

Small-angle neutron scattering from micellar solutions

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Abstract. Micellar solutions are the suspension of the colloidal aggregates of the surfactant molecules in aqueous solutions. The structure (shape and size) and the interaction of these aggregates, referred to as micelles, depend on the molecular architecture of the surfactant molecule, presence of additives and the solution conditions such as temperature, concentration etc. This paper gives the usefulness of small-angle neutron scattering to the study of micellar solutions with some of our recent results.

Keywords. Small-angle neutron scattering; surfactant; micelle.

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1. Introduction

Micellar solutions are the suspension of the colloidal aggregates of the surfactant molecules in aqueous solutions. Surfactant molecules consist of a polar hydrophilic head group and a long hydrophobic chain connected to the head group. The coexistence of the two opposite types of behavior (hydrophilic and hydrophobic) in the same molecule leads to the self-aggregation of the surfactant molecules when dissolved in water. The aggregates are called as micelles [1]. The micelles are formed by the delicate balance of opposing forces: the attractive tail–tail hydrophobic interaction provides the driving force for the aggregation of the surfactant molecules, while the electrostatic repulsion between the polar head groups limit the size that a micelle can attain. As a result, the characteristics of these aggregates are easily controlled by the change in the solution conditions such as temperature, concentration and ionic strength. The aggregates formed are of various types, shapes and sizes such as spherical or ellipsoidal, cylindrical or thread-like micelle, disk-like micelle, membrane and vesicles [2–5]. The study of formation of these different structures is important as the surfactant solutions are widely used in various household, industrial and research applications [6].

Small-angle neutron scattering (SANS) covers a length-scale, where most of the micelle structures starting from spherical to rod-like or disk-like shapes are formed [7,8]. SANS gives information about the shapes and sizes of the micelles and the

interactions between the micelles [9,10]. SANS is an ideal technique for studying the structural aspects of micellar solutions. The contrast between the micelle and the solvent can be easily enhanced by deuterating either the micelle or the solvent. Further, multi-component micellar systems can be simplified to study them by selectively contrast-matching the components with the partial deuteration of the components.

SANS has been used extensively to study a variety of micellar solutions [11–30]. The micellar solutions of different types of surfactants of recent interest and the effect of solution conditions such as concentration, temperature and presence of various additives in these micellar solutions have been studied. The surfactants that have been investigated are the conventional surfactants [11–16], mixed surfactants [17–19], block copolymers [20–22] and the newly synthesized gemini [23–27] and multi-headed surfactants [28–30]. This paper brings out the usefulness of SANS to the study of micellar solutions and some of our recent results on micelles as studied by this technique.

2. Small-angle neutron scattering

SANS is a diffraction experiment, which involves scattering of a monochromatic beam of neutrons from the sample and measuring the scattered neutron intensity as a function of the scattering angle. The wave vector transfer Q ($= 4\pi\sin\theta/\lambda$, where λ is the incident neutron wavelength and 2θ is the scattering angle) in these experiments is small, typically in the range of 10^{-3} to 1.0 \AA^{-1} . The wavelength of neutrons used for these experiments are usually 4–10 \AA . Since the smallest Q values occur at small scattering angles ($\sim 1^\circ$), the technique is called small-angle neutron scattering. An indigenously built SANS instrument [31] has been operating at Dhruva reactor, BARC, and is being regularly used by BARC and university scientists.

In SANS experiment one measures the coherent differential scattering cross-section ($d\Sigma/d\Omega$) as a function of wave vector transfer Q . For a system of monodisperse particles, it is given by [32]

$$\frac{d\Sigma}{d\Omega}(Q) = n(\rho_p - \rho_s)^2 V^2 P(Q)S(Q), \quad (1)$$

where n is the number density of the particles, ρ_p and ρ_s are, respectively, the scattering length densities of the particle and the solvent, and V is the volume of the particle. $P(Q)$ is the intraparticle structure factor and is decided by the shape and size of the particle. $S(Q)$ is the interparticle structure factor, which depends on the spatial arrangement of particles and is thereby sensitive to interparticle interactions. In case of dilute solutions, interparticle interference effects are negligible, and $S(Q) \sim 1$.

