salts. The aggregates form liquid crystalline structures as the surfactant concentration increases. The formation of ordered mesophases is driven by the relief of interaggregate repulsions. With respect to the ‘science of laundry detergents’, detailed knowledge of liquid crystalline behavior is required for the formulation of liquid detergents (characterized by high surfactant concentrations), whereas washing performance critically depends on the aggregate morphology in the wash liquor.

1.5.1 Micellar shape and geometric packing constraints. To a first approximation, the ability of amphiphiles to form aggregates of a well-defined morphology depends on the molecular architecture of the surfactant molecules. The packing properties of surfactants result from a balance between the optimal cross-sectional surface area of the headgroups $a_0$, the volume $v$ of the hydrocarbon chains, and the maximum length $l_c$ that the chains can attain. The dimensionless packing parameter $p = v/a_0l_c$ characterizes the surfactant’s ability to form spherical micelles (cone-shaped surfactant molecules,

![Figure 1.12](image)

The packing parameter approach: the morphology of the surfactant aggregates is determined by the geometrical shape of the constituent monomers.
p<1/3), worm-like micelles (truncated cone, 1/3<p<1/2) or bilayers (1/2<p<1). Figure 1.12 graphically illustrates the packing parameter approach.59

By input of mechanical energy, flat bilayers close to form spherical structures entrapping an aqueous ‘pool’.60 These so-called vesicles may be uni- or multilamellar, depending on the number of concentric bilayers forming the structure.61 Moreover, depending on the size, one distinguishes between small unilamellar (Figure 1.13), large unilamellar and giant vesicles.62 SUVs (20-50 nm), LUVs (60-1000 nm) and GVs (> 1 μm). We stress, however, that vesicles formed from chemically pure amphiphiles are metastable, and with time, they return to the flat bilayer state.63 This spontaneous change can be explained in terms of geometrical factors. A bilayer is composed of two monolayers (bilayer leaflets), stuck together through hydrophobic interfaces. Each monolayer is characterized by an equilibrium spontaneous curvature which in general is non-zero. A bilayer composed of identical monolayers is frustrated because the monolayer curvatures are equal in magnitude, but of opposite sign. In terms of symmetry, the flat bilayer is least frustrated (i.e., has the lowest Gibbs energy) when its spontaneous curvature is zero!64

Is the packing parameter explanation of surfactant aggregate morphologies satisfactory? In general, the answer is ‘yes’. There are many (recent) examples of a wide variety of surfactant molecules which obey these geometrical rules. For example, C_{12}EO_3 forms vesicles, whereas C_{12}EO_7, having a larger headgroup, forms worm-like micelles.65 Even polystyrene-b-poly(acrylic acid) diblock copolymers form bilayer structures (PS-b-PAA = 400-b-16) or worm-like micelles (200-b-15) depending on the ‘hydrophobic chain length’ (ca. PS content) at constant ‘head group area’ (ca. PAA content).66

In cases where the approach is unsatisfactory, it is still valid in reality, but the sensitivity of both the geometry and packing of surfactant molecules to the experimental conditions may be underestimated!67 Thus, micelles of NaDoBS in dilute aqueous solutions can be transformed into bilayer aggregates by addition of alkali metal chlorides.68 An increase in ionic strength leads to an increase in counterion binding to the micellar surface and a concomitant decrease of the hydration of the headgroups (and Coulombic inter-headgroup repulsions). Consequently the effective optimal cross-sectional surface area of the headgroup decreases, the packing parameter increases and the morphology of the aggregate is altered.69 The soap boilers used this principle. By adding large amounts of NaCl to a concentrated micellar solution of soap, the packing parameter of the surfactant molecules increases and large bilayer structures are formed, which phase separate to form a solid-like material. For nonionic surfactants, temperature plays an important role. Headgroup hydration (and a_o) decreases rapidly with increasing temperature. Consequently, the aggregate size increases.70 At even higher temperatures, the aggregates become so large that (at the cloud point) phase separation occurs.71, 72, 73 Finally, mixing of two different amphiphiles may result in aggregate properties that can only be understood on the basis of a larger-than-mean average packing parameter. For example, the electrostatic repulsions between ionic surfactants, and
the steric repulsions between nonionic surfactants are strongly diminished when these molecules are mixed, because repulsive forces are completely different! Thus, admixing solutions containing nonionic and anionic surfactants, individually forming spherical micelles, produces a solution containing worm-like micelles.\(^{74,75}\)

