

Role of counterion of the surfactant molecule on the micellar structure in aqueous solution

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This article reports the sizes and shapes of micelles of anionic surfactants of LiDS, NaDS, KDS, RbDS and CsDS in aqueous solutions as studied by the technique of small-angle neutron scattering. The micelles of these surfactants are made up of negatively charged DS⁻ ions, while the positively charged ions such as Na⁺ (referred to as counterions) tend to stay near the micellar surface. The present study shows that the distribution of counterions around the micelle depends on hydrophilicity of the counterions, and this in turn decides the micellar structure.

SURFACTANT molecules (e.g. CTAB, SDS, etc.) when dissolved in water above a certain concentration, referred to as critical micellar concentration (CMC), self-aggregate into supramolecular structures. The simplest aggregate of these surfactant molecules is called a micelle and the dispersion of these aggregates in aqueous solution is referred to as a micellar solution¹⁻³. The self-aggregation of the molecules arises because of the fact that the surfactant molecule consists of two parts, which are distinctly different in character. It consists of a polar hydrophilic head group and a non-polar hydrophobic tail. A variety of surfactant molecules differing in their head groups or tails is available. They are broadly classified as ionic or non-ionic depending on whether the head group has a net charge or not. Ionic surfactants are further classified as cationic (e.g. CTAB) or anionic (e.g. SDS) depending on whether the head group is positively or negatively charged. Micellization results because of competition of two forces: the hydrophobic interaction between the tails provides the driving force for aggregation and the electrostatic or steric repulsion between the head groups limits the size that the micelle can attain. It is thus expected that the size and shape of a micelle will depend on the architecture of the surfactant molecule and the charge on the head group. In earlier studies, we have examined the role of molecular architecture on the micellar structure⁴⁻⁷. This paper deals with the study of the effect of head-group charge on the size and shape of the micelles. The charge on the head group is varied by varying the counterion of the surfactant molecule.

Anionic surfactant sodium dodecyl sulphate (SDS or NaDS), CH₃(CH₂)₁₁SO₄⁻Na⁺, ionizes in water and the

NaDS micelle is an aggregate of negatively charged dodecyl sulphate (DS⁻) ions. The positively charged Na⁺ ions, referred to as counterions, tend to stay near the micellar surface. In principle, the distribution of counterions around the micelle decides the effective charge on the head group (SO₄⁻), and this in turn decides the micellar structure. To examine if a change in counterion distribution has an effect on the micellar structure, we have studied the sizes and shapes of DS⁻ micelles in solutions of LiDS, NaDS, KDS, RbDS and CsDS. The distribution of counterions in these solutions arises because of the differences in hydrophilicity of the counterions, from Li⁺ to Cs⁺ ions. The sizes and shapes of micelles have been studied using the technique of small-angle neutron scattering (SANS), which is known to be ideal for such studies^{8,9}.

Experiment

NaDS, as obtained from Fluka, had purity better than 99% and was used as supplied. The other surfactants LiDS, KDS, RbDS and CsDS were synthesized by repeated crystallization of solutions of NaDS with Li, K, Rb or Cs salts respectively. Solutions were prepared by dissolving the required amounts of the above surfactants in D₂O. The use of D₂O instead of H₂O provides a better contrast between the micelle and the solvent during SANS experiments. D₂O (> 99.4% atom %D) was obtained from Heavy Water Division of Bhabha Atomic Research Centre. The SANS experiments were carried out using SANS diffractometer at Dhruva reactor, Trombay¹⁰ in wave vector transfer Q ($= 4\pi \sin \theta / \lambda$, where 2θ is the scattering angle and λ is the incident neutron wavelength) range of 0.018–0.32 Å⁻¹. Measurements were made on micellar solutions of LiDS, NaDS, KDS, RbDS and CsDS for a fixed surfactant concentration of 0.3 M. The sample temperature was maintained at 30 ± 1°C for all the measurements. A quartz cell of 5 mm path length was used to hold the sample. The data were corrected for background, empty-cell contribution and sample transmission, and normalized to absolute cross-section units¹⁰.