Scattered neutron intensity in the SANS experiment depends on $(\rho_p - \rho_s)^2$ – the square of the difference between the average scattering length density of the particle and the average scattering length density of the solvent. This term is referred to as the contrast factor. It is equivalent to the contrast term in optics where it is decided by the difference in the refractive indices of the particle and the solvent. Due to the

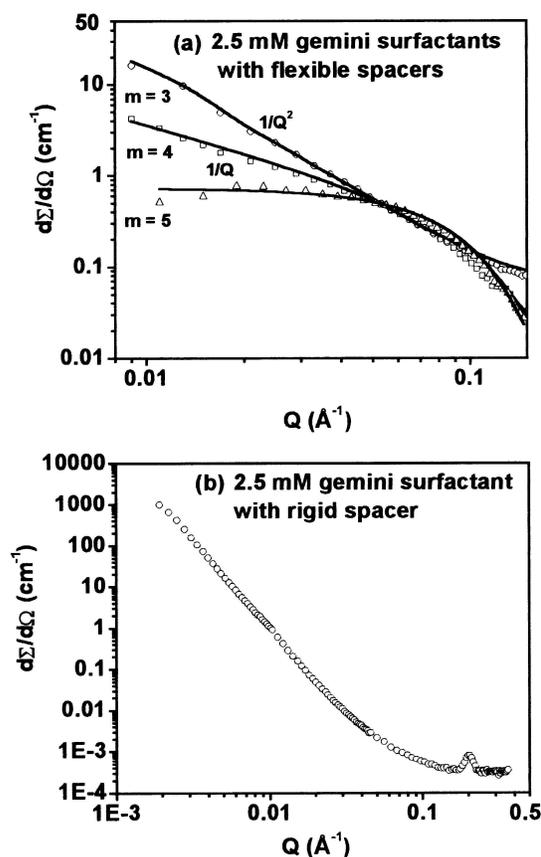


Figure 1. (a) SANS data from 16- m -16, 2Br^- gemini surfactants with varying spacer length $m = 3, 4$ and 5 and (b) SANS data from gemini surfactants with rigid spacers.

fact that the scattering length is negative ($= -0.3723 \times 10^{-12}$ cm) for hydrogen and positive ($= 0.6674 \times 10^{-12}$ cm) for deuterium, SANS is ideally suited for studying the structural aspects of hydrogenous materials such as micellar solutions [10].

3. Results

SANS is a versatile technique in obtaining various information on the micellar solutions. Herein, we show some of the capabilities of SANS to the study of micellar solution with suitable examples.

3.1 Shape and size of the micelles of gemini surfactants

This example is to show the capability of SANS in determining the shape and size of the micelles as has been applied to the gemini micelles. Gemini or dimeric

surfactants consist of two hydrophobic chains and two hydrophilic head groups covalently connected by a spacer [33]. Gemini surfactants are called the surfactants of the next generation because of the various exceptional properties that they manifest. Additionally, the gemini format allows for expanded structural diversity in surfactant chemistry, as head groups, hydrophobic chains, spacers and counterions can be varied in search for enhanced performance. We have studied in detail the effect of (a) spacer length, (b) flexibility vs. rigidity of the spacer, (c) hydrophobicity vs. hydrophilicity of the spacer and (d) role of change of the head group from cationic to anionic on the micellar structures of gemini surfactants [23–27]. Depending on the nature of spacer and head groups, length of hydrophobic chains and spacer lengths, various types of aggregates, have been observed. Figure 1a shows the SANS data from 2.5 mM micellar solutions of 16-*m*-16, 2Br⁻ gemini surfactants consisting of polymethylene spacer for spacer length $m = 3, 4$ and 5 [24]. The measurements were carried out at low concentration to ensure the micellar solutions are dilute (i.e. $S(Q) \sim 1$), so that the scattered intensity is only governed by $P(Q)$. It is seen that the cross-section ($d\Sigma/d\Omega$) and the slope of the SANS data at low Q region ($Q < 0.05 \text{ \AA}^{-1}$) decreases as m is increased. This suggests that micellar structures are widely different in these systems. For $m = 3$ and 4, SANS distributions are straight lines in the low Q range of 0.01 to 0.05 \AA^{-1} . For $m = 3$, $d\Sigma/d\Omega$ varies as $1/Q^2$ and for $m = 4$, it varies as $1/Q$. These observations on Q dependence of the cross-section suggest micelles are disc-like for $m = 3$ and rod-like for $m = 4$. The small values of $d\Sigma/d\Omega$ at low Q region for $m = 5$ is an indication of smaller micelles in these systems than those for $m = 3$ and 4. It is found that micelles are ellipsoidal for $m = 5$.

