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Micelle to Lamellar Aggregate Transition of an Anionic Surfactant in Dilute Aqueous Solution Induced by Alkali Metal Chloride and Tetraalkylammonium Chloride Salts

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Micelles of the anionic surfactant sodium dodecylbenzenesulfonate (NaDoBS) in dilute aqueous solution can be transformed into lamellar aggregates by the addition of alkali metal chloride (LiCl to CsCl) and tetraalkylammonium chloride (alkyl is methyl or n-butyl) salts. Depending on the type of cation, concentration of salt, and isomeric purity of the alkyl chain of the surfactant, different types of phases are observed: large unilamellar vesicles, multivesicular vesicles, and flocculated multimamellar vesicles (lamellar droplets). Over limited concentration ranges, some salts induce phase separation in a surfactant-rich and a surfactant-lean phase. The formation of the different phases was monitored by turbidity and fluorescence depolarization measurements, whereas the phases were characterized by light microscopy, freeze-fracture electron microscopy, and confocal scanning laser microscopy. Thermodynamic aspects of aggregation, in particular the counterion binding characteristics, were studied by microcalorimetry and conductivity. On a molecular level, the packing in a lamellar array can be explained largely in terms of a change in counterion binding and, to a lesser extent, by a decrease of the hydration of the headgroup and the counterion. A better understanding of the structural variation in the lyotropic series stems from the fact that the cation hydration alters the interaction between headgroup and the counterion, and extends with two tetraalkyl ammonium chloride salts (TAACl, alkyl being methyl or n-butyl). The reason for this structural variation originates from the fact that the hydration of the headgroup and the counterion, and extends with two tetraalkyl ammonium chloride salts (TAACl, alkyl being methyl or n-butyl). The reason for this structural variation originates from the fact that the cation hydration alters dramatically along this series, from highly hydrated for Li+ to weakly hydrated for Cs+ to more hydrophobically hydrated for the TAA+ ions. As a rule of thumb, less hydrated ions lead to higher counterion binding in surfactant aggregates. This will have drastic consequences for the transition into a lamellar arrangement of the surfactant molecules. Several reports in the literature indicate that the change from Na+ to other alkali metal cations, especially Cs+, induces changes in aggregates of anionic surfactants, which are related to the hydration characteristics of the specific counterions. A similar role is played by anions in the aggregation behavior of molecules by salts finds an important commercial application in liquid laundry detergents.

Introduction
The aggregation of surfactants in a lamellar array can be facilitated if one of the following requirements is met. First of all, a high surfactant concentration in water often leads to a lyotropic lamellar liquid-crystalline phase. Numerous phase diagrams can be listed, where, as a function of composition and/or temperature, a lamellar phase is observed.1,2 Double-tailed amphiphiles usually form bilayer sheets, as their most hydrated state allows the molecules to pack only in a lamellar arrangement. Upon closing, these sheets form vesicles.3,5 Lamellar aggregates are also formed from delicate mixtures of anionic and cationic surfactants in water6 or mixtures of ionic surfactants and long-chain alcohols in water7 or electrolyte solution.8 Some surfactant molecules in aqueous solution are spontaneously transformed from micelles into a lamellar array in the presence of a high salt concentration.9 On a molecular scale, this change in aggregate morphology is facilitated by an increase in counterion binding and dehydration of the surfactant headgroups and bound counterions. On a larger scale, interactions between lamellae occur, leading to the formation of either unilamellar vesicles (small or large) or multilayered systems (oligo- and multimamellar vesicles, lamellar droplets, or a continuous lamellar phase, Lα). The induction of a lamellar arrangement of surfactant...
alkyltrimethylammonium salts in water, where changing from the common bromide counterion to the better hydrated hydroxide ion leads to smaller micelles with higher curvature.

Also the isomeric purity of the hydrophobic tail of the surfactant can have a profound influence on the aggregation behavior. This will be illustrated by comparing the aggregation behavior of the polydisperse NaDoBS with that of the isomerically pure 5/6 sodium dodecylbenzenesulfonate.

In addition to the rearrangement on a molecular scale, the interactions between aggregates or between bilayers, are influenced by the nature of the interaggregate or the interbilayer medium, in this case, type of salt and its concentration. The interactions between bilayers (and aggregates in general) are governed by several factors, as reviewed by Israelachvili. These interactions are comprised of an attractive van der Waals force, acting on any two bodies over a different medium, and, on the repulsion side, involve the electrical double layer forces.

On a shorter distance, the hydration force is considered, as proposed by Rand and Parsegian, but these effects are controversial. Repulsions which are due to thermally-induced motions of the surfactant molecules and of the bilayers are the steric forces, divided in three different types: proton repulsion and peristaltic membrane motions, both acting on rather small distances, and (Helfrich) undulation repulsion, which can act over substantially larger distances for flexible bilayers.

This study aims at explaining what are the physical factors determining the aggregation behavior of the anionic surfactant sodium dodecylbenzenesulfonate (NaDoBS) in different aqueous salt solutions.

Experimental Section

Materials. The anionic surfactant was a commercial dodecylbenzenesulfonic acid (HDoBS, MARLON AS3, Hüls, Hilts, 98.3% pure, provided by Unilever Research Laboratory, Vlaardinghen, The Netherlands) with an average composition as sketched, containing a few tenths of a percent sulfuric acid and the remaining part is non-surface-active organic material.

Solutions were adjusted to a pH of approximately 7 with sodium hydroxide, yielding an aqueous solution of the sodium salt (NaDoBS). The solid NaDoBS was also prepared by reaction of dodecylbenzenesulfonic acid (HDoBS, MARLON AS3, Hüls, Hilts, 98.3% pure, provided by Unilever Research Laboratory, Vlaardinghen, The Netherlands) with an average composition as sketched, containing a few tenths of a percent sulfuric acid and the remaining part is non-surface-active organic material.

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Sample Preparation. Samples were prepared by either dissolving approximately 4 mmol of NaDoBS (solid) per kg of water (m) or diluting a concentrated HDOS solution, neutralized by NaOH, to approximately 4 mmol. No differences in phase behavior were found for the surfactants obtained by the two methods of preparation. The phase behavior of NaDoBS in dilute solution was studied by turbidity and fluorescence depolarization measurements. Solutions were labeled with DPH by vortexing the surfactant solution for at least 10 min over a film of fluorophore, made by evaporation of the solvent from a solution of DPH in THF, under a stream of nitrogen. The fluorophore/surfactant ratio was about 1:10000. Fluorescence cuvettes were filled with 2 g of surfactant solution. Then the salt concentration was increased stepwise by addition of the particular salt in small, precisely weighed amounts, either as a solid or, when phase changes occur over short salt concentration ranges, in a concentrated solution of known composition. After dissolution of the salt and homogenization, the turbidity and fluorescence depolarization value were determined immediately (see below). Samples were kept at ambient temperature. Reflective indices of 1.0 m XCl salt solutions were measured with a conventional Zeiss refractometer at 25 °C.