1.5.2 Formation of liquid crystals from surfactant aggregates. Upon gradually increasing the concentration of ‘well-behaved’ surfactant above the CMC, more and more spherical micelles are formed. As a result, the mean distance between aggregates decreases. To accommodate the micelles, the system undergoes a disorder/order transition.\(^{76}\) For example, micelles can pack in a cubic array,\(^{77}\) to form a lyotropic (solvent-dependent) liquid crystal. The molecular order is not perfectly long-range (as in a crystal), nor isotropic (as in a liquid), but somewhere in between.\(^{78}\)

For the purposes of this thesis, the lamellar liquid crystalline phase is most important. The continuous lamellar phase is formed by a stack of ordered bilayer aggregates (Figure 1.14). The ‘neat soap’ phase depicted in Figure 1.2 is an example of a continuous lamellar phase. Alternatively, separate entities are formed upon closure of the bilayer sheets. Multilamellar vesicles appear when several bilayers pack around one another, rather like in an onion. Part of this thesis deals with multilamellar vesicles with many layers, henceforth called lamellar droplets. The thickness of the water layers between the surfactant lamellae (0.2-100 nm) may well exceed the bilayer thickness (2-3 nm), depending on, for example, surfactant concentration.\(^{79}\)

1.5.3 Phase behavior of liquid crystalline lamellar droplets in ‘structured’ liquid detergents. ‘Concentrated’ liquid laundry detergent formulations may contain over 30 wt% of surfactants. Hence, interaggregate interactions produce liquid crystalline phases. The resulting colloidal dispersions are colloidally unstable: phase-separation will occur due to flocculation (\textit{vide infra}). Two approaches are taken in practice to circumvent this problem. The lyotropic phase can be broken down by addition of intercalating\(^{80}\) water-soluble compounds such as sodium p-xylenesulfonate.\(^{81}\) The presence of these so-called hydrotropes results in the formation of an isotropic liquid. Another possibility is to induce the formation of liquid crystalline lamellar droplets, and to make the dispersion physically stable. In this way, an internally or surfactant-structured liquid detergent formulation is obtained.\(^{82}\) We focus attention on the latter approach.

The remainder of this chapter introduces the lamellar dispersions which have been studied in this thesis, and previously by Van de Pas.\(^{82}\) These systems are models for commercial structured liquid laundry detergents. In studies of the microstructure, the physical stability and the rheology of such
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detergent formulations, the number of components can be reduced to four: an anionic and a nonionic surfactant, water, and electrolyte. Specifically, the model lamellar dispersion under study consists of 28 parts (by weight) of NaDoBS, 12 parts of Synperonic A7, 60 parts of water and 20 parts of trisodium citrate: the 40/60/20 system.

In the next stage we turn attention to the aggregation and phase behavior of the surfactant mixture in the aqueous salt solution. Sodium citrate breaks down the hydration layer of the poly(oxyethylene) headgroup of the nonionic surfactants (‘salting-out’ or Hofmeister effect). At the electrolyte concentrations employed, dehydration occurs to such an extent that the headgroups cannot be kept in solution. Demixing occurs, according to the same mechanism as for temperature-induced ‘clouding’. Moreover, the reduction of the optimal headgroup area results in an increase of the packing parameter, which explains the transition to bilayer structures (arranged in a lamellar fashion) (Figure 1.15). Lamellar droplets are formed instead of a continuous lamellar liquid crystalline phase for two reasons. We recall that formation of curved bilayer structures from a chemically pure surfactant is thermodynamically unfavorable. Indeed, one might argue that the lamellar droplets are metastable, their formation being induced by the mechanical agitation involved in dissolving sodium citrate in a micellar surfactant solution. However, the lamellar droplets are stable for more than 5 years, providing strong indications that the droplets are thermodynamically stable. The reason is that a surfactant mixture is used, and if the compositions of the two monolayers are allowed to differ then, possibly, the spontaneous
curvature of the bilayer will be non-zero, thus favoring the formation of finite size vesicles.\textsuperscript{87}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{dispersion_lamellar_droplets.png}
\caption{Schematic representation of a dispersion of lamellar droplets. Reproduced from ref. [82a].}
\end{figure}
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Spontaneous vesicle formation has been observed in dilute aqueous mixtures of (i) cationic and anionic surfactants, and (ii) mixtures of ionic surfactants and alcohol cosurfactants with brine. This enthalpic stabilization mechanism was originally proposed by Safran et al. who showed theoretically that the Gibbs energy of a two-component bilayer may sometimes be minimized in a state of nonzero curvature, due to the spontaneous formation of different chemical compositions in the outer and inner leaflets.