The presence of aromatic rings at the spacer changes the spacer from flexible to rigid. Figure 1b shows the SANS data for a gemini surfactant with rigid spacer. It is seen that the features of SANS data with rigid spacer are quite different than those with the flexible spacers. The data in figure 1b show large scattering in the low Q region and a Bragg peak at the large Q value of 0.20 \AA^{-1} . These observations suggest that the gemini surfactants with rigid spacer form the multi-lamellar vesicles and not the micelles as formed with the flexible spacers. The position of the Bragg peak gives the repeat distance ($\sim 31 \text{ \AA}$) of the lamella in the multi-lamellar vesicles.

3.2 Structure and interaction of ionic micelles in the presence of electrolytes

One of the unique advantages of SANS to the micellar solutions is its capability to determine both structure and interaction of micelles. In fact, this feature of SANS has been widely used to understand the structure of ionic micelles in aqueous electrolyte solutions. Ionic micelles (e.g. CTABr) are nearly spherical in pure micellar solutions. These micelles become elongated and grow in length on addition of electrolytes such as KBr, sodium salicylate (NaSal) etc. The effect of different electrolytes is interestingly quite different. This provides one of the easiest ways for practical applications to control the properties of the micellar solutions by the addition of the electrolytes. We have used SANS to address some of the specific questions in these systems [11–16]. For example, it was not clear why CTABr or CTACl micelles grow with the addition of small quantities of KBr, but not with KCl even at high concentrations? SANS results from these systems in terms of the

structures and interactions of the micelles showed that differences in micellar growth of CTABr or CTACl in the presence of KCl and KBr are connected with the different counterion sizes of Cl^- and Br^- ions [11,13,15]. The smaller the hydrated size of the counterion, higher will be its tendency to screen the charge on the micelle, and hence larger the size of the micelles. The other example, where we have used the SANS is to understand the structures and the interactions in the viscoelastic CTABr/NaSal micellar solutions. This system shows a striking double peak behaviour of the zero-shear viscosity as a function of NaSal concentration. It is found that beyond the first viscosity maximum micelles behave as living polymers [12]. In the living polymer regime, micelles break and coalesce on a time-scale smaller than the time-scale of diffusional motion. The micelles are highly polydispersed in this regime and their length distribution is exponential. These studies further suggest that the variation in viscosity after the first viscosity maximum is connected with the change in the intermicelle interactions.

Figure 2 shows a typical SANS data from a micellar solution of 100 mM CTACl to compare the effect of the addition of KBr and KCl [15]. The correlation peak in the data is an indication of strong repulsive interaction between the positively charged CTACl micelles. The peak usually occurs at $Q_m \sim 2\pi/d$, where d is the average distance between the micelles. The peak shifting to lower Q values with KBr is an indication of the growth of the micelles in CTACl/KBr solutions. The broadening of the peak is due to the screening of the repulsive interaction between the micelles in the presence of the electrolyte. The same is not the case in the CTACl/KCl solutions, where the peak broadens without a significant shift in the peak position. This shows that CTACl micelles do not grow with the addition of KCl. The quantitative information about the structure and the interactions of the micelles is obtained by fitting the experimental data in terms of eq. (1) using suitable models for $P(Q)$ and $S(Q)$ [11–16]. The solid lines in figure 2 are a fit to the experimental data.

3.3 Study of micellar solutions with two components as surfactants and block copolymers

Most important characteristic of SANS is to study the multi-component micellar solutions. This is possible with the contrast variation method of the SANS. The triblock copolymer P85 [(EO)₂₆(PO)₃₉(EO)₂₆] is usually dissolved as unimers at low temperatures (say 20°C). This is because both the PEO and PPO blocks are hydrophilic at low temperatures. On the other hand, anionic surfactant sodium dodecyl sulfate (SDS) forms the micelles at 20°C. It is interesting to know what structure will be formed when the SDS and P85 are mixed together? There are three possibilities: (i) SDS does not do anything to P85 and the mixed system consists of P85 unimers and SDS micelles, (ii) SDS induces the micellization of P85 and the mixed systems have both P85 and SDS micelles and (iii) SDS makes the mixed micelles with P85. The contrast variation technique of SANS can be used to identify one of these structures, which is formed in the above system.