Turbidity Measurements. Turbidity measurements were performed at 25 °C with a Philips PU 8740 UV/VIS spectrophotometer. Turbidity is expressed as the optical density at 400 nm in absorption units.

Fluorescence Depolarization. An SLM Amicon SPF-500C spectrophotometer equipped with a polarization device was used for fluorescence depolarization experiments. Measurements were performed as described before. The excitation wavelength was 360 nm; emission was determined at 428 nm.

Light Microscopy. After the occurrence of the different phases was monitored by turbidity and fluorescence depolarization studies, specific samples were examined by light microscopy with a Zeiss Axioskop or a Zeiss Axioplan light microscope equipped with an automatic photocamera, using the bright field, the phase contrast (Axioplan), and the crossed polars mode. To prevent the collapse of aggregates, a thin strip of Parafilm was employed in several cases as a spacer between the microscope slide and the coverglass. In this way the possibility was created to observe the structures in unperturbed surroundings. A disadvantage of the method is that the aggregates above and below the plane of focus can obscure the image.

Electron Microscopy. Freeze-fracture replicas were made as described previously; samples were examined in a Philips EM 201 electron microscope, operating at 60 kV.

Confocal Scanning Laser Microscopy. Several solutions were examined by confocal scanning laser microscopy (CSLM). The procedure has been described before; samples were stained with Rhodamine-B analogously to the solutions employed for fluorescence depolarization (see above).

Microcalorimetry. The enthalpy of aggregation (ΔHagg) and the critical aggregation concentration (cac) were determined using a MicroCal Omega titration microcalorimeter (MicroCal, Inc., Northampton, MA). Procedures have been described in detail by Bijma et al. In short, a degassed solution of known surfactant concentration (using the NaDoBS surfactant) in the particular containing phase, water or electrolyte solution (roughly 10 times the cac), was injected in fixed increments (usually 4 μL) into a reservoir with overflow, containing 1.3249
mL of degassed continuous phase at 25.0 ± 0.1 °C. After each injection the instrument records the heat released or dissipated by the solution, in this case the breakup of aggregates and dilution. ΔH_agg and the cac can be extracted from the raw data using the method described by van Os et al. Notice that concentrations for microrheometry and conductivity studies are in mol/L (molar) whereas all the other concentrations are expressed in mol/kg (molal). Measurements were performed in duplicate or sometimes in triplicate.

Conductometry. Critical micelle concentrations (cmc) and the fraction of counterion binding, β, were determined by a Wayne Kerr Autobalance Universal Bridge B 642 conductometer. A solution of NaDoBS, with known concentration in water or 3.5 mM salt solutions, was injected in fixed increments into the isotonic continuous phase at 25.0 ± 0.1 °C. After homogenization the conductance was measured (in mS). Concentrations were corrected for volume changes. The cmc was taken from the intercept of the lines fitted through an array of points before and after an array of points after the break in a conductivity versus concentration plot. β was calculated as 1 - (slope after/slope before breakpoint). cmc values in electrolyte concentrations higher than 3.5 mM cannot be measured by conductivity, because the variation in conductivity is too small compared to the scale of the instrument necessary to measure conductance.

Results

The addition of salts to a solution of NaDoBS in water induces different types of surfactant aggregates, easily observable as solutions as dilute as 4 mM (only twice the cmc in water). These changes can be probed when the salts are added in small steps by monitoring the turbidity and the fluorescence depolarization of a fluorescent probe (DPH) bound to the surfactant assembly. As an example, the behavior of RbCl is depicted in Figure 1. The DPH fluorescence depolarization, which reflects the microviscosity of the hydrophobic surroundings of the probe, and the turbidity of the same sample are combined in one concentration plot. β was calculated as 1 - (slope after/slope before breakpoint), cmc values in electrolyte concentrations higher than 3.5 mM cannot be measured by conductivity, because the variation in conductivity is too small compared to the scale of the instrument necessary to measure conductance.

Figure 1. Fluorescence depolarization and turbidity (optical density at 400 nm) of a 4 mM NaDoBS solution in water as a function of RbCl concentration: ■, polarization, left axis; ●, turbidity, right axis.

The eff...
microscopy (CSLM) reveals a clear picture for the packing of surfactant molecules in this surfactant-rich phase. NaCl induces the formation of multilamellar aggregates straight after the micellar phase. There is a small but significant increase in $P$ between 0.2 and 0.35 $m$, before the multilamellar stage is entered, which can be attributed to a tighter packing of surfactant molecules leading to micelles with different geometry (for instance, with a more rod- or disk-like shape). A similar change in shape has been observed by light scattering. This feature is observed for the LiCl solutions as well.

The other alkali metal chlorides induce the formation of unilamellar aggregates, before higher salt concentrations turn these structures into multilamellar aggregates. Large unilamellar vesicles are observed by light microscopy, although these are often too small and moving too fast to catch them by photography; see Figure 3A. Figure 4A shows an FFEM micrograph of these vesicles. These unilamellar aggregates are colloidal more stable and the aggregates flocculate and cream completely from the electrolyte solution within an hour. The transition to multilamellar aggregates becomes less cooperative going toward CsCl. Addition of urea breaks down the multilamellar aggregates into micelles. This interesting phenomenon has not been examined in more detail.

Compared to the commercial, rather polydisperse NaDoBS, the isomerically pure 5/6 NaDoBS forms salt-induced lamellar aggregates at much lower NaCl concentrations than the polydisperse type; see Figure 2B. Most remarkable is that initially, at 0.05 $m$ NaCl, unilamellar aggregates are formed, characterized by a rather high $P$ and a rather low turbidity. At 0.25 $m$ NaCl, multilamellar aggregates form, which flocculate and precipitate from the solution, as indicated by a sharp increase in turbidity. Again, $P$ does not change at the transition from unilamellar to multilamellar aggregates.

