Chapter - III

SANS Studies on Sodium Dodecyl Sulfate – Quaternary Ammonium Bromide Systems
Introduction

Micelles are often drawn as static structures of spherical aggregates of oriented molecules near cmc. In case of ionic micelles, the morphology is generally modified by the addition of suitable counterions.\textsuperscript{142} Depending on their exact nature, counterions may bind differently to the micelle and have important consequences on electrical double-layer, and both on inter- and intra-micellar interactions as well.\textsuperscript{303}

The long range forces that are acting in micellar systems are the electrostatic repulsion and the attractive dispersion interactions. The former is very strong at short distances but in salt solutions it decays exponentially due to screening. The dispersion forces are weaker but they decay more slowly. The driving forces for the formation of a periodic structure is then a damping of repulsive forces within the boundaries of the solvent medium. Addition of salt should reduce the repulsion among the aggregates and thus the system is less prone for formation of ordered structures. On the other hand, salt addition causes micellar growth which in itself should increase the tendency of forming ordered structures. It is not straight forward to judge which of the two effects is dominating and, depending on the system, addition of salt can both destroy and induce micellar structuring in the solution. As a rule of thumb, less hydrated ions lead to higher counterion binding in surfactant aggregates.\textsuperscript{174} This will have drastic consequences towards the micellar growth. Several reports indicate that change from Na\textsuperscript{+} to Cs\textsuperscript{+} induces micellar growth which is
related to the hydration of specific counterion. A similar role is played by anions in aggregation behavior of cationic surfactants.

In contrast to inorganic counterions, \( R_4N^+ \) ions are essentially non-hydrated. These have been found to displace loosely bound \( Na^+ \) in the micelles composed of decylphosphate monoanions by increasing the ionic strength and lowering the cmc but cannot displace \( Na^+ \) ions tightly associated with the head groups. \( R_4N^+ \) ions are "wrapped in a plastic bag" and cannot interact specifically, but only coulombically with anionic head groups and hydrophobically with exposed hydrocarbons at the micellar surface. A detailed account of SDS micelles in presence of simple inorganic counterions can be found in the literature. Recently, counterion effect with \( R_4N^+ \) type cations is gaining recognition in micellar systems. An interesting cloud-point phenomenon and micellar growth behavior was reported by Yu and Xu with \( n-Bu_4NBr \) and anionic surfactant. Structural interactions in aqueous solutions of these ions have been interpreted as showing that solvent-induced attractive forces exist between two hydrophobic solutes and repulsive forces between a hydrophobic solute and a hydrophilic one. These interpretations would suggest that structural interactions are involved in salting-out of non-electrolytes capable of hydrophobic interactions by hydrophilic salts, e.g., \( NH_4Br \) and \( Me_4NBr \); and salting-in by hydrophobic salts, e.g., \( n-Pr_4NBr \) and \( n-Bu_4NBr \). The effectiveness of cations to salt-out is in the order:
\[ K^+ > Na^+ > NH_4^+ \sim Me_4N^+ > Et_4N^+ > n-Pr_4N^+ > n-Bu_4N^+ \]

The sequence shows that the salting-out efficiency decreases with increase in both the ion size\textsuperscript{286} and the ability of the ion to alter the degree of structure in water (hydrophobic bonding). \( R_4N \) salts exhibit an ambivalent nature in aqueous solutions. In these ions the single positive charge is buried in a paraffin shell. The salting-in effects of these salts are in contrast to the salting-out effects of the small inorganic salts.

Mostly, shape/size of the micelles depends upon the actual packing parameters in the micellar assembly.\textsuperscript{131,132} The addition of different types of molecules leads to large deviations of packing parameters. Many counterions/cosurfactants are strongly adsorbed at the micellar interface: depending on the amount of penetration, this may change the mean distance between the polar head groups or increase the volume of the micellar core.\textsuperscript{115,206,260,316}

In many studies it was shown that, above a single concentration of electrolytes, micellar shape transforms from spherical to cylindrical.\textsuperscript{134,177,184,311,317} Typical values of 1:1 electrolyte concentrations to initiate spherical to cylindrical transitions are relatively high. Most of the time these studies were performed using inorganic salts. Since \( R_4N^+ \) cations modify the structure of water around them in a similar way as some simple hydrocarbons do, it could be of considerable interest to see how this interaction affects the shape/size of the micelles. The reason for selecting \( R_4N \) salts in this study originates from the fact that
the degree of hydrogen bonding in water alters dramatically along this series of salts, \(^{318}\) e.g., \(\text{NH}_4^+\) to \(\text{n-Bu}_4^+\).