Figure 3a shows the effect of addition of SDS on aqueous solution of block copolymer P85. It is seen that the scattering profile of mixed SDS and P85 is significantly

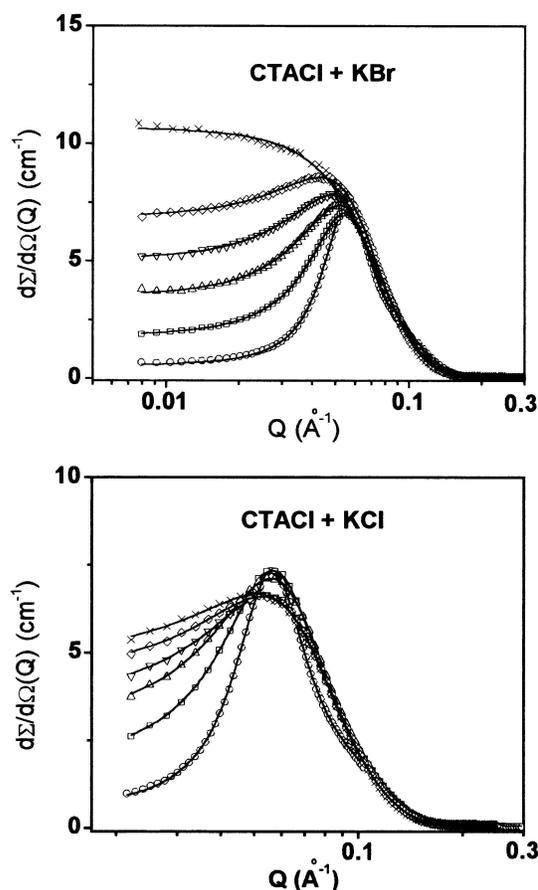


Figure 2. Comparison of SANS data from 100 mM CTACl micellar solution in the presence of varying concentration of KBr and KCl. The data from bottom to top correspond to the salt concentrations of 0, 20, 40, 60, 80 and 100 mM, respectively.

different from those of the individual components. To identify the structure in the mixed system, the surfactant is contrast-matched to the solvent, using the deuterated surfactant. The SANS data with deuterated surfactant are shown in figure 3b. The fact is that the SANS data of matched contrast to surfactant with block copolymer does not match with that of the block copolymer. This rules out the possibility that the mixed system consists of P85 unimer and SDS micelles. It is observed that the scattering features of the data of mixed SDS and P85 with and without deuterated surfactants are the same. In fact, these data can be scaled to each other. This suggests that the mixed system can not have the individual P85 and SDS micelles. The scaling of the two data sets is possible when the mixed micelles are formed with P85 and SDS and the distribution of the components is uniform.

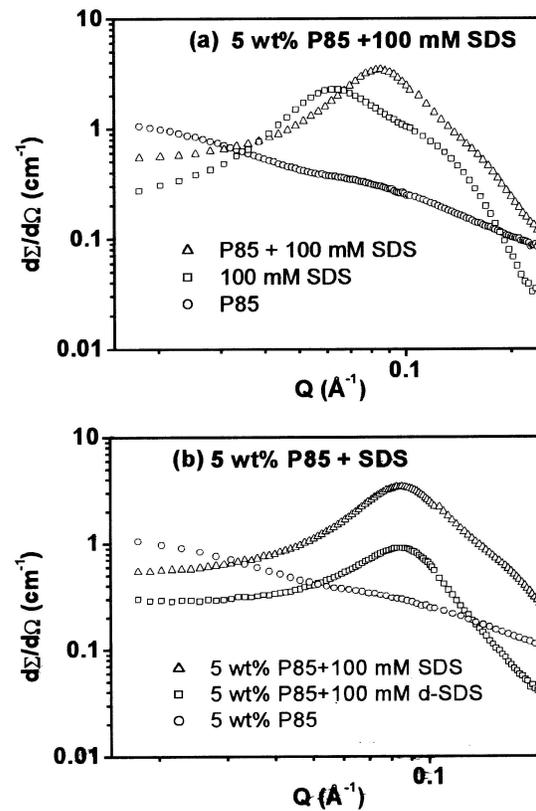


Figure 3. (a) SANS data from P85, SDS and the mixture of P85 and SDS, (b) SANS data of P85 are compared with and without the deuterated SDS.

4. Summary

SANS is a powerful technique to the study of micellar solutions. This arises due to the contrast between the micelle and the solvent that can be easily enhanced deuterating either the micelle or the solvent. Further, the multi-component micellar systems can be simplified to study them by selectively contrast-matching the components with the partial deuteration of the components. SANS can be used to obtain the various information on the micelles such as shape and size of the micelles, structure with interaction in micellar solutions and composition of the multi-component micellar solutions. Some of our recent SANS results on micelles have been discussed.

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