Tetraalkylammonium chloride salts (alkyl = methyl or $n$-butyl) have a peculiar influence on the aggregation behavior of NaDoBS in water that differs substantially from the aggregation behavior of NaDoBS in alkali metal chloride solutions. Initially NaDoBS remains in the micellar phase up to 0.03 $m$ TBuACl and 0.9 $m$ TMACl, addition of more salt at ambient temperature leads to phase separation into a surfactant-rich and surfactant-lean phase. At still higher salt concentrations (1.6 $m$ for TBuACl and 2.2 $m$ for TMACl), the clouding gradually gives way to a physically stable dispersion of unilamellar vesicles and multivesicular vesicles, as can be clearly seen from Figures 3B and 4C. The vesicles are also nicely observable with CSLM (not shown); however, no bilayer undulations are found on the resolution scale of this technique, as was observed for the system described previously. At high salt concentrations (TMACl, 3 $m$; TBuACl, 1.5 $m$) these vesicles are physically and colloidal more stable for at least a year. Still higher salt concentrations (up to 7 $m$ TMACl) lead to dissolution of the aggregates and no multilamellar aggregates are observed. More and more surfactant molecules are dissolved as monomers, and, of course, at 7 $m$ TMACl (43% by weight) we can hardly speak of an aqueous solution anymore.

As was indicated by the fluorescence depolarization value $P$, the microviscosity inside the hydrophobic domains in the surfactant-rich phase is higher than in micellar aggregates but lower than in lamellar aggregates. Therefore, the packing of molecules is more regular and denser than in the micellar phase, but less than in a bilayer.

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Micelle to Lamellar Aggregate Transition

Critical aggregation concentration, enthalpies of aggregation, and fraction of counterion binding for NaDoBS in electrolyte solutions at 25.0 ± 0.1°C (unless stated otherwise)

<table>
<thead>
<tr>
<th>Solution</th>
<th>Phase</th>
<th>cac (mM)</th>
<th>$\Delta H_{aggr}$ (kJ/mol)</th>
<th>cmc (mM)</th>
<th>b'</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaDoBS in water</td>
<td>mic</td>
<td>2.21</td>
<td>-0.9*</td>
<td>2.25</td>
<td>0.36</td>
</tr>
<tr>
<td>LiCl, 0.0035 M</td>
<td>mic</td>
<td>1.53</td>
<td>-0.8*</td>
<td>1.70</td>
<td>0.31</td>
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<tr>
<td>0.2 M</td>
<td>mic</td>
<td>0.17</td>
<td>-1.2*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaCl, 0.0035 M</td>
<td>mic</td>
<td>1.30</td>
<td>-1.2*</td>
<td>1.36</td>
<td>0.34</td>
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<tr>
<td>0.01 M</td>
<td>mic</td>
<td>0.73</td>
<td>-1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.05 M</td>
<td>mic</td>
<td>0.28</td>
<td>-2.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1 M</td>
<td>mic</td>
<td>0.23</td>
<td>-2.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2 M</td>
<td>mic</td>
<td>0.16</td>
<td>-2.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.3 M</td>
<td>mic</td>
<td>0.12</td>
<td>-2.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KCl, 0.2 M</td>
<td>lam</td>
<td>0.15</td>
<td>-5.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RbCl, 0.2 M</td>
<td>lam</td>
<td>0.15</td>
<td>-6.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CsCl, 0.0035 M</td>
<td>mic</td>
<td>0.96</td>
<td>-2.4**</td>
<td>1.53</td>
<td>0.43</td>
</tr>
<tr>
<td>0.01 M</td>
<td>mic</td>
<td>0.55</td>
<td>-2.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.05 M</td>
<td>mic</td>
<td>0.27</td>
<td>-4.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.075 M</td>
<td>lam</td>
<td>0.21</td>
<td>-5.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1 M</td>
<td>lam</td>
<td>0.20</td>
<td>-6.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.15 M</td>
<td>lam</td>
<td>0.14</td>
<td>-6.8</td>
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<tr>
<td>0.2 M</td>
<td>lam</td>
<td>0.11</td>
<td>-6.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.3 M</td>
<td>lam</td>
<td>0.09</td>
<td>-6.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TMACl, 0.0035 M</td>
<td>mic</td>
<td>0.82</td>
<td>-2.9**</td>
<td>0.97</td>
<td>0.38</td>
</tr>
<tr>
<td>2.0 M (2.65 m)</td>
<td>lam</td>
<td>0.07</td>
<td>-5.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CsDoBS in water</td>
<td>mic</td>
<td>1.55</td>
<td>-4.3</td>
<td>1.53</td>
<td>0.43</td>
</tr>
<tr>
<td>TMADoBS in water</td>
<td>mic</td>
<td>1.45</td>
<td>-3.9</td>
<td>1.61</td>
<td>0.40</td>
</tr>
<tr>
<td>5/6 NaDoBS, water</td>
<td>mic</td>
<td>1.80</td>
<td>+2.4*</td>
<td>2.39</td>
<td>0.26</td>
</tr>
<tr>
<td>ide m, 35°C</td>
<td>mic</td>
<td>2.28</td>
<td>-4.9*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ide m, 45°C</td>
<td>mic</td>
<td>2.07</td>
<td>-11.0*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2 M NaCl</td>
<td>mic</td>
<td>0.13</td>
<td>-4.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*a Type of aggregate, micellar or lamellar. b Critical aggregation concentration determined by microcalorimetry; critical micelle concentration determined by conductometry. c Errors in the values for $\Delta H_{aggr}$ and cac are usually less than 10 and 5%, respectively, for cac values below 0.2 mM the absolute heat effects are becoming quite small leading to error margins that can be as large as 25%. d Pre-cmc slope, see text; **, negative post-cmc values, see text. e Fraction of counterions bound to the aggregate surface.

The data are used predominantly to shed light on the difference in the behavior of cations and not

Similar characteristics were found in NMR line broadening experiments but will not be discussed here.

