A SANS study on growth of anionic micelles with quaternary ammonium bromide

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The micellar growth of sodium dodecyl sulphate in presence of inorganic (KBr) and quaternary ammonium bromides (R₄NBr, R = CH₃ or n-C₄H₉) has been studied by small-angle neutron scattering measurements at 30°C. The data has been analysed using Hayter–Penfold model. After combining the results of previous and present studies, no direct relationship between length of alkyl part (R) and aggregation number (n₀) of the micelles is found. It is proposed that both the inorganic and quaternary counterions (with R ≤ C₄H₉) cause micellar growth due to screening of micellar surface charge while latter ones (especially with longer R) do it by screening and increased hydrophobic interaction. Also, n₀ increases with increase in [R₄NBr].

MICELLAR morphology is generally modified by the addition of suitable counterions. Depending on their nature, counters may bind differently to the micelle and have important consequences on electrical double-layer, as well as for both inter- and intramicellar interactions. Mostly, shape/size of the micelles depends upon the actual packing parameters in the assembly. Many counterions/cosurfactants are strongly adsorbed at the micellar surface and, depending on the extent of penetration, this may change the mean distance between the polar head groups or increase the volume of the micellar core.

Detailed accounts of sodium dodecyl sulphate (SDS) micelles in presence of simple inorganic counterions can be found in the literature. As a rule of thumb, counterions having less affinity to water lead to higher binding to the micelles. This will have significant consequence towards micellar growth. In contrast to inorganic counterions, quaternary ammonium ions (R₄N⁺) are essentially non-hydrated and amphiphilic. In these ions the positive charge is buried in a paraffin shell. Interestingly, SDS micellar solutions show clouding in presence of such counterions.

In our recent small-angle neutron scattering (SANS) measurements carried out on SDS-R₄NBr (R = H, CH₃ or n-C₄H₉) systems, one of the observations was that aggregation number (n₀) of 0.3 M SDS micelle increased with all the salts (at 0.1 M).

In the present investigation, the effect of presence of inorganic and quaternary ammonium (R₄N⁺) counterions on the growth behaviour in 0.3 M SDS micellar solution has been investigated. Motivation of the work mainly came from the fact that these two types of counterions can influence the behaviour of micellar surface region with the concomitant influence on the SDS-micelle.

For this purpose we have performed SANS experiments on 0.3 M SDS-micellar solutions with different inorganic and R₄NBr salts.

SDS was the same as used in earlier studies. Tetraethylammonium bromide (> 99%) and tetra-n-propylammonium bromide (> 99%) were obtained, respectively, from BDH (England) and Merck-Schuchardt (Germany). KBr (> 99%) was obtained from E-Merck (India). The salts were dried and stored as detailed elsewhere. Solvent D₂O of 99.4% purity was supplied by the Heavy Water Division, Bhabha Atomic Research Centre (BARC), Mumbai.

The measurements were performed on the SANS spectrometer at CIRUS reactor, BARC. The experiments used incident neutrons of mean wavelength (λ) 5.2 Å with sample-to-detector distance 1.8 m. The angular distribution of the scattered neutrons was recorded with a one-dimensional position-sensitive detector. Under the present experiments, the data were recorded in the wave vector transfer (Q) range of 0.02–0.3 Å⁻¹ (Q = 4π sinθ/λ, where θ is the scattering angle). The data for Q ≥ 0.2 Å⁻¹ are not shown as the signal-to-background ratio was very poor.
To have a good contrast between the micelles and the solvent, all samples were prepared in D_{2}O. The samples were held in a 0.5 cm path-length quartz cell. The cell was properly stoppered and thermostated at 30 ± 0.5°C. All the samples contained a constant concentration of 0.3 M SDS but various amounts of R_{4}NB r salts. Samples with 0.1 M inorganic salts were also studied to compare their effect on aggregation number (n_{a}) and other parameters.

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 the coherent differential scattering cross-section, dΣ/dΩ, vs Q was obtained^{26}

The relevant SANS theory is summarized below. For homogenous monodisperse interacting micelles of volume V_{m} (volume seen by neutrons, i.e., micellar core) present at number density n_{m} and of the scattering length-density ρ_{m}, dispersed in a medium of scattering length-density ρ_{s}, the coherent differential scattering cross section (dΣ/dΩ) may be written as^{37-32}

\[
dΣ/dΩ = n_{m}V_{m}(ρ_{m} - ρ_{s})^{2}[(F(Q)^{2})
+ \langle F(Q) \rangle^{2}(S(Q) - 1)] + B, \tag{1}
\]

where F(Q) is the single particle form factor which depends on the size and shape of the particle, S(Q) the interparticle structure factor, B a constant term representing the incoherent scattering background (which is mainly due to hydrogen atoms in the sample). For the analysis, we assume the micelles to be monodispersed prolate ellipsoids, (a = b ≠ 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 monodispersed, but eq. (1) is not valid for polydispersed system. 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 parameters in the analysis.