Visualizing the significant properties of \(\text{R}_4\text{N}^+\) cations it was thought worthwhile to pursue a study in order to understand the role of counterion size in concentrated micellar solutions. In the following pages SANS studies performed on 0.3 M SDS solutions containing varying amounts of \(\text{R}_4\text{N}\) bromides (\(\text{R} = \text{C}_2\text{H}_5\) and \(\text{n-C}_3\text{H}_7\)) are described.

**Results**

The SANS spectra for the 0.3 M SDS/D\(_2\)O with and without added \(\text{R}_4\text{NBr}\) salts are shown in Figs. 3.1 and 3.2. The presence of a peak in the measured distribution is indicative of the formation of aggregates within the solution.\(^{182}\) The peak shifts to lower Q values on addition of salts. This indicates that micelles grow in size by salt addition. The positions and change in the measured distribution as a function of Q depends not only on the structure, size, and number of aggregates but also on interactions between them. These parameters can be determined by analyzing the SANS curves with the aid of models.

**Data treatment**

The raw data were corrected for the background, empty cell scattering and sample transmission. The corrected intensities were normalized to absolute cross-section units and thus \(d\Sigma/d\Omega\) vs. Q was obtained. The experimental data points were fitted by adopting the routines as described by Hayter and Penfold\(^{293,319}\) and Chen and coworkers.\(^{182,320}\) The data have not been corrected for resolution
Fig. 3.1. SANS spectra from 0.3M SDS + (C_2H_5)_4NBr systems at 30 °C as a function of (C_2H_5)_4NBr concentration. Solid lines are theoretical fits based on Hayter and Penfold-type analysis. The spectra are shifted vertically by 0, 2, 4 and 6 units, respectively for clarity of presentation.
Fig. 3.2. SANS spectra from 0.3M SDS + (n-C₃H₇)₄NBr systems at 30 °C as a function of (n-C₃H₇)₄NBr concentration. The spectra are shifted vertically by 0, 2, 4 and 6 units, respectively.
effects. Analysis of a limited set of data showed that resolution corrections do not alter the aggregation number of the micelle, especially when SANS data show a peak. The residuals in the fitting were negligible.

**Data Analysis**

The relevant SANS theory is summarized as: For homogeneous monodisperse micelles of volume $V_p$ present at number density $n_p$ and of coherent length density $\rho_p$, dispersed in a medium of scattering length density $\rho_{m}$, the coherent differential scattering cross-section ($d\Sigma/d\Omega$) may be written as $^{180,291,293,298,319,321}$

$$
\frac{d\Sigma}{d\Omega} = n_p \, V_p^2 \, (\rho_p - \rho_m)^2 \, P(Q) \, S(Q) + B
$$

(3.1)

where $P(Q)$ is the single (orientationally averaged) particle form factor which depends on the size and shape of the particle and $S(Q)$ is the interparticle structure factor. $B$ is a constant term that represents the incoherent scattering, which is mainly due to hydrogen atoms in the sample. For the analysis, we assume the micelles to be monodisperse prolate ellipsoids, $(a=b\neq c)$, where the sphere is a special case. It may be mentioned, however, that elongated micelles usually tend to be of varying sizes and may not be monodisperse, but eq. (3.1) is not valid for the polydisperse system. It was further assumed that the micelles have a hydrophobic core composed of hydrocarbon tails of the dodecyl sulfate and a hydrated hydrophilic shell composed of head groups ($\text{OSO}_3^-$), some fraction of Na$^+$, $R_4\text{N}^+$, and the solvent molecules ($D_2O$). In fact, the interfacial thickness of the pure SDS micelle is about 5.5Å.$^{182}$ Also, ionic radii of the salt cations are 4.0 Å ($R = \text{C}_2\text{H}_5$) and 4.52 Å ($R = n-\text{C}_3\text{H}_7$).$^{322}$ In the
light of these facts it is conceivable that most of these ions will find shelter in the hydrophilic shell. The scattering contribution from the hydrophilic shell is much weaker than that of micellar core for neutron scattering. Consequently, the scattering from the species other than the micellar core is treated as a flat background contributed to B. Although we are aware of the limitations of such assumptions, it is not possible to get information on size distributions of micelles from the present data because of the involvement of too many unknown parameters in the data analysis. Thus, in the present analysis we have assumed the system to be monodisperse to avoid additional complexities.