As can be inferred from Figure 2, most changes in aggregation type occur above 0.1 m salt concentration, that is always a 25-fold excess or more of bulk cations. (The only exception is TBUAIC, for which phase changes occur at 0.03 m.) At this point it seems safe to assume that the bound Na+ ions are exchanged substantially for the other cation X+ (except for the LiCl case, see below). Information on the extent of the exchange can be obtained in the very dilute salt regime by conductivity and for a somewhat higher salt concentration with microcalorimetry. Listed in Table 1 are data obtained by those techniques. The values are extracted from raw data by models and calculations which are still under discussion. Here the data are used predominantly to shed light on the difference in the behavior of cations and not

Table 1. Critical Aggregation Concentrations, Enthalpies of Aggregation, and Fraction of Counterion Binding for NaDoBS in Electrolyte Solutions at 25.0 ± 0.1°C (Unless Stated Otherwise)

Figure 4. Freeze-fracture electron microscopy (FFEM) micrographs of (A) 2 mm NaDoBS in 0.1 m CsCl, unilamellar vesicles; (B) flocculated lamellar droplets (multilamellar vesicles) of NaDoBS in 1.2 m RbCl; (C) 4 mm NaDoBS in 3.3 m TMACl, large unilamellar and multivesicular vesicles. The bar represents 1 μm.
concentration examined. Formally this is not correct, because the first injection will show a rather high dilution effect, finally going to zero after an infinite number of injections when the concentration of the stock solution and in the reservoir have become equal. However, the practical error introduced by this interpretation is negligible.

The heat effect caused by deaggregation is the reverse of the effect of aggregation \( \Delta H_{\text{agg}} = -\Delta H_{\text{agg}} \). Consider the effect of aggregation occurring at the cac: the driving force for surfactant aggregation is a delicate compromise of entropic and enthalpic contributions. The exact nature of this driving force, hydrophobic bonding, remains a point of debate in the literature.\(^\text{22}\) The enthalpic parts of the aggregation process can be divided into several exothermic and endothermic contributions. The exothermic contribution predominantly stems from the dispersion forces which bind the hydrophobic tails in the core of the aggregate. For various aggregate morphologies this favorable enthalpy contribution will be different and will increase going from sphere- to rod-\(^\text{33}\) to disk-like micelles and finally to lamellar aggregates.

The building up of an electrical double layer around the aggregate involves an important endothermic contribution. It originates from the repulsion of bringing the headgroups together and an endothermic contribution of the (entropy driven) buildup of the diffuse part of the electrical double layer. The endothermicity will decrease further if the surrounding medium is an electrolyte solution and if the counterion binding is high. Moreover, the less hydrated counterions, that display a higher hydration enthalpy upon binding to the aggregate surface. This stock solution will consist of micelles in 0.2 M NaCl, and \( \Delta H_{\text{agg}} \) is isomerically pure 5/6 NaDoBS in 0.2 M NaCl, \( \Delta H_{\text{agg}} \) in CsCl, \( \Delta H_{\text{agg}} \) is isomerically pure 5/6 NaDoBS in 0.2 M NaCl, \( \Delta H_{\text{agg}} \) in CsDoBS in water, and \( \Delta H_{\text{agg}} \) in 0.2 M RbCl.

A remarkable result is the endothermic \( \Delta H_{\text{agg}} \) for the isomerically pure 5/6 NaDoBS in water at 25 °C, illustrative for the importance of a positive entropy of aggregation as the driving force for aggregation. The endothermic effect can (at least partially) be explained by the significantly lower counterion binding (\( \beta = 0.26 \)). This will give rise to a highly charged (thus enthalpically unfavorable) electrical double layer around the micelle, although isomeric purity would facilitate better packing and thus more hydration per cation.

Marked with a double asterisk in Table 1 are two measurements with an exothermic post-cac heat effect, going along with a larger increase in \( \Delta H_{\text{agg}} \) for only a small increase in electrolyte concentration. Both measurements deal with stock solutions containing a 4- to 9-fold excess of NaDoBS as compared to the background CsCl or TMACl solution. This stock solution will consist of micelles dressed with both Na\(^+\) and Cs\(^+\) or TMA\(^+\) counterions. Upon the first injections into the 3.5 mM electrolyte solution in the reservoir, the micelles simply fall apart into dissociated monomers. Above the cmc, however, the Na\(^+\) ions bound to the newly injected micelles, will be replaced by Cs\(^+\) or TMA\(^+\) ions which are present in excess in the bulk electrolyte solution. The removal of the Na\(^+\) ions from the surface of the micelle will be an endothermic process, since the exothermic hydration of the Na\(^+\) ions is less favorable than the endothermic contribution of the loss of electrostatic binding. On the other hand, more Cs\(^+\) or TMA\(^+\) ions bind to the micellar surface (exothermic) than Na\(^+\), with less dehydration (endothermic) per cation. Furthermore, as a result of the increased counterion binding, the surfactant headgroups experience overall less repulsion and this will allow a better packing of the molecules in the aggregate. The overall process of cation exchange will be exothermic, as is borne out by experiment. Another indication for the exchange of bound Na\(^+\) ions for Cs\(^+\) or TMA\(^+\) ions is the absence of a pre-cmc slope as discussed above, since this is an indication for higher counterion binding in the stock solution, which must be caused by the preferential binding of Cs\(^+\) or TMA\(^+\) ions. A similar conclusion can be drawn from conductometry, although this is less clear for the 3.5 mM TMACl case. However, this may be attributed to the TMA\(^+\) ions that bind to the micellar surface, releasing more mobile Na\(^+\) ions, which have a higher contribution to the conductivity of the solution.

A higher counterion binding is also apparent for both CsDoBS and TMADoBS in water: the \( \Delta H_{\text{agg}} \) is about 3 kJ/mol more favorable than for NaDoBS. This is readily reconcilable with the absence of a premicellar slope in the enthalpogram and with the higher \( \beta \) value obtained by conductometry.

A remarkable result is the endothermic \( \Delta H_{\text{agg}} \) for the isomerically pure 5/6 NaDoBS in water at 25 °C, illustrative for the importance of a positive entropy of aggregation as the driving force for aggregation. The endothermic effect can (at least partially) be explained by the significantly lower counterion binding (\( \beta = 0.26 \)). This will give rise to a highly charged (thus enthalpically unfavorable) electrical double layer around the micelle, although isomeric purity would facilitate better packing and thus grant a more exothermic contribution to the \( \Delta H_{\text{agg}} \). Going to higher temperatures, \( \Delta H_{\text{agg}} \) for 5/6 NaDoBS turns exothermic, as is commonly encountered for a variety of surfactants.\(^\text{24,25,29,32}\)