The aggregation number n_{a} for the micelle is related to the V_{m} by the relation n_{a} = V_{m}/v, where v is the volume of the hydrocarbon tail of the surfactant monomer. F(Q) for anisotropic micelles (e.g., ellipsoidal)

\[
\langle F(Q)^{2} \rangle = \frac{1}{0} [F(Q, μ)^{2}] dμ, \tag{2}
\]

\[
\langle F(Q) \rangle^{2} = \left[ \int_{0}^{1} F(Q, μ) dμ \right]^{2}. \tag{3}
\]

The form factor F(Q, μ) is given by eq. (4):

\[
F(Q, μ) = 3 \left( \sin μ - μ \cos μ / μ^{2} \right), \tag{4}
\]

where μ = Q(c^{2}μ^{2} + a^{2}(1-μ^{2}))^{1/2} (a and c are, respectively, the semi-minor and semi-major axes of ellipsoid of revolution while μ is the cosine of the angle between the direction of c and Q). Therefore, F(Q) is dependent on μ and c. The value of a used is 16.7 Å, which is equal to the length of the hydrocarbon tail of the surfactant monomer^{35}. The volume v was taken to be 350.2 Å^{3}, given by Tanford’s formula^{33}. A correlation peak in the SANS spectrum is indicative of ionic character of micelle in solution^{32}. The peak arises because of the corresponding peak in the S(Q). The S(Q) value depends on the spatial distribution of micelles and it is Fourier transform of the radial distribution function g(r) for the mass centres of the micelles. In the present analysis, for ellipsoidal micelles, we calculated S(Q) using rescaled mean spherical approximation as developed by Hayter and Penfold^{59}. The ellipsoidal micelle is approximated by an equivalent sphere of radius R = (ac^{2})^{1/3}, and intermicellar interaction is modeled through a dimensionless screened Coulombic potential, which is given by

\[
u(r) = u_{0}2R \exp[-κ(r - 2R)/r], \quad r > 2R, \tag{5}
\]

where κ is the Debye–Huckel inverse screening length, calculated by

\[
κ = [8πN_{A}e^{2}I/10^{7}ek_{B}T]^{1/2}, \tag{6}
\]

and u_{0}, the contact potential, given by

\[
u_{0} = Z^{2}e^{2}/(8πεκ_{B}R(1 + κR^{2})). \tag{7}
\]

(N_{A} is the Avogadro number, e the electronic charge, ε the dielectric constant of the medium, k_{B} the Boltzmann’s constant, T the temperature, ε_{k} the permittivity of free space, I the ionic strength of the solution, and Z the micellar charge).

In this analysis the calculated spectra have only two parameters, viz., the effective charge per monomer (α = Z/n_{a}), and either the semi-major axis (c) or the aggregation number n_{a}.

The SANS spectra for the 0.3 M SDS/D_{2}O with and without added R_{4}NB r salts are shown in Figures 1 and 2. Data were analysed using the method discussed above and parameters α and c, were computed. Solid lines in Figures 1 and 2 are the calculated curves. The values of n_{a}, α, a (b = c), and c/a are given in Table 1.

Specific counterion effects on a variety of micellar properties generally follow a Hofmeister series^{34}, i.e., for counterions of the same valence, the magnitude of the effect (critical micelle concentration (cmc), micellar growth, etc.) increases with bare counterion size and the ease of dehydration of the counterion. We can see from Table 1 the n_{a} values of 0.3 M SDS micelle with 0.1 M

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salt increase but the magnitude of increase is dependent on the nature of the salts. With inorganic salts (NaBr or KBr), the \( n_i \) value decreases with the hydrated size of the counterion (see Figure 3) which is expected due to the fact that K\(^+\) is less hydrated and can bind strongly than Na\(^+\) to the micellar surface. This is in agreement with the reported trend\(^{35,36}\). The cation hydration of R\(_n\)NBr salts decreases progressively with the lengthening of R (ref.

\[\text{Table 1. Micellar parameters for 0.3 M SDS with R}_n\text{NBr obtained from Hayter-Penfold type analysis at 30°C (data of NaBr and KBr are also included)}\]