SANS data analysis

We consider a micellar solution containing n micelles per unit volume of the solution. Each micelle is made up of N (referred to as aggregation number) surfactant mole-

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cules. That is, if C is the surfactant concentration (number of molecules per unit volume), number density of micelles is given by $n = C/N$. Volume V of the micelle is equal to Nv , where v is the volume of the surfactant molecule. In a SANS experiment from such a solution one measures the differential scattering cross-section per unit volume ($d\Sigma/d\Omega$) as a function of scattering vector Q . For a system of monodisperse interacting micelles, $d\Sigma/d\Omega$ is given by^{8,11}:

$$\frac{d\Sigma}{d\Omega} = n(\rho_m - \rho_s)^2 V^2 [\langle F^2(Q) \rangle + \langle F(Q) \rangle^2 \langle S(Q) \rangle - 1] + B, \quad (1)$$

where ρ_m and ρ_s are the scattering length densities of the micelle and the solvent respectively, and V is the volume of the micelle. $F(Q)$ is the single-particle form factor and $S(Q)$ is the inter-particle structure factor. B is a constant term that represents the incoherent scattering background, which is mainly due to hydrogen in the sample. The single-particle form factor has been calculated by treating the micelle as a prolate ellipsoid. For such an ellipsoidal micelle,

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

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

$$F(Q, \mu) = \frac{3(\sin x - x \cos x)}{x^3}, \quad (4)$$

$$x = Q[a^2\mu^2 + b^2(1-\mu^2)]^{1/2}, \quad (5)$$

where a and b are the semi-major and semi-minor axes of the ellipsoidal micelle respectively, and μ is the cosine of the angle between the directions of the major axis and the wave vector transfer Q .

In general, micellar solutions of ionic surfactants show a correlation peak in the SANS distribution. The peak arises because of the corresponding peak in the inter-particle structure factor $S(Q)$, and indicates the presence of electrostatic interactions between the micelles¹¹. $S(Q)$ specifies the correlation between the centres of different micelles and it is the Fourier transform of the radial distribution function $g(r)$ for the mass centres of the micelle. In the analysis for ellipsoidal micelles, $S(Q)$ has been calculated using mean spherical approximation as developed by Hayter and Penfold¹². In the approximation, the micelle is assumed to be a rigid equivalent sphere of diameter $\sigma = 2(ab^2)^{1/3}$ interacting through a screened Coulomb potential, which is given by

$$u(r) = u_0 \sigma \frac{\exp[-\kappa(r-\sigma)]}{r}, \quad r > \sigma, \quad (6)$$

where κ is the Debye-Hückel inverse screening length given by

$$\kappa = \left[\frac{8\pi N_A e^2 I}{10^3 \epsilon k_B T} \right]^{1/2}, \quad (7)$$

where N_A is the Avogadro's number, e the electronic charge, ϵ the dielectric constant of the solvent medium, k_B the Boltzmann's constant and T the sample temperature. The ionic strength I of the solution is determined by

$$I = CMC + \frac{1}{2}\alpha C. \quad (8)$$

The fractional charge α ($= Z/N$, where Z is the micellar charge) is the charge per surfactant molecule in the micelle and is a measure of the dissociation of the counterions of the surfactant in the micelle. C is the concentration of the surfactant in the solution. The contact potential u_0 in eq. (6) is given by

$$u_0 = \frac{Z^2 e^2}{\pi \epsilon \epsilon_0 \sigma (2 + \kappa \sigma)^2}, \quad (9)$$

where ϵ_0 is the permittivity of free space.

Although micelles may form polydisperse systems, we have assumed them to be monodisperse systems for simplicity of calculation and to limit the number of unknown parameters in the analysis. The dimensions of the micelle, aggregation number and the fractional charge have been determined from the analysis. The semi-major axis (a) and the fractional charge (α) are the variable parameters in analysing the SANS data. The semi-minor axis ($b = c$) is kept fixed, as obtained from the length of the surfactant molecule.

