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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 (R_4NBr , $R = C_2H_5$ or $n-C_3H_7$) 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 (n_s) of the micelles is found. It is proposed that both the inorganic and quaternary counterions (with $R \leq C_2H_5$) cause micellar growth due to screening of micellar surface charge while latter ones (specially with longer R) do it by screening and increased hydrophobic interaction. Also, n_s increases with increase in $[R_4NBr]$.

MICELLAR morphology is generally modified by the addition of suitable counterions¹. Depending on their nature,

counterions may bind differently to the micelle and have important consequences on electrical double-layer, as well as for both inter- and intramicellar interactions². Mostly, shape/size of the micelles depends upon the actual packing parameters in the assembly^{3,4}. 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^{5–8}.

Detailed accounts of sodium dodecyl sulphate (SDS) micelles in presence of simple inorganic counterions can be found in the literature^{9–16}. 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^{17,18}. In contrast to inorganic counterions, quaternary ammonium ions (R_4N^+) are essentially non-hydrated and amphiphilic¹⁴. In these ions the positive charge is buried in a paraffin shell. Interestingly, SDS micellar solutions show clouding in presence of such counterions^{19–22}.

In our recent small-angle neutron scattering (SANS) measurements carried out on SDS- R_4NBr ($R = H, CH_3$ or $n-C_4H_9$) systems²³, one of the observations was that aggregation number (n_s) 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 (R_4N^+) 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 R_4NBr salts.

SDS was the same as used in earlier studies^{8,23}. 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 elsewhere²⁴. 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, BARC²⁵. 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 ($Q = 4\pi \sin\theta/\lambda$, where 2θ is the scattering angle). The data for $Q \geq 0.2$ Å⁻¹ are not shown as the signal-to-background ratio was very poor.

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To have a good contrast between the micelles and the solvent, all samples were prepared in D₂O. 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 R₄NBr salts. Samples with 0.1 M inorganic salts were also studied to compare their effect on aggregation number (n_s) 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, $d\Sigma/d\Omega$, vs Q was obtained²⁶.

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 ($d\Sigma/d\Omega$) may be written as²⁷⁻³²

$$\begin{aligned} d\Sigma/d\Omega = n_m V_m^2 (\rho_m - \rho_s)^2 [\langle F(Q)^2 \rangle \\ + \langle F(Q) \rangle^2 (S(Q) - 1)] + B, \end{aligned} \quad (1)$$

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, ($a = b \neq c$), 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 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_s for the micelle is related to the V_m by the relation $n_s = V_m/v$, where v is the volume of the hydrocarbon tail of the surfactant monomer. $F(Q)$ for anisotropic micelles (e.g., ellipsoidal)

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

$$\langle F(Q) \rangle^2 = \left[\int_0^1 F(Q, \mu) d\mu \right]^2. \quad (3)$$

The form factor $F(Q, \mu)$ is given by eq. (4):

$$F(Q, \mu) = 3 (\sin\omega - \omega \cos\omega)/\omega^3, \quad (4)$$

where $\omega = Q[c^2\mu^2 + a^2(1-\mu^2)]^{1/2}$ (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 a and c . The value of a used is 16.7 Å, which is equal to the length of the hydrocarbon tail of the surfactant monomer³³. The volume v was taken to be 350.2 Å³, given by Tanford's formula³³. A correlation peak in the SANS spectrum is indicative of ionic character of micelle in solution²⁹. 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 Penfold²⁹. The ellipsoidal micelle is approximated by an equivalent sphere of radius $R = (ca^2)^{1/3}$, and intermicellar interaction is modeled through a dimensionless screened Coulombic potential, which is given by

$$u(r) = u_0 2R \exp[-\kappa(r - 2R)]/r, \quad r > 2R, \quad (5)$$

where κ is the Debye-Hückel inverse screening length, calculated by

$$\kappa = [8\pi N_A e^2 I / 10^3 \epsilon k_B T]^{1/2}, \quad (6)$$

and u_0 , the contact potential, given by

$$u_0 = Z^2 e^2 / (8\pi \epsilon \epsilon_0 R (1 + \kappa R)^2). \quad (7)$$

(N_A is the Avogadro number, e the electronic charge, ϵ the dielectric constant of the medium, k_B the Boltzmann's constant, T sample temperature, ϵ_0 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 ($\alpha = Z/n_s$), and either the semi-major axis (c) or the aggregation number n_s .