<table>
<thead>
<tr>
<th>[Salt]/M</th>
<th>( n_i )</th>
<th>( \alpha )</th>
<th>( a = b/\AA )</th>
<th>( c/\AA )</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(^+) (Na(^+) radius: bare, 0.95 (\AA); hydrated, 3.6 (\AA))</td>
<td>0.1</td>
<td>127</td>
<td>0.16</td>
<td>16.7</td>
<td>36.7</td>
</tr>
<tr>
<td>KBr (K(^-) radius: bare, 1.33 (\AA); hydrated, 3.3 (\AA))</td>
<td>0.1</td>
<td>150</td>
<td>0.14</td>
<td>16.7</td>
<td>44.4</td>
</tr>
<tr>
<td>H(^+) (NH(_3)(^+) radius: bare, 1.48 (\AA); hydrated, 3.31 (\AA))</td>
<td>R = CH(_3)(^+) (CH(_3)(_3)N(^+) radius: bare, 3.47 (\AA); hydrated, 3.67 (\AA))</td>
<td>0.1</td>
<td>130</td>
<td>0.15</td>
<td>16.7</td>
</tr>
<tr>
<td>R = C(_2)H(_5) (C(_2)H(_3)(_3)N(^+) radius: bare, 4.00 (\AA); hydrated, 4.00 (\AA))</td>
<td>0.1</td>
<td>128</td>
<td>0.15</td>
<td>16.7</td>
<td>38.4</td>
</tr>
<tr>
<td>0.2</td>
<td>133</td>
<td>0.14</td>
<td>16.7</td>
<td>39.9</td>
<td>2.39</td>
</tr>
<tr>
<td>0.3</td>
<td>135</td>
<td>0.14</td>
<td>16.7</td>
<td>40.5</td>
<td>2.43</td>
</tr>
<tr>
<td>R = n-C(_2)H(_n) (n-C(_2)H(_n)N(^+) radius: bare, 4.52 (\AA); hydrated, 4.52 (\AA))</td>
<td>0.1</td>
<td>134</td>
<td>0.15</td>
<td>16.7</td>
<td>40.2</td>
</tr>
<tr>
<td>0.2</td>
<td>145</td>
<td>0.12</td>
<td>16.7</td>
<td>43.5</td>
<td>2.61</td>
</tr>
<tr>
<td>0.3</td>
<td>148</td>
<td>0.11</td>
<td>16.7</td>
<td>44.3</td>
<td>2.65</td>
</tr>
<tr>
<td>R = n-C(_2)H(_n)(^+) (n=C(_2)H(_n)N(^+) radius: bare, 4.94 (\AA); hydrated, 4.94 (\AA))</td>
<td>0.1</td>
<td>192</td>
<td>0.07</td>
<td>16.7</td>
<td>57.8</td>
</tr>
</tbody>
</table>

\(^a\)Data from ref. 23.

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Figure 1. SANS spectra of 0.3 M SDS + (C\(_2\)H\(_3\))\(_n\)NBr systems at 30°C as a function of (C\(_2\)H\(_3\))\(_n\)NBr 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.

Figure 2. SANS spectra of 0.3 M SDS + (n-C\(_2\)H\(_n\))\(_n\)NBr systems at 30°C as a function of (n-C\(_2\)H\(_n\))\(_n\)NBr concentration. The spectra are shifted vertically by 0, 2, 4 and 6 units, respectively, for clarity of presentation.

Figure 3. Variation of aggregation number \( (n_i) \) of 0.3 M SDS + 0.1 M XBr (X may be inorganic or quaternary ammonium counterion) with hydrated counterion radius \( (r) \).
Our results with such salts do not fit the generalization mentioned above for inorganic salts as $\eta$ first decreases with $R = H$ to $R = C_2H_5$ and then increases with $R = n-C_6H_{13}$ or $n-C_8H_{17}$ (Table 1). This shows that more than one factor is controlling the growth of SDS micelles. The important electrostatic interaction in ionic micelles is the screening of head group repulsions, which is determined by the effective charge density at the surface provided by the counterion. A large counterion cannot approach the head group as closely as a small one (like Na$^+$) and so one can assume that larger counterions will be less effective in screening the repulsions. Probably this effect is operating in decreasing the $\eta$ up to $R = C_2H_5$ but progressively larger values of $\eta$ obtained with $R = n-C_6H_{13}$ or $n-C_8H_{17}$ cannot be explained by considering the screening mechanism only.

As observed experimentally, the micelles are, however, longer (the c-values are higher, see Table 1) with the last two counterions: this demands exploration of other possibilities. There is a compensatory effect due to larger size (less screening) and lesser hydration (increased accessibility). The larger hydrocarbon chains of such R$_n$N$^+$ counterions give rise to increased hydrophobic interactions with the exposed hydrocarbon chains at the micellar surface – this additional effect seems to dominate resulting in higher $\eta$ values.

Figure 3 shows variation of $\eta$ with counterion hydrated radius. It could be seen that the counterions having hydrated radii closer to each other, e.g. Na$^+$ (3.6 Å) and (CH$_3$)$_3$N$^+$ (3.67 Å) or K$^+$ (3.3 Å) and NH$_4^+$ (3.31 Å) show similar effect on the $\eta$, value of SDS micelle$^{6,38}$. No doubt, $\eta$ depends on the hydrated radius of a counterion as well as on its nature.

We conclude that inorganic and quaternary counterions interact with micellar surface via different mechanisms dependent on size and hydration state of the added counterion.


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