Finally, we examine the reasons why these spontaneously formed multilamellar vesicles phase separate. We have an indication of the factors that are at play on a colloidal level. Generally, in stable dispersions, repulsive forces between particles are dominant. If attractive forces dominate, the particles flocculate (reversibly) or coagulate (irreversibly). Van der Waals attraction is always experienced between identical particulate matter. The attraction is due to ‘dispersion forces’ originating from electron correlations. At any given instant, the electronic configuration of atom \( a \) corresponds to an instantaneous dipole moment \( \mu(a, \text{inst}) \). The electric field corresponding to \( \mu(a, \text{inst}) \) polarizes atom \( b \) and induces a dipole moment \( \mu(b, \text{ind}) \). The instantaneous energy of interaction \( E(\text{inst}) \) is then the dipole-dipole energy corresponding to \( \mu(a, \text{inst}) \) and \( \mu(b, \text{ind}) \):

\[
E(\text{inst}) = -\frac{\alpha_b \mu(a, \text{inst})^2}{(4\pi\epsilon_0)^2 R^6}
\]

where \( \alpha_b \) denotes the frequency-dependent polarizability with a frequency corresponding to the rate of change of \( \mu(a, \text{inst}) \). The Van der Waals attraction between two semi-infinite flat surfaces can be written in the form:

\[
E_{\text{vdW}} = \frac{-A}{12 \pi D^2}
\]

where \( D \) is the distance between the surfaces and \( A \) is the Hamaker constant, which is a measure of the strength of the Van der Waals interaction. The Hamaker constant has a frequency-dependent and a zero-frequency term. In the presence of 0.5 M of electrolyte, the zero-frequency term is almost completely shielded at a separation of 1 nm. However, the frequency-dependent term hardly varies with salt concentration since the ions are too massive to follow redistributions of electrons. Overall, the Hamaker constant is \( 4.5 \times 10^{-21} \) J in pure water, and is reduced to \( 3.10^{-21} \) J in the 40/60/20 model system.

The electrical double layer repulsion \( (E_{\text{el}}) \) is the major long-range repulsion for charged particles. The electrical double layer comprises the charged bilayer and the (partially bound) counterions. For entropic reasons not all counterions are tightly bound. Hence the charge density (exponentially) decays from the surface. The ‘non-condensed’ counterions comprise the diffuse part of the double layer. Where the diffuse parts of either double layers of adjacent surfactant bilayers overlap, the counterion concentration starts to build up, and an osmotic flow of solvent into the overlap region keeps the surfaces apart. When an electrolyte is added to the system, counterion binding increases, the surface charge density is reduced and the electrical double layer repulsion is diminished. This pattern is true for
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bilayer-bilayer interactions in lamellar droplets and for inter-droplet interactions.

In the absence of salt, there is steric repulsion between the nonionic headgroups. The steric interaction energy has several components: (i) a volume restriction term which is due to the loss of configurational entropy of the PEO chains that occurs on head-to-head approach of the nonionic surfactants \( E_v \), and (ii) an osmotic interaction \( E_o \), which results from an increase in the local concentration of PEO segments in the region where the headgroups overlap.\(^9\) (The osmotic term is generally most important.) However, in the presence of high electrolyte concentrations, water is a ‘bad solvent’ for the poly(ethylene oxide) moieties; the PEO chains contract, the osmotic interaction may become attractive, and the volume restriction term becomes insignificant at distance larger than 3 nm. Again, both intra- and inter-droplet repulsions are greatly reduced upon addition of salt.