Results and discussion

The measured SANS data for 0.3 M micellar solutions of LiDS, NaDS, KDS, RbDS and CsDS as a function of Q are shown in Figure 1. It is seen that the distributions

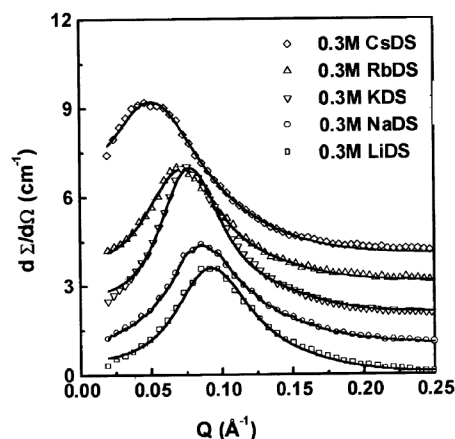


Figure 1. SANS distribution from LiDS, NaDS, KDS, RbDS and CsDS micellar solutions. Distributions for NaDS, KDS, RbDS and CsDS are shifted by 1, 2, 3 and 4 units respectively.

Table 1. Structural parameters of the micelle. The semi-minor axes are kept fixed ($b = c = 16.7 \text{ \AA}$)

Micellar system	Aggregation number N	Fractional charge α	Length of semi-major axis a (\AA)	Axial ratio a/b	Bare counterion radius (\AA)	Hydrated counterion radius (\AA)
LiDS	76	0.31	23.6	1.41	0.68	3.8
NaDS	88	0.28	27.3	1.63	0.97	3.6
KDS	127	0.23	29.4	1.76	1.33	3.3
RbDS	144	0.13	43.3	2.59	1.48	3.3
CsDS	244	0.04	73.5	4.40	1.67	3.3

show a peak and the position of the peak shifts to lower Q values as one goes from LiDS to CsDS. This peak arises because of a corresponding peak in $S(Q)$, the position of which, $Q_m (= 2\pi/d)$, depends on the inter-micellar distance (d). The shift in peak position in the present data indicates that as one goes from LiDS to CsDS, the inter-micellar distance increases, which in turn implies the number density of micelles decreases. These observations and the fact that surfactant concentration is the same in all the samples, suggest that micelle size (or the aggregation number N of the micelle) increases as one goes from LiDS to CsDS.

A quantitative analysis of the SANS data has been carried out using the method given earlier. The semi-minor axes of the micelle ($b = c = 16.7 \text{ \AA}$) was assumed to be equal to the length of the DS tail, as it is known that one dimension of the micelle is nearly equal to the length of the surfactant molecule. The data analysis involved fitting of the calculated $d\Sigma/d\Omega$ to the measured distributions with semi-major axis (a) and the effective charge α on the head group as variable parameters. Solid lines in Figure 1 are the fitted curves and the values of extracted parameters are given in Table 1. The aggregation number N was obtained from a knowledge of the micelle volume ($V = \frac{4}{3}\pi a^2 b$) and the volume ($v = 350.2 \text{ \AA}^3$) of the DS⁻ ion. The values of aggregation number $N = 76$ for LiDS and $N = 88$ for NaDS micelles are in good agreement with reported values of $N = 78$ (ref. 13) and $N = 84$ (ref. 14) in the literature.

Table 1 shows that the head-group charge α decreases as one goes from LiDS to CsDS, suggesting that the Cs⁺ ion is more effective in screening micellar charge compared to Li⁺ ion. We believe that this arises because of change in counterion distribution around the micelle. Comparison of sizes (Table 1) of hydrated and unhydrated monovalent ions¹ indicates that hydrophilicity of these ions decreases as one goes from Li⁺ to Cs⁺ ions. We understand that while anions having higher hydrophilicity have more affinity to remain in the bulk of the micellar solution with water, the anions having less hydrophilicity tend to stay more near the micelle, and thereby as the hydrophilicity of counterions decreases they provide a

better screening of the micellar charge. The decrease in head-group charge in going from LiDS to CsDS as seen in Table 1, is thus connected with the differences in the counterion distributions around the micelle which results from the differences in hydrophilicity of the counterions. It is noted that a decrease in head-group charge gives rise to an increase in semi-major axis and the aggregation number of the micelle.

In short, these studies have shown that counterion distribution in LiDS-type of micellar solutions changes as one goes from LiDS to CsDS, and this results in an increase in micelle size. The small-angle X-ray scattering (SAXS) experiments and the combined analysis of SANS and SAXS data for directly obtaining the counterion distribution in these systems as suggested by Aswal *et al.*¹⁵, are planned.

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