Overall, the data in Table 1 show that lamellar aggregates formed from the dodecylbenzenesulfonate has been published by Bijma et al.\(^\text{34}\) This effect will be larger if the aggregates in the stock solution have a relatively low counterion binding and therefore be less close to an ideal solution than in the case of a higher counterion binding, as is borne out by the data in Table 1. This is also reflected in the lower \( \beta \) values found with conductometry. Higher counterion binding (by a change in type and/or change in background electrolyte concentration) and the background electrolyte itself (a less ideal solution) mute this effect.
**Table 2. Characteristic Features of the Cations and Their Chloride Salts in Aqueous Solutions**

<table>
<thead>
<tr>
<th>Ion</th>
<th>hydrating number</th>
<th>hydrated radius (nm)</th>
<th>relative osmolality</th>
<th>Refractive index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li⁺</td>
<td>a 7.4 b 5-6</td>
<td>0.38</td>
<td>1.123</td>
<td>1.3416</td>
</tr>
<tr>
<td>Na⁺</td>
<td>a 6.5 b 4-5</td>
<td>0.36</td>
<td>1</td>
<td>1.3427</td>
</tr>
<tr>
<td>K⁺</td>
<td>a 6.0 b 3-4</td>
<td>0.33</td>
<td>0.932</td>
<td>1.3424</td>
</tr>
<tr>
<td>Rb⁺</td>
<td>a 4.7</td>
<td>0.33</td>
<td>1.3427</td>
<td></td>
</tr>
<tr>
<td>Cs⁺</td>
<td>a 4.3 b 1-2</td>
<td>0.33</td>
<td>0.907</td>
<td>1.3452</td>
</tr>
<tr>
<td>TMA⁺</td>
<td>a 1.8</td>
<td>0.37</td>
<td>1.3471</td>
<td></td>
</tr>
<tr>
<td>TBUA⁺</td>
<td>a 0.0</td>
<td>0.47</td>
<td>1.3695</td>
<td></td>
</tr>
</tbody>
</table>

*a Derived from limiting partial molar ionic volumes, data from Marcus.*

**Discussion**

Cations and their Hydration Numbers. How can the aggregation behavior of NaDoBS in different salt solutions be explained? The key lies in the hydration numbers of the cations used in this study. Unfortunately, the magnitude of the hydration number depends on the experimental technique used to determine this property. Listed in Table 2 are some hydration characteristics of different ions, showing discrepancies between several reports in the literature, but the general trend appears to be clear: an increasing atomic number (and atom size) leads to a decreased hydration number, and a slightly decreased size of the hydrated ion. The less hydrated an ion, the better it binds to an oppositely charged surface.

Exchange of Counterion. To understand the influence of salt concentration and the nature of the cation on the phase behavior of dilute NaDoBS solutions, we consider the two equilibria given in Scheme 1, where [RS⁻] is the dodecylbenzenesulfonate surfactant molecule in an aggregate (micelle or lamellar aggregate) and X⁺ the cation of the XCl salt added to induce the phase changes. Notice that the equilibrium constants should be expressed in activities because these highly concentrated solutions are far from thermodynamically ideal. These equilibria are the main issues for explaining the aggregation behavior. Of major importance are (i) changes in counterion binding, (ii) dehydration of the headgroup as a consequence of the addition of a salting-out electrolyte, and (iii) the influence of a salt on the physical interactions between molecules and between aggregates. Formally we should also consider the exchange equilibrium of cations between the electrical double layer and bulk solution far away from the aggregate surface.

Scheme 1

\[ [RS^-] + X^+(aq) + Cl^-(aq) ↔ [RS^-] + Na^+(aq) + Cl^-(aq) \]

Aggregation Behavior on the Molecular Scale. The shape of the surfactant molecule primarily determines the aggregate morphology under equilibrium conditions. The geometrical effects can be expressed in terms of an experimental geometrical packing parameter \( P = v/l, \) where \( v \) is the volume of the hydrophobic chain of the surfactant molecule, and \( l \) is the optimal cross-sectional area that the hydrated headgroup occupies at the aggregate-aqueous-phase interface, and \( l \) is the maximum effective length of the hydrocarbon chain in a fluid state. Included in the value for \( a \) are factors such as counterion binding and nonoptimal hydration of the headgroup when the solution conditions change, for instance by a salting-out electrolyte present in a high concentration or when the surfactant concentration is so high that it can form other lyotropic liquid crystalline phases. The surfactant used in this study is an important industrial product with many commercial applications and is nonmonodisperse; its dodecyl chain can be attached on any of the carbon atoms to the benzenesulfonate moiety. Therefore, the surfactant can be considered double-tailed, which usually leads to a bilayer-forming amphiphile. Sodium dodecylbenzenesulfonate, however, forms micelles in water, as also has been reported frequently in the literature, albeit with different micellar shapes.

**References**


Also the length and volume of the hydrophobic moiety of the alkylbenzenesulfonate are crucial parameters which are hard to be accounted for correctly in the packing parameter. For a truly cylindrically shaped amphiphile, an increase in chain length cancels the increase in volume of the hydrophobic moiety, so that the packing parameter remains constant with increasing chain length. For a truncated-cone shaped amphiphile, as discussed here, the volume also scales with the length above a certain alkyl chain length. Nevertheless, an alkylbenzenesulfonate with a longer tail such as SHBS (sodium 4-[(1′-heptyl)benzenesulfonate] is known to aggregate in a lamellar arrangement in water,1,2,13 whereas it has exactly the same topology as 5/6 NaDoBS and thus both surfactants will have a practically identical packing parameter. Nonetheless, 5/6 NaDoBS forms micelles in water. The influence of counterion binding has been illustrated nicely by the addition of a cryptand to a dispersion of SHBS in water.14 The sodium counterion will be dragged away from the aggregate surface, giving way to electrostatic repulsions between the sulfonate headgroups and probably to an increase in hydration of the headgroups. This leads to a higher curvature of the aggregate surface and a concomitant dissolution of the lamellar aggregates into micelles.