The aggregation number (n) for the micelle is related to the $V_p$ by the relation $n = V_p/v$, where $v$ is the volume of surfactant monomer. $P(Q)$ for anisotropic micelle (e.g., ellipsoidal) is given by.

$$P(Q) = \int_0^1 [F(Q, \mu)]^2 \, d\mu \quad (3.2)$$

The form factor $F(Q, \mu)$ is given by

$$F(Q, \mu) = 3 \left( \sin \omega - \omega \cos \omega \right) / \omega^3 \quad (3.3)$$

where $\omega = Q \left[ a^2 \mu^2 + c^2 \left( 1 - \mu^2 \right) \right]^{1/2}$ and $\mu$ is the cosine of the angle between the axis of revolution and $Q$. Therefore, $P(Q)$ is dependent on $a$ and $c$.

The value of $a$ used is 16.7 Å, which is equal to the length of the surfactant monomer ($l_c$). The volume of SDS monomer was taken to be 350.2 Å³, as given by Tanford's formula. S(Q) was calculated using standard methods. This theory is applicable if there is no angular correlation between the micelles which is reasonable for charged micelles. It may be mentioned that a
satisfactory data analysis method for charged rod shaped micelles have not yet been developed.

In this analysis the calculated spectra have only two free parameters, *viz.*, $\alpha$ and $c$ or $n$.

Discussion

The model discussed above was fitted to our experimental data and yielded excellent agreement with all scattering curves, as evidenced in Figs. 3.1 and 3.2, where the solid lines are always the calculated curves. The values of $n$, $\alpha$, $a(=b)$, $c$ and $c/a$ are given in Table 3.1. The $n$ value of 0.3 M SDS micelle with 0.1 M $R_4NBr$ first decreases and then increases as the length of $R$-part increases. As expected, less hydrated ions lead to stronger counterion binding to head groups in the micelles.\textsuperscript{174,304} For such cases higher micellar growth were reported\textsuperscript{142,323} As one moves from $R = H$ to $R = n-C_3H_7$, the cation hydration decreases dramatically.\textsuperscript{324} Therefore, $n$ should increase continuously for $R = H$ to $R = n-C_3H_7$. If we consider the hydrated size of the counterion as parameter of increasing $n$,\textsuperscript{97,144} then it should decrease from $R = H$ to $R = n-C_3H_7$. Our results for $n$ do not fit in any of the above generalizations. This shows that more than one factor is controlling the growth of SDS micelles. From $R = H$ to $R = C_2H_5$, the $n$ value decreases which seems to be governed by increase in hydrated size. In this case the adsorption of counterion on negatively charged SDS micelle is the dominant factor, as bigger size of the ion will cause it to be less effective in reducing the steric constraints (damping of electrostatic interactions which is responsible for large micelles). Therefore, $n$ value will be more with $R = H$ than $R = C_2H_5$ and support the earlier findings.\textsuperscript{97,144} The increase in $n$ values with
TABLE - 3.1
Micellar parameters for 0.3 M SDS with $R_n$NBr obtained from Hayter-Penfold type analysis at 30°C (data of NaBr and KBr are also included$^a$)

