MONOMER DYNAMICS IN SDS MICELLAR SOLUTION:
QUASIELASTIC NEUTRON SCATTERING STUDY

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Abstract

Monomer dynamics in sodium dodecyl sulfate (SDS) micellar solution at room temperature as studied by quasielastic neutron scattering (QENS) technique is reported here. The elastic incoherent structure factor (EISF) obtained from the analysis of QENS data suggests that the SDS chain performs uniaxial rotational diffusion along the long molecular axis. The rotation diffusion coefficient is found to decrease with the increase in the concentration of the surfactants. It is also observed that on addition of electrolyte the motion is arrested. Addition of salt is known to induce the growth in SDS micelles, here it is found to affect the dynamics of monomers also. This is understood in terms of combined effect of closer packing of the monomers within the micelle and the tendency of amphiphilic molecules to stabilize due to the presence of electrolytes.

Keywords: Micelles, Quasi Elastic Neutron Scattering, EISF, Electrolyte.

Introduction

Amphiphilic molecules have the ability to undergo self association under specific conditions to create a variety of structures including micelles, liposomes, bilayers, wormlike micelles and so on. Surfactants and their aggregates are widely used as a significant component in variety of applications such as detergency, pharmaceutical formulations, biomedical applications, and materials synthesis [1-2]. In particular, viscoelastic wormlike micellar solutions find application as oil field fracturing fluids, drag reducing agents and personal care formulations [3]. One particular example of commonly used surfactant is the sodium dodecyl sulfate (SDS) which is an anionic surfactant that is used in industrial products including engine degreasers, floor cleaners, and car wash soaps; as well as in household products such as toothpastes, shampoos, shaving foams, dissolvable aspirins, fiber therapy caplets, and bubble baths for its thickening effect and its ability to create a lather. The molecule has a tail of 12 carbon atoms, attached to a sulfate group, giving the molecule the amphiphilic properties required of a detergent. The critical micelle concentration (CMC) in pure water at 25°C is 0.0082 M, and the aggregation number is around 60.

By tailoring the molecular architecture and interaction between the amphiphiles, discrete structures with specific size, shape and order can be created. The geometry of the aggregates formed by the amphiphilic molecules is a result of a delicate balance between two opposing forces. The attractive tail-tail hydrophobic interaction provides the driving force for the aggregation of surfactant molecules, while the electrostatic repulsion between head groups puts a lower limit on the size that a micelle can attain. Charged spherical micelles can grow into elliptical rod like structures by addition of electrolytes that screen the electrostatic repulsion. Formation of worm like micelles can be induced in ionic micellar solutions by changing
the electrostatic interaction between the head groups of individual amphiphiles. The addition of inorganic or organic salts to an ionic surfactant solution facilitates the transition from spherical to rod-like micelles by shielding the repulsions between the charged headgroups. Recently, we reported a sphere-to-rod like transition in anionic sodium dodecyl sulfate (SDS) micelles induced by the addition of the aromatic salts aniline hydrochloride (AHC) and its ortho, meta and para substituted analogues, o-toluidine hydrochloride (OTH), m-toluidine hydrochloride (MTHC) and p-toluidine hydrochloride (PTHC). Dynamic light scattering (DLS) and SANS studies revealed that the growth of the micelles is much more pronounced with the addition of PTHC as compared to AHC, OTHC and MTHC [4].

Though the structure and macroscopic behavior of assemblies are extensively studied, the fast segmental dynamics of surfactants in assemblies and their correlation with microstructure is poorly understood. Different kinds of motion exist in micellar solution such as the translation and rotation motion of whole aggregates, segmental motion of monomers within micelles, etc. In general global motions are much slower than the segmental motion of micelles and exist typically at few microseconds. Most commonly, nuclear magnetic resonance (NMR) relaxation method, micro viscosities, dynamic light scattering, etc. techniques are used to study molecular motions in these systems. However, to study surfactant systems by NMR requires some special instrumentation, micro viscosity measurements only give qualitative information and like others, dynamic light scattering is also limited to probe slower global motions. To probe such faster local motions in the presence of such global motions, which is interesting as it could influence the release of solubilized drugs and other molecules in micelles, quasielastic neutron scattering (QENS) is one of the best suitable techniques that is generally used to study the fast motions [5]. For example, earlier we have studied alkyl chain dynamics on monolayer protected metal clusters (MPC) [6-8] using QENS technique. It was found in these studies that the alkyl chains protecting the metal clusters undergo uniaxial reorientation motion with reorientation times of the order of a few picoseconds. Further, it was observed that the temperature at which the dynamical freedom sets in is different for isolated clusters, superlattices and thiolates, being maximum for thiolates and minimum for isolated clusters. However in SDS micelles there are no such metal cores and there exists no fixed end of the alkyl chain as it exists in case of MPC. Unlike in MPCs where high structural order prohibits long-range motion, SDS micelles can perform long-range translational motion. However, translational and rotational motions of the whole aggregates are reported to be slow ($10^{-7}$ s) and will not be within the range of QENS. The time window available for a QENS spectrometer is generally $10^{-10}$ - $10^{-13}$ s and only fast local motion such as the reorientation of the monomers can be detected by QENS out of all possible motions existing in a micellar solution.