Interactions between Lamellae and between Aggregates. As explained in the introduction, four factors dominate the interactions between aggregates and bilayers in particular: van der Waals attractions, electrical double layer repulsions, hydration, and thermally induced steric repulsions. The influence of salt on all these forces will determine the overall aggregate behavior, and different salts will display different influences. The attractive van der Waals force will be lower in electrolyte solution than in water. The van der Waals interaction of two bodies (here the bilayers or the different aggregates) acting across a different medium (the electrolyte solution) can be described by the Hamaker constant. This Hamaker constant is composed of two terms: a zero-frequency part and a nonzero or high-frequency part. Ions in aqueous solutions are too massive to follow high-frequency oscillations, and therefore will not influence the high-frequency contribution to the Hamaker constant; this term will be comparable for water and aqueous electrolyte solutions. On the other hand, the electrolyte solution will screen the zero-frequency contribution substantially (compared to water).24 Moreover, this zero-frequency part is an important contribution to the Hamaker constant for hydrocarbons acting across aqueous media.18,44 In our study, we address the question whether this decrease in van der Waals attraction at increasing salt concentration changes as a function of the type of cation dissolved in the interlamellar medium. This screening of the zero-frequency part is related to the number of electrons per ion, which is also a feature determining the refractive index of that particular aqueous electrolyte solution. Therefore it is expected that, at equal concentrations, different cations might cause different van der Waals attractions. However, whether this effect is large enough to be observed in practice, is not clear. This view is supported by the fact that the refractive indices hardly vary for 1 m alkali metal chloride salts (Table 2). Van der Waals attraction between bilayers consisting of alkylbenzenesulfonates can be large compared to attractions between bilayers built up of alkyl chains since London dispersion interactions between aromatic moieties are relatively strong due to the high polarizability of the aromatic system. This difference is also seen in the different refractive indices (and dielectric constants).11 1.482 vs. 1.422 for dodecylbenzene and dodecane, respectively. Although the van der Waals attraction decreases at increasing electrolyte concentration, it obviously is the predominant interaction and does not decrease as much as all combined long-range repulsions since for all alkali metal cations, the attraction ultimately vindicates over repulsion, because flocculated multilamellar aggregates are finally formed in all cases.

On the repulsive side, hydration forces operate only over rather short distances (below 3 nm). Since the headgroups and most ions will not have the maximum number of solvating water molecules available at high electrolyte concentrations, hydration repulsions between surfactant aggregates will be appreciably less than in a purely aqueous environment. The Helfrich undulation repulsion can act over somewhat longer ranges,18 especially if the bilayers are highly flexible, i.e., possess a low bending modulus. Bilayer rigidity depends inter alia, on the thickness of the bilayer, which is rather low for a bilayer formed from NaDoBS molecules (ca. 1.9 nm1). There is no reason, however, to expect the bending modulus to change on increasing the background electrolyte concentration or changing the type of background electrolyte, except probably for a small contribution of a lower surface charge density for bilayers decorated with Cs+ ions compared to Na+ ions. Also peristaltic and protrusion factors operate over small distances (less than 3 nm), though no differences are expected for different type or concentration of background electrolyte, at least not for the alkali metal salts. For the TAA salts, protrusion might become a factor to take into account. Since these salts are salting-in electrolytes, monomer solubility increases and the interfacial tension decreases in a TAACl solution compared to water, leading to the possibility for the saltant molecules to jump out of the lamellar layer.8

The origin of the electrical double layer forces lies in the balance between electrostatic and entropic forces of the dissociated counterions, leading to an osmotic repulsion when two, here negatively charged, aggregate surfaces approach. Increasing counterion binding and concomitantly decreasing surface charge density will decrease the electrical double layer repulsions. The electrical double layer repulsion depends on the difference between the number of cations in the double layer vs. the number of cations in the bulk electrolyte solution. Thus, an increase of background electrolyte concentration reduces this osmotic repulsion. An additional factor to take into account is the change in osmotic force when the cations in the positive layer vary from Li+ to Cs+. Would this lead to a drastic change in repulsion, would for instance Cs+ give rise to a much larger osmotic repulsion? A comparison of the osmotic pressure values listed in Table 2 for several 1 m XCl solutions does not make this a tempting idea: a CsCl solution can exert an osmotic pressure which is only 91% of the osmotic pressure which is exerted by an NaCl solution of equal molar concentration. It is a small difference, but nevertheless, it acts in the wrong direction to explain the experimental observations (see also the Section on Experiments).

The interactions between bilayers or aggregates as a function of interbilayer or -aggregate distance is a
compilation of the forces mentioned above. We will both consider the interactions between bilayers in one aggregate (intraaggregate) and the interactions between bilayers of separate aggregates (interaggregate), as being of similar nature. The net interaction is pictured in Figure 6 for two extreme cases. Curve A represents the interactions experienced by bilayers where only repulsions are dominant. This state is sometimes called extremely swollen or fully unbound. Curve B pictures the case where attraction allows bilayers to approach each other until at short distance the repulsions take over. Thus multilayers or stacks of bilayers are formed and the aggregates tend to flocculate. This entropically unfavorable state occurs at relatively high alkali metal chloride concentrations, where strongly flocculated multilamellar aggregates the equilibrium distance is approximately 1.5 nm. The depth of the well, shallow or deep, is also an important factor determining whether, respectively, unilamellar or multilamellar aggregates are formed. Repulsions at low distances (solvation and steric) prevent complete collapse and full squeezing out of water.

Figure 6. Interaction energy vs distance for surfactant aggregates acting across the aqueous electrolyte solution: (A) relative low salt concentration, lamellar layers (and separate aggregates) repel; (B) high salt concentration, lamellar layers (and aggregates) experience a net attractive force, in the case of flocculated multilamellar aggregates the equilibrium distance is approximately 1.5 nm. The depth of the well, shallow or deep, is also an important factor determining whether, respectively, unilamellar or multilamellar aggregates are formed. Repulsions at low distances (solvation and steric) prevent complete collapse and full squeezing out of water.

Five Different Cases for Electrolyte-Induced Effects on Surfactant Aggregation. We return to Scheme 1 in an attempt to explain the differences in aggregation behavior as discussed above. Five cases will be considered: (i) no electrolyte added; (ii) NaCl solutions; (iii) solutions with alkali metal cations with a higher atomic number than Na⁺; (iv) LiCl solutions; (v) tetraalkylammonium chloride solutions.

(i) No Electrolyte. In plain water only the left-hand side equilibrium (Scheme 1) matters but counterion binding will be low. Therefore, large electrostatic and hydration repulsions between surfactant headgroups occur, leading to the formation of micelles. In terms of the packing parameter analysis, these micelles will be nonspherical.