<table>
<thead>
<tr>
<th>[Salt] (M)</th>
<th>n</th>
<th>$\alpha$</th>
<th>$a=b$ (Å)</th>
<th>c (Å)</th>
<th>c/a</th>
</tr>
</thead>
<tbody>
<tr>
<td>no salt</td>
<td>110</td>
<td>0.14</td>
<td>16.7</td>
<td>33.4</td>
<td>2.00</td>
</tr>
<tr>
<td>NaBr 0.1</td>
<td>127</td>
<td>0.16</td>
<td>16.7</td>
<td>36.7</td>
<td>2.20</td>
</tr>
<tr>
<td>KBr 0.1</td>
<td>153</td>
<td>0.13</td>
<td>16.7</td>
<td>45.3</td>
<td>2.71</td>
</tr>
<tr>
<td>$R = H^b$ 0.1</td>
<td>150</td>
<td>0.14</td>
<td>16.7</td>
<td>44.4</td>
<td>2.66</td>
</tr>
<tr>
<td>$R = CH_3^b$ 0.1</td>
<td>130</td>
<td>0.15</td>
<td>167</td>
<td>.390</td>
<td>2.33</td>
</tr>
<tr>
<td>$R = C_2H_5$ 0.1</td>
<td>128</td>
<td>0.15</td>
<td>16.7</td>
<td>38.4</td>
<td>2.30</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>133</td>
<td>16.7</td>
<td>39.9</td>
<td>2.39</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>135</td>
<td>16.7</td>
<td>40.5</td>
<td>2.43</td>
</tr>
<tr>
<td>$R = n-C_3H_7$ 0.1</td>
<td>134</td>
<td>0.15</td>
<td>16.7</td>
<td>40.2</td>
<td>2.41</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>145</td>
<td>16.7</td>
<td>43.5</td>
<td>2.61</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>148</td>
<td>16.7</td>
<td>44.3</td>
<td>2.65</td>
</tr>
</tbody>
</table>

$^a$V.K. Aswal, private communication.

$^b$Data from ref. 145.
R = n-C₃H₇ cannot be explained with the above mechanism. However, it is experimentally observed that micelles are bigger (of greater c value, Table 3.1) with this counterion; therefore, exploration of other possibilities is required. Compared to earlier members (R = CH₃ or C₂H₅), the latter (R = n-C₃H₇) is essentially less hydrated and, therefore, will have comparatively less objections against binding to the micelle. Further, the latter ion can also interact hydrophobically with few exposed hydrocarbon chains at the micellar surface. For such type of counterions an effect on the electrostatic energy is also possible, both directly, because the bulkiness of the ions keeps the +ve and -ve charges apart, and indirectly, via a decrease of the electric permittivity at the micelle surface when the bigger R-part gets inserted between the head groups (intercalation). The intercalation of such counterions will decrease the electrostatic interactions in addition to increased hydrophobic interactions. The decrease in α-values with R = n-C₃H₇ supports the point. It may be mentioned here that a favorable conformation of such ions near micellar surface is hard to predict, but it is proposed that few of these short chains can penetrate the micellar surface.¹⁴⁵,³¹³

Fig. 3.3 shows the variation of n with the counterion hydrated radii.¹⁷⁷,³²² It could be seen that counterions having closer hydrated radii (i.e., Na⁺ (3.6 Å) and (CH₃)₄N⁺(3.67 Å) or K⁺(3.3 Å) and NH₄⁺ (3.31 Å)) show similar effect on n value of SDS micelle. At first sight it looks that n depends distinctly on the hydrated radius of a counterion, but weakly on its nature (whether it belongs to inorganic or quaternary ammonium category). This seems true only for hydrated counterions.
Fig. 3.3. Variation of aggregation number (n) of 0.3M SDS + 0.1M XBr (X may be inorganic or quaternary ammonium counterion) with hydrated counterion radius (r): $K^+$ (●), $NH_4^+$ (●), $Na^+$ (●), ($CH_3)_4N^+$ (●), ($C_2H_5)_4N^+$ (●), ($n-C_3H_7)_4N^+$ (●).
It was suggested earlier that the free alkyl chains near micellar surface can act as a bridge linking two micelles together.\textsuperscript{312} Our data do not suggest such a possibility as this situation will increase n value drastically. The dependence of n on length of R with increasing \([R_4NBBr]\) (Table 3.1) suggests that a situation may arise where increase in number of carbon atoms in R or increase in [SDS] may cause closer contact of micelles (or a collapse of micelles in the extreme situation).

The start of an increase in n for \(n-C_3H_7\) salt suggests that the idea of partial intercalation of counterions is reasonable. Studies on such systems may produce few \(R_4NBBr + SDS\) combinations where cloud-point phenomenon may occur (which are rarely seen with ionic surfactants). The idea has indeed found strong support as appearance of cloud-point phenomenon in SDS + \((n-C_4H_9)_4NBBr\) system has successfully been demonstrated in our laboratory.\textsuperscript{325}