The SANS spectra for the 0.3 M SDS/D₂O with and without added R₄NBr 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_s , 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 series³⁴, 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_s values of 0.3 M SDS micelle with 0.1 M

salt increase but the magnitude of increase is dependent on the nature of the salts. With inorganic salts (NaBr or

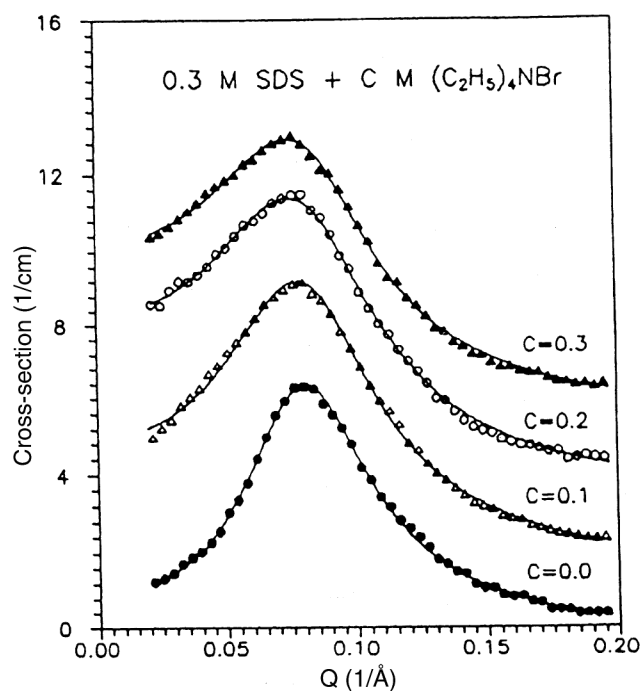


Figure 1. SANS spectra from 0.3 M SDS + $(\text{C}_2\text{H}_5)_4\text{NBr}$ systems at 30°C as a function of $(\text{C}_2\text{H}_5)_4\text{NBr}$ concentration. Solid lines are theoretical fits based on Hayter and Penfold type analysis. The spectra are shifted vertically by 0, 2, 4 and 6 units, respectively, for clarity of presentation.

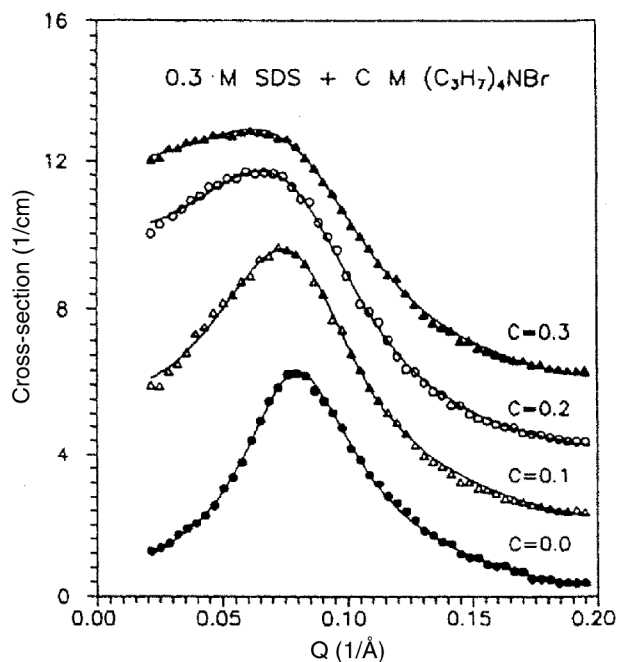


Figure 2. SANS spectra from 0.3 M SDS + $(n\text{-C}_3\text{H}_7)_4\text{NBr}$ systems at 30°C as a function of $(n\text{-C}_3\text{H}_7)_4\text{NBr}$ concentration. The spectra are shifted vertically by 0, 2, 4 and 6 units, respectively, for clarity of presentation.