(ii) NaCl Solutions. Again only the left equilibrium (Scheme 1) matters. However, this will shift more and more to the left-hand side as the NaCl concentration increases. Furthermore, the entropic (osmotic) force to maintain the electrical double layer will diminish if the background electrolyte concentration increases. A higher counterion binding will result. At higher concentrations, the salting-out property of NaCl will tend to dehydrate all ions, particularly the surfactant headgroups. As a result of both the higher counterion binding and partial dehydration, surfactant headgroups can be packed more tightly, leading to packing in a lamellar array at 0.3 m NaCl concentration. The van der Waals attraction probably increases substantially when the aggregate structure changes from micelles to lamellar aggregates. This can be due to two factors: the lamellar aggregates are larger and possess a closer molecular packing than the micelles. At this point the interlamellar van der Waals attraction is now suddenly large enough to overcome the repulsions (predominantly the electrical double layer repulsion), resulting in the formation of flocculated multilamellar aggregates. How delicate this simultaneous change in packing and the change in magnitude of the repulsions is can be inferred from the fact that the isomERICally pure 5/6 NaDoBS shows at the same NaCl concentration a unilamellar region where relatively large repulsions operate although the molecules are already in a lamellar arrangement. In addition, the unilamellar to multilamellar transition occurs at lower salt concentration (0.25 vs 0.30 m for 5/6 NaDoBS and the polydisperse analogue, respectively, see Figure 2B); thus the van der Waals attraction between 5/6 NaDoBS lamellae will be slightly larger than for polydisperse commercial surfactant.

(iii) KCl, RbCl, or CsCl Solutions. For all the other salts the right-hand side equilibrium comes into play. As was illustrated by microcalorimetry and conductivity, this effect will play a crucial role already at low concentrations of KCl, RbCl, and CsCl. Going from Na⁺ to K⁺ to Rb⁺ to Cs⁺, i.e., going toward less hydrated cations, the equilibrium will shift more and more to the far right hand side, induced by increasingly favorable counterion binding. At relatively low salt concentration, Na⁺ will be preferably depleted as a counterion (see for instance the large heat effects for the 3.5 mM CsCl experiment, Table 1). The increased counterion binding will lead to decreased interheadgroup repulsions, and going toward Cs⁺, the surfactant molecules have a propensity to aggregate in lamellae at decreasing concentrations of added salt. Large unilamellar vesicles are formed (Figures 3A and 4A), with a net repulsion between lamellae and between vesicles. The slow sedimentation points to a physically instable dispersion, gravity can overcome the dispersive action between the aggregates, vesicles precipitate but do not fuse or turn into multilamellar structures. The interaction is probably well described by curve B in Figure 6, with a minimum so shallow that thermal motions can keep the aggregates apart.

The transition from unilamellar to multilamellar aggregates occurs at an increasingly higher concentration of added electrolyte, upon going from Na⁺ to Cs⁺. Since the van der Waals attraction decreases with salt concentration largely independent of the type of alkali metal cation, the dominant factor inducing the differences in unilamellar to multilamellar transition will be repulsive in nature. Furthermore, the type of alkali metal cation will not noticeably influence the steric repulsions, and since these repulsions operate only over small distances, these effects can be neglected in a first approximation. The possibility to dehydrate the headgroup will decrease going from NaCl toward the CsCl, so the hydration repulsion will become larger going into that same direction, albeit that this repulsion operates over fairly small distances.

As discussed before, the osmotic pressure and surface charge density decrease going from a double layer with Na\(^+\) ions to one with Cs\(^+\) as the counterions. Thus, a lower electrical double layer repulsion is expected for Cs\(^+\) relative to Na\(^+\). This therefore cannot explain the experimental observation that the transition from unilamellar to multimellar aggregates occurs at a higher salt concentration for CsCl as compared to NaCl (Figure 2A). Lowering the surface charge density by changing to Cs\(^+\) as counterions instead of Na\(^+\) or by increasing the electrolyte concentration will lead to more flexible bilayers and a concomitant increased undulation repulsion. This, however, cannot be a dominant factor since at higher density, the repulsion between the counterions and the van der Waals attraction can obviously overcome the repulsions, and undulation repulsions are only expected to increase, if they change at all. What remains as an explanation? Left out of the discussion thus far is a possible contribution due to the hydrophobic attraction between bilayers, or more particularly, between parts of the hydrophobic tails that are exposed to water.\(^{18}\),\(^{40}\) It is reasonable to expect a higher hydrophobic attraction between bilayers with a relatively low number of bound counterions (the Na\(^+\) case), which shield the hydrophobic interior less effectively than, for instance, the case with high counterion binding (Cs\(^+\)).

(iv) LiCl Solutions. For the strongly hydrated Li\(^+\) ion, hydration repulsion may be a more important factor.\(^{45}\) At relatively low concentrations, Li\(^+\) has only a minor effect on the position of the equilibria shown in Scheme 1. Only at higher LiCl concentrations can a shift toward the right-hand side be expected, which is due simply to the large excess of Li\(^+\) (i.e. at 1 m LiCl and 4 m mm NaDoBS, a 250-fold excess). Thus at a relatively high concentration of LiCl, a small counterion binding is still expected. If a cation binds, it most likely will be a Li\(^+\) which drags along a considerable hydration shell. We contend that even at high concentrations of LiCl, micelles with highly curved surfaces will remain. A similar effect has been observed for strongly hydrated ions as hydroxide and acetate, inducing enhanced bilayer curvature of (positively charged) didodecyldimethylammonium bromide (DDAB) lamellae.\(^{38}\) Nonetheless, along with the increasing LiCl concentration also the electrical double layer repulsion will disappear and at 1.1 m, the van der Waals attractions between micelles will triumph over repulsions, and the micelles will phase separate from solution before packing in a lamellar array has been completed. Further addition of Li\(^+\) leads to the headgroup dehydration and alkali metal and all other ions. At these high salt concentrations, even the hydration of the Li\(^+\) ions in the bulk will decrease, which facilitates higher counterion binding, giving way to less steric constraints and less electrostatic repulsions between headgroups, with ultimately, the formation of a lamellar arrangement of the surfactant molecules. However, the interaggregate repulsions have already been overcome and therefore only multilamellar aggregates form, which flocculate and precipitate. This idea is supported by the increase in the fluorescence depolarization value \(P\) over the concentration range where the phase separation occurs.