Changes in the interaction between amphiphiles within an aggregate could alter the local dynamics of amphiphiles and other solubilized molecules within the assemblies. Earlier, Taboney et al [9] had reported monomer dynamics in tetradecyl trimethyl ammonium bromide (TTAB) micelles and sodium bis (2 ethylhexyl) sulfo succinate (AOT) reverse micelles. Freda et al [10] had shown hydration dependent internal dynamics of AOT reverse micelles in deuterated cyclohexane (C$_6$D$_{12}$). For the anhydrous sample, quasielastic broadening is attributed entirely to the global motion of AOT reverse micelles. With increase in hydration above a threshold, onset of internal motion of the micelles along with the global motion is observed. Confined diffusion within a sphere is reported by Brocca et al., [11] in case of ganglioside micellar solution. But the effect of concentration of surfactant and salts on the local dynamics has not been reported yet to the best of our knowledge. Here, we report QENS studies on sodium dodecyl sulfate (SDS or NaDS) (C$_{12}$H$_{25}$SO$_4$Na) micelles to investigate the monomer motions in micelles and changes in the local motion of the surfactants in aggregates with different morphologies which was achieved by varying surfactant concentration and adding electrolytes.

**Experimental details**

Sodium dodecyl sulfate (electrophoresis grade) was obtained from Sisco Research Labs, Mumbai, India. Schematic of the molecular structure of SDS is shown in Fig. 1. For QENS measurements micelles were prepared...
by dissolving SDS in D$_2$O (99.4% atom D purity). QENS experiments were carried out using the QENS spectrometer [12] at Dhruva reactor, Trombay. This spectrometer is used in multi angle reflecting crystal (MARX) mode, which essentially uses a combination of a large analyser crystal and a position sensitive detector. In the present configuration, the spectrometer has an energy resolution of 200 $\mu$eV with an incident neutron wavelength of 4 Å. QENS measurements were carried out on 5% (w/w), 10% (w/w) aqueous SDS solution in D$_2$O in absence and presence of 0.8 M NaCl in a wave vector transfer ($Q$) range of 0.67 – 1.8 Å$^{-1}$ at room temperature. We have also recorded QENS spectra for pure D$_2$O as a reference. The samples were contained in flat aluminium rectangular sample cells of dimension (50 × 15 × 5) mm.

Results and Discussion

QENS spectra obtained with D$_2$O were subtracted from the data taken with 5% (w/w) SDS solution in order to observe the dynamics within the SDS micelles. The subtracted data showed significant quasi elastic broadening over instrument resolution suggesting the presence of fast dynamics of surfactant chains inside micelles. Typical quasielastic broadening at $Q=1.32$ Å$^{-1}$ is shown in Fig. 2.

To analyse the data, first the measured spectra were separated into elastic and quasielastic components, by using the following general scattering law and convoluting it with the measured instrumental resolution function, by least squares fits.

\[
S(Q,\omega) = A(Q)\delta(\omega) + [1 - A(Q)]L(\Gamma,\omega)
\]

(1)

Here \(L(G,\omega)\) is the Lorentzian with half width at half maximum (HWHM) \(\Gamma\). The fits for 5% (w/w) SDS solution at some typical $Q$ values along with the separated elastic and quasi-elastic components are shown in Fig. 3.

The parameters obtained from the fits are the EISF \(A(Q)\) and the HWHM \(\Gamma\) of the Lorentzian. A non-zero value of EISF is obtained, which indicates the presence of localized motion. The variation of the EISF thus obtained was then compared with various models for rotational motions. It was found that the uniaxial rotation diffusion in which SDS chain performs uniaxial rotation along the molecular axis with a radius of gyration $r = 1.4$ Å fits the EISF very well. Fig. 4 shows the variation of the experimentally obtained EISF along with the fits with uniaxial rotational diffusion model.