The total interaction energy per unit area \( E_{tot} \) when two bilayers approach each other may be approximated by:

\[
E_{tot} = E_{vdW} + E_v + E_{vr} + E_o
\]

Typically, the net interaction energy as a function of interparticle separation follows the profile outlined in Figure 1.16. As follows from the discussion above, Van der Waals and osmotic attractions dominate the repulsion in the presence of electrolyte. Hence, multilamellar stacks of bilayers are formed. The location of the primary minimum, i.e. the interparticle separation where the energy is lowest, is of the

![Figure 1.16](image_url)  
**Figure 1.16** Total interaction energy as a function of distance between bilayers.
order of several nm, according to X-ray diffraction measurements (Chapter 6). However, there are also (weaker) net attractive forces between the lamellar droplets, as indicated by the presence of the secondary minimum. This secondary minimum appears to be quite deep (= several kT): it is usually observed that the lamellar droplets are flocculated, and can hardly be redispersed upon shaking. The extent of flocculation is determined by the same forces as those which act between bilayers. The interactions between the lamellar layers and the lamellar droplets are of the same kind: the interaction forces are coupled. The only difference is that the curvatures of two opposite layers within the droplet are of opposite sign, whereas the curvatures of two layers in opposite layers have the same sign. As a consequence, in the presence of electrolyte, the net attractive forces between lamellar droplets are smaller than those between lamellae within droplets. Hence, the secondary minimum is more shallow than the primary minimum.

1.5.4 Deflocculation of lamellar droplets by addition of decoupling polymers. The mutual aggregation of lamellar droplets can be prevented by the addition of polymers which - due to the presence of hydrophobic side-chains - adsorb onto the periphery of the multilamellar aggregates, while a water-soluble backbone protrudes into the solution. Adsorption of these ‘hairy’ polymers prevents close approach of the droplets by a mechanism called steric stabilization. Provided that the aqueous electrolyte solution is a ‘good’ solvent for the polymer, i.e. the polymer coil is not collapsed, the same type of steric/osmotic forces as described for PEO segments in salt-free aqueous solutions becomes operative, and two repulsive (volume restriction and osmotic) interaction terms $E_{vr,pol}$ and $E_{os,pol}$ are added to the total interaction potential. However, provided that the polymers do not penetrate 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, see Figure 1.17.
Figure 1.17  Schematic representation of a lamellar dispersion in a good solvent (A), in a poor solvent (B) and in a poor solvent with added decoupling polymer (C). (Solvency is noted with respect to the surfactants.) The polymers are depicted in a thick line style. For a legend to surfactant structures, see Figure 1.15. Taken from ref. [82a].
Van de Pas has developed a random copolymer of lauryl methacrylate and sodium acrylate of molecular weight 4000; the LMA/NaA monomer ratio is 1:25. This polymer, RAN4000, efficiently stabilises lamellar droplets in a 40/60/20 system when added on top in concentrations of 0.5-2 wt.%.

In fact, this polymer is used in commercial concentrated structured liquid detergents.

1.6 Polymer-surfactant interactions in (liquid) laundry detergent science. Outline of this thesis.

So far, we have explored the broad area of laundry detergent science with respect to the wash liquor and the formulation of structured liquid laundry detergents. With regard to the wash liquor, we are concerned with dilute surfactant solutions (concentration < 10 CMC). Hydrophobic interactions between surfactant molecules and/or micelles and hydrophobic soil are involved in the actual detergency process. However, a large number of components are present in detergent formulations. Therefore, we anticipate many interactions between these additives, the surfactants, the soil and the fabric in the wash liquor. Thus, a detailed understanding of detergency, taking into account all processes and interactions in the wash liquor, presents an enormous challenge.