KBr), the n_s 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_4NBr salts decreases progressively with the lengthening of R (ref.

Table 1. Micellar parameters for 0.3 M SDS with R_4NBr obtained from Hayter–Penfold type analysis at 30°C (data of NaBr and KBr are also included)

[Salt]/M	n_s	α	$a = b/\text{Å}$	$c/\text{Å}$	c/a
No salt	110	0.14	16.7	33.4	2.00
NaBr ^a (Na^+ radius: bare, 0.95 Å; hydrated, 3.6 Å)					
0.1	127	0.16	16.7	36.7	2.20
KBr (K^+ radius: bare, 1.33 Å; hydrated, 3.3 Å)					
0.1	153	0.13	16.7	45.3	2.71
$\text{R} = \text{H}^+$ (NH_4^+ radius: bare, 1.48 Å; hydrated, 3.31 Å)					
0.1	150	0.14	16.7	44.4	2.66
$\text{R} = \text{CH}_3^+$ ($(\text{CH}_3)_4\text{N}^+$ radius: bare, 3.47 Å; hydrated, 3.67 Å)					
0.1	130	0.15	16.7	39.0	2.33
$\text{R} = \text{C}_2\text{H}_5$ ($(\text{C}_2\text{H}_5)_4\text{N}^+$ radius: bare, 4.00 Å; hydrated, 4.00 Å)					
0.1	128	0.15	16.7	38.4	2.30
0.2	133	0.14	16.7	39.9	2.39
0.3	135	0.14	16.7	40.5	2.43
$\text{R} = n\text{-C}_3\text{H}_7$ ($(n\text{-C}_3\text{H}_7)_4\text{N}^+$ radius: bare, 4.52 Å; hydrated, 4.52 Å)					
0.1	134	0.15	16.7	40.2	2.41
0.2	145	0.12	16.7	43.5	2.61
0.3	148	0.11	16.7	44.3	2.65
$\text{R} = n\text{-C}_4\text{H}_9$ ^a ($(n\text{-C}_4\text{H}_9)_4\text{N}^+$ radius: bare, 4.94 Å; hydrated, 4.94 Å)					
0.1	192	0.07	16.7	57.8	3.46

^aData from ref. 23.

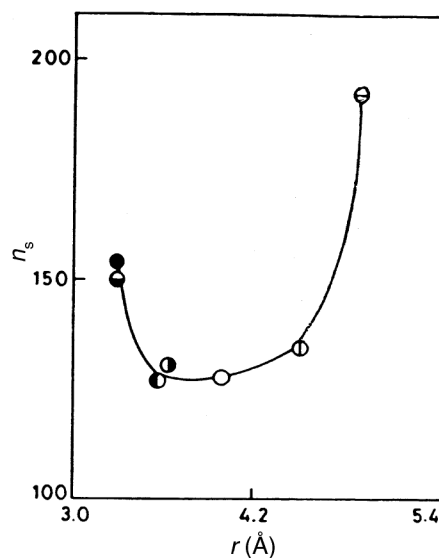


Figure 3. Variation of aggregation number (n_s) of 0.3 M SDS + 0.1 M XBr (X may be inorganic or quaternary ammonium counterion) with hydrated counterion radius (r).

37). Our results with such salts do not fit the generalization mentioned above for inorganic salts as n_s first decreases with $R = H$ to $R = C_2H_5$ and then increases with $R = n-C_3H_7$ or $n-C_4H_9$ (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 n_s up to $R = C_2H_5$ but progressively larger values of n_s obtained with $R = n-C_3H_7$ or $n-C_4H_9$ 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_4N^+ 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 n_s values.

Figure 3 shows variation of n_s 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 $(CH_3)_4N^+$ (3.67 Å) or K^+ (3.3 Å) and NH_4^+ (3.31 Å) show similar effect on the n_s value of SDS micelle^{16,38}. No doubt, n_s 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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