(v) TAACI Solutions. The aggregation behavior in tetraalkylammonium chloride (TAACI) salts is remarkable. It seems clear that an explanation as given above for the behavior of NaDoBS in aqueous alkali metal chloride salt solutions does not apply here. The tetraalkylammonium ions, particularly the TBuA\(^+\) ion, have a salting-in character and enhance the solubility of otherwise poorly water-soluble compounds.\(^{39}\) One clue, delivered by microcalorimetry, is the high counterion binding. Compared to the other cations, the TAA ions are poorly hydrated and therefore will have only limited objections against binding to the micellar surface. On the other hand, the ions have a low charge density. The right-hand side equilibrium (Scheme 1) shifts farther to the right and becomes dominant, the effect being larger for TBuA\(^+\) than for TMA\(^+\) ions. As a result rather hydrophobic particles will be created, which, in first instance, do not dissolve in the aqueous solution. TAACI solutions located aggregates phase separate, probably with the withdrawal of several water molecules still sticking to the polar surface of the aggregate. Only at higher TAACI concentrations can the salting-in character of TAACI become an important factor. As a consequence, the propensity of the headgroups to remain in contact with the aqueous electrolyte solution increases as the TAACI concentration increases. Since the tails still prefer to be in an aqueous alkali metal salt, the phase separation occurs. The concentration range where the phase separation has only a minor effect to Na\(^+\) as the counterions. Thus, a lower gel-to-liquid crystalline phase transition for TMA-diheptadecyl phosphate vesicles, as compared to the corresponding Na\(^+\) salt. In addition, Kachar et al.\(^{50}\) state that the tetrathio-ethylene sulfonate counterion is located further out from the surface of a 4-(1-heptylpyrrol)-benzenesulfonate aggregate, inducing noticeable curvature of the bilayer surface. Finally, Jansson et al.\(^{52}\) argue that attractive hydrophobic interactions occurring between emulsion droplets are enhanced with the adsorption of

these hydrophobic ions. A similar explanation is obviously not valid here, since the observed vesicles will indeed have a highly hydrophobic surface, with TAA cations bound to the surface, but still a large repulsion must exist (curve A in Figure 6) since no sign of aggregation is observed over a period of a year.

**Transition between Aggregates on a Molecular Scale.** A final remark on the observed transitions from one type of aggregate to another on a molecular scale seems in order. The formation of unilamellar vesicles can be attributed to an initial change in micellar shape, upon increasing salt concentrations toward a rod- or disklike micelle. The size of the aggregate will then grow dramatically, turning to a large flat aggregate, a pancake structure or a bilayer fragment, which will close spontaneously to form large unilamellar vesicles. This spontaneous closure is induced by thermal fluctuations of the bilayer pancake, the driving force can be the minimization of edge effects.53

It is remarkable that at higher salt concentrations the unilamellar vesicles do not aggregate (flocculate) but transform to multilamellar aggregates, which subsequently flocculate and fall out of solution. This transition from unilamellar to multimamellar aggregates must involve enormous rearrangements of molecules between different layers. In this process, we envisage passages in which whole patches of lamellarly arranged molecules protrude from one bilayer and insert into another. Local instabilities in the bilayer and local packing mismatches, both amplified by undulation and peristaltic motions of the bilayer and by potential differences arising from salt concentration differences between solution inside and outside a vesicle, could be nuclei for short lived intermediate structures, resembling temporary L3 phase-like bicontinuous structures with bilayer curvature in both directions. These bypasses presumably will facilitate the flow of surfactant molecules from one bilayer to the other.

**Conclusions**

The formation of a lamellar phase from the micellar phase of the anionic surfactant sodium dodecylbenzene-sulfonate (NaDoBS) in dilute solutions can be induced by various alkali metal chlorides and tetraalkylammonium chloride salts. A distinction has to be made between the influence of salt on a molecular scale and on a larger scale, i.e., the aggregate level.

On a molecular level, an increase in alkali metal cation concentration induces the packing of molecules into a lamellar array, which is facilitated by an increase in counterion binding and to a lesser extent by dehydration of the headgroups induced by the addition of a salt. Both effects will facilitate a closer packing of the surfactant headgroups, which leads to the rearrangement of the surfactants into micelles into lamellae. An excess of foreign ion X− will replace Na+ as the counterion, as illustrated by Scheme 1. An exception is the highly hydrated Li+ ion which at low concentrations is not capable of replacing the Na+ ion. The observed transformations of the assemblies can be described as the phase behavior of the surfactant XDoBS in XCl solution. A change toward a less hydrated ion X− parallels an increase in counterion binding. This translates into the packing in a lamellar array which occurs at a decreasing electrolyte concentration going from LiCl to CsCl.

On the aggregate level, the interactions between lamellar layers and between aggregates lead to the formation of large unilamellar vesicles when long range repulsions are stronger than attractions (curve A in Figure 6) and to flocculated multimamellar vesicles, called lamellar droplets, when bilayers and aggregates experience an attractive force down to a short distance, when short range repulsions take over (curve B in Figure 6). Figure 2A summarizes the observed phases as a function of salt for dilute NaDoBS solutions. Electrostatic double layer repulsions are expected to be smaller when the surface potential is lower, which is expected for high counterion binding. In addition, the osmotic repulsion is expected to be lower for a double layer consisting of Cs+ ions as compared to the Na+ case. It is argued that other interactions do not change significantly by a change of the type of cation. In contrast to expectations, the phase behavior in CsCl shows strong long range repulsions up to the highest concentration. A possible explanation for this paradox, lies in a lower hydrophobic attraction between bilayers and between aggregates for the situation where Cs+ ions are bound to the bilayer surface (compared to the Na+ case), or a lower van der Waals attraction between two bilayers acting over a CsCl solution, compared to a NaCl solution of equal molality.

Between 1.1 and 1.6 m LiCl, dilute NaDoBS solutions phase separate into a surfactant-rich and a surfactant-lean phase. At higher LiCl concentrations, regular flocculated lamellar droplets are formed. The surfactant-rich phase is formed when the interaggregate attractions can overcome repulsions, even before the molecules can pack in a lamellar array.

The phase behavior in tetraalkylammonium chloride salt solutions appears to be a regular cloud point phenomenon as is observed for nonionic poly(ethylene oxide)-based surfactants. The behavior is rationalized by a high counterion binding which creates a rather hydrophobic moiety, which causes a high attraction between the surfactant aggregates and leading to phase separation. At higher TAACl concentrations, the salting-in effect increases the headgroup solubility, leading to stable dispersions of large unilamellar and multivesicular vesicles.

The difference between the phase behavior of the polydisperse NaDoBS and of the isomERICally pure 5/6 NaDoBS (Figure 2B) illustrates the importance of the packing of the hydrophobic tails in a lamellar arrangement, which is hampered by the polydispersity of the alkyl chain.

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