In a first attempt to gain some insight into the complicated interaction landscape, we studied the interactions between surfactant monomers, micelles and vesicles, and hydrophobically-modified water-soluble polymers (HMP) in dilute solutions. The decoupling polymers constitute one example of this class of polymers; they have an amphiphilic nature and are expected to interact with surfactant molecules or aggregates through hydrophobic interactions. We will see that decoupling polymers can form micelle-like structures which are called hydrophobic microdomains. Interactions with single-tailed micelles critically depend on the presence of these domains, to which surfactant monomers may bind. Consequently, the concentration of free surfactant monomers in solution is reduced. Moreover, the viscosity of the wash liquor may be influenced by the polymer, and the solution viscosity may be altered by the polymers interacting with surfactants. A titration microcalorimetric / fluorescence spectroscopic study on HMP-surfactant monomer and HMP-micelle interactions is reported in Chapter 2.

Chapter 3 describes the interactions between surfactant bilayers and hydrophobically-modified polymers in dilute solutions as studied by titration microcalorimetry and differential scanning microcalorimetry. The aim of this research is to study the factors that determine the efficiency of anchoring of hydrophobic side chains into (small unilamellar) vesicle bilayers. The underlying idea is that the efficiency of anchoring of the polymer into the vesicle bilayer is of immediate relevance for steric stabilization.

Chapters 4 and 5 are concerned with microstructural and rheological properties of concentrated lamellar dispersions with added decoupling polymers. We have developed a decoupling polymer that is specifically hydrophobically end-capped, in contrast to the commercial product RAN4000 which is less well-defined because it contains, apart from ‘anchorless’ poly(sodium acrylate), fractions bearing more than one anchor per polymer. Using this end-capped polymer, we have studied in detail the effects of adsorbed polymer on the average lamellar droplet size, as a function of polymer concentration and molecular weight. Moreover, the rheological properties of the model dispersions are interpreted in terms of interparticle forces (Chapter 5). Finally, we show that by rational design of polymer structure, shear-thinning properties of a lamellar dispersion can be amplified, so that solid particles can be suspended in
a liquid laundry detergent.

Most of this work has been or will be published.\textsuperscript{100}

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### 1.7 Notes and references

13. See, for example, the online Microsoft Encarta encyclopedia: http://encarta.msn.com/index/concise/0vol0E/01b45000.asp. One might also surf to: http://www.schwaben.de/home/kepi/water4.htm.
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Van Os and Haak have compiled a large number of data regarding aggregation of many different amphiphiles: Van Os, N.M.; Haak, J.R.; Rupert, L.A.M. *Physico-Chemical Properties of Selected Anionic, Cationic, and Nonionic Surfactants*, Elsevier: Amsterdam, 1993. Paul Huibers’ homepage on the Internet provides access to interesting sites related to amphiphiles: [http://web.mit.edu/huibers/www/surfsite.htm](http://web.mit.edu/huibers/www/surfsite.htm). At the time of writing, the site has links to 193 people in the field, 183 business sites, 98 sites on surfactant applications, 78 publishers and publications, 40 conference sites, 19 professional societies and 81 universities and research centers.


Small-angle neutron scattering was used to provide direct evidence for the spherical nature of micelles from sodium dodecyl sulfate aqueous solution: Corti, M.; Degiorgio, V. *J. Phys. Chem. 1981* 85, 1442.


‘Optimal’ refers to the condition where two opposing forces are in equilibrium. Hydrated and/or charged headgroups repel each other, tending to increase the headgroup area. On the other hand, the hydrocarbon/water interface strives to be minimized.


In Figures 1.12 and 1.13, the bilayers are shown composed of single-tailed surfactants, for ease of drawing. We stress that more generally, (vesicle) bilayers are composed of double-tailed amphiphiles.
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64. Safran, S.A. Statistical Thermodynamics of Surfaces, Interfaces and Membranes, Addison-Wesley: Reading (MA), 1994.


69. At the same time, a reduction of repulsive forces between headgroups lowers the CMC: Ruckenstein, E.; Beunen, J.A. Langmuir 1988, 4, 77.


76. Initially, worm-like micelles will be formed.


78. Thermotropic liquid crystals are formed when molecular solids are heated in the absence of solid. We refer the reader to Collings, P.J. Liquid Crystals, Natures Delicate Phase of Matter, Adam Hilger: Bristol, 1990.


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