The scattering law [13] for uniaxial rotational diffusion is given by

\[
S(Q,\omega) = J_0(Qr\sin\theta)\delta(\omega) + 2\sum_{l=1}^{\infty} J_l(Qr\sin\theta)\frac{Dl^2}{(Dl^2)^2 + \omega^2} + \delta(\omega)
\]

(2)

where $r$ is the radius of gyration and the $J_l$ s are Bessels function of the first kind. Here the behavior of the elastic and the quasielastic structure factors strongly depends on the angle \(\theta\) between the direction of $Q$ and the axis of rotation. For a powder sample, one has to take an isotropic
average over angle $\theta$. Unfortunately, no formal analytical expression exists for the average. However, it is possible to use the expressions of the scattering law for a jump model over $N$ equally spaced sites, with $N$ sufficiently large, at least in the limit of $Qr < \pi$. The scattering law for jump diffusion model [13] can be written as,

$$S(Q, \omega) = A_0(Qr)\delta(\omega) + \frac{1}{\pi} \sum_{i=1}^{N} A_i(Qr) \frac{1/\tau_i}{(1/\tau_i)^2 + \omega^2}$$

where $A_i(Qr) = \frac{1}{N} \sum_{n=1}^{N} j_0(2Qr \sin \pi n/N) \cos(2\pi nl/N)$

the correlation times can be evaluated as $\tau_i^{-1} = 2\tau^{-1} \sin^2 (l \pi / N)$. The rotational diffusion constant $D_r$ can be identified with the jump rate probability $1/t_1$, as $D_r = 1/t_1 = (2/t) \sin^2 (\rho/N)$.

In the present case, with the maximum possible wave vector $Q = 1.8 \text{ Å}^{-1}$ and the radius of gyration $r = 1.4 \text{ Å}$, for all possible $Q$ values, $Qr$ is always less than $\pi$. Therefore, the scattering law for the jump models with large jump sites ($N > 6$) can be used as a scattering law for uniaxial rotational diffusion. It was found that the uniaxial rotational model describes the experimental QENS spectra very well supporting our results that the motion is related to uniaxial rotation of surfactant along the molecular axes. A rotation diffusion coefficient $D_r = 7.4 \times 10^{10} / \text{sec}$ was obtained from the fit of uniaxial rotational model with the experimental QENS data.

Earlier, it was shown [4,14] that a change in concentration of salts or surfactant induced the growth of micelles, which changed the shape of micelles. Therefore, it will be interesting to see the effect of concentration and salts on the local dynamics of micelles. With that view, a QENS experiment was also carried out on 10% (w/w) SDS micelles solution in absence and presence of salts. QENS spectra of 10% (w/w) SDS solution subtracted from $D_2O$ were separated into elastic and quasielastic parts. It was found that the behavior of the EISF is more or less the same as described by uniaxial rotational diffusion model with a radius of gyration 1.4 Å and the variation is shown in Fig. 4. The value of rotational diffusion coefficient, $D_r$, as obtained from the fitting with the model scattering law is found to be 5.1 $\times 10^{10} / \text{sec}$. Uniaxial fits of typical QENS data for 10% (w/w) SDS micellar solution and fits assuming uniaxial rotational diffusion at some $Q$ values are shown in Fig. 5.

It was found that the rotational diffusivity of the monomer is reduced with an increase in the concentration of the surfactant, while the nature of the monomer motion remains unaltered. This can be explained due to changes in the packing density of the monomers within the micelles, which is also supported by a small angle neutron...
scattering study [15]. More counter ions in case of 10% (w/w) SDS micellar solution lead to higher screening of the electrostatic repulsion compared to 5% (w/w) SDS solution and thus provide lesser spacing between the monomers in the micelles compared to 5% (w/w) SDS solution. Closer packing of the monomers within the micelle causes hindrance in the reorientation motion of the monomer. This has been further verified by the addition of electrolyte, NaCl (0.8 M NaCl). Addition of salt leads to more counter ions in the micellar solution without changing the concentration of SDS. It is observed that on addition of NaCl, the motion is arrested and no quasielastic broadening is observed. The screening of repulsive interactions between the head groups by the addition of salt leads to the monomers coming too close to be able to move. Thus addition of salt, which is known to induce growth in SDS micelles, is found to affect the local dynamics as well. The amount of salt (0.8 M NaCl) used in our experiment is probably too high, which results in the freezing of the motions. A systematic study with smaller quantities of salt is presently being pursued by us to study the effect of salt on the local dynamics of SDS micelles.

Subsequently we have carried out QENS measurements using high-resolution backscattering spectrometer IRIS, at ISIS facility, UK. We found in addition to the monomer dynamics the micelle also show global motion. We have developed a model considering both global and internal dynamics and able to describe the observed data successfully at different temperatures and concentration of SDS.

Conclusion

Internal dynamics of SDS micelles has been studied using quasielastic neutron scattering technique. It has been found that a model in which the SDS chain performs uniaxial rotational motion about the long chain axis fits the experimental data best. The rotational diffusion coefficient has been obtained by fitting the experimental data with the uniaxial rotational diffusion model. Internal motion of the SDS chain is seen to be affected with the presence of counter ions in the micellar solution. With more counter ions available in the solution, screening between the head groups increases which allows the surfactant to pack more closely. Due to the closer packing of the surfactants, hindrance in the motion increases which leads to decrease in the diffusivity of the monomers.

References


