Micellar structure and inter-micelle interactions in micellar solutions: Results of small angle neutron scattering studies

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Micelles are aggregates of surfactant molecules suspended in water. The structure (shape and size) of a micelle depends both on the architecture of the constituent surfactant molecule and the solution conditions such as temperature, presence of impurities, etc. The inter-particle interaction between micelles also depends on several different parameters. It is of interest to study the structure and inter-micellar interactions in micellar solutions both from the point of view of basic research and the applications. It has been found that the technique of Small Angle Neutron Scattering (SANS) is ideally suited for the above studies. This paper gives an introduction to the technique of SANS and discusses the results of typical SANS studies dealing with the micellar structure and the inter-micellar interactions.

1. Introduction

SURFACTANT molecules (e.g. CTAB, SDS, Triton X-100, etc.) self-aggregate into supermolecular structures when dissolved in water or oil. The simplest aggregate of these surfactant molecules is called a micelle; and the dispersion of the aggregates in water or oil is referred to as a micellar solution[1–4]. An excellent introduction to micelles is given in an article[5] by Moulik published in this journal in 1996. A typical micelle has size of ~ 50 Å and is made of about 100 surfactant molecules. In general, these pseudo-particles could be spherical, cylindrical, ellipsoidal or disc-like in shape. It may be mentioned that self-aggregation of surfactant molecules in water/oil arises because of dual affinity of these molecules for water and oil. The surfactant molecule consists of two parts, namely, a polar hydrophilic head group and an apolar hydrophobic tail (hydrocarbon chain). A schematic representation of a surfactant molecule and a micelle is shown in Figure 1.

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The intermolecular forces between surfactant molecules in presence of water (high dielectric constant) are weak (~ k_BT) and can be easily modified by manipulating them by addition of salts (that is, by reducing or increasing electrostatic effects). Hence, micellar solutions exhibit interesting properties on addition of salts or with a change in temperature. For example, the micellar solutions of cetyltrimethylammonium bromide (CTAB) become extremely viscous on addition of small quantities of sodium salicylate[6–8]. Triton X-100 micellar solutions separate into two phases – one rich and the other dilute in micellar concentration (analogous to

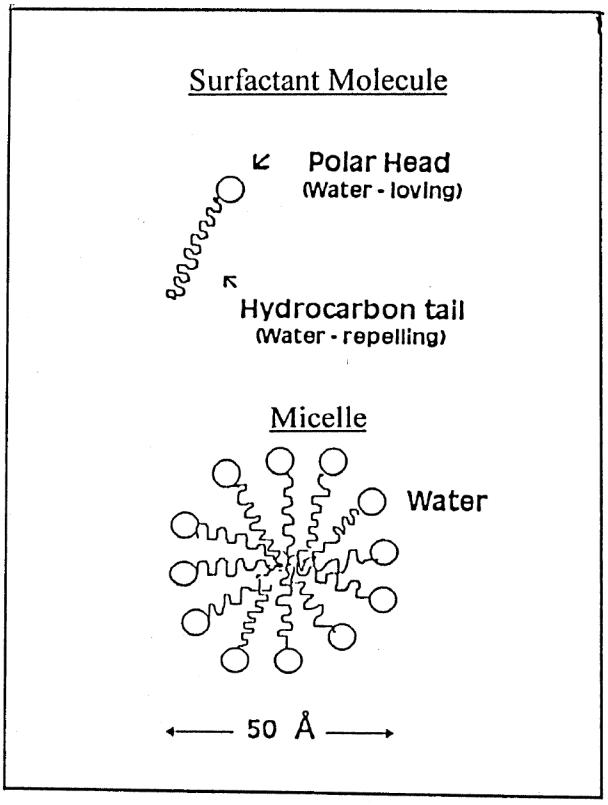

Figure 1. A schematic structure of a micelle and a surfactant molecule.

gas–liquid transition) on heating or beyond a well defined temperature T_{cp}, called cloud point[9,10]. These observations suggest that there are significant changes in the micelle structures and inter-micellar interactions on addition of salt or with a change in temperature.

The study of micellar solutions is of interest both from the point of view of basic research and applications of surfactants. A variety of experimental techniques have been used for studying the micellar systems[3]. Among these, Small Angle Neutron Scattering (SANS) technique is an important tool for studying the micellar structures (size and shape) and the inter-micellar interactions[11,12]. This paper gives an introduction to the technique of SANS and shows results of some of the studies undertaken by us at BARC, Trombay on micellar solutions. The plan of the paper is as follows. An introduction to different types of surfactant molecules is given in the next section. The characteristic parameters of these molecules and their role in deciding the shape of micelles is discussed in §3. A brief discussion on the various terms contributing to inter-micellar interactions is also given in §3. §4 gives a detailed introduction to the experimental and theoretical aspects of SANS. The results of typical SANS studies on micellar solutions are given in §5. Lastly, a summary of the paper is given in §6.

2. Surfactants used in formation of micelles

As already mentioned, the surfactant molecule consists of a polar hydrophilic head group and a non-polar hydrophobic tail. A variety of surfactant molecules have been synthesized. Schematic representations of some of these molecules are given in Figure 2. Surfactant molecules are classified as ionic or non-ionic depending on whether the head group has a net charge or not. The ionic surfactants are further classified as cationic or anionic depending on whether the head group is positively or negatively charged. CTAB is an example of a cationic surfactant and sodium dodecyl sulphate (SDS) that of an anionic surfactant. Most of these ionic surfactants have a single tail and a single head group. However, it is possible to synthesize surfactant molecules having double or branched hydrophobic tails or those having multiple head groups. The Gemini surfactants consist of two hydrophobic tails and two hydrophilic head groups covalently attached by a hydrophobic or hydrophilic spacer[13,14]. Triton X-100 is an example of a non-ionic micelle. Non-ionic micelles are neutral. Unlike ionic surfactants, where the head consists of a small molecular group, the hydrophilic part of the non-ionic surfactant molecule consists of a long chain. In addition to Triton X-100, diblock (PEO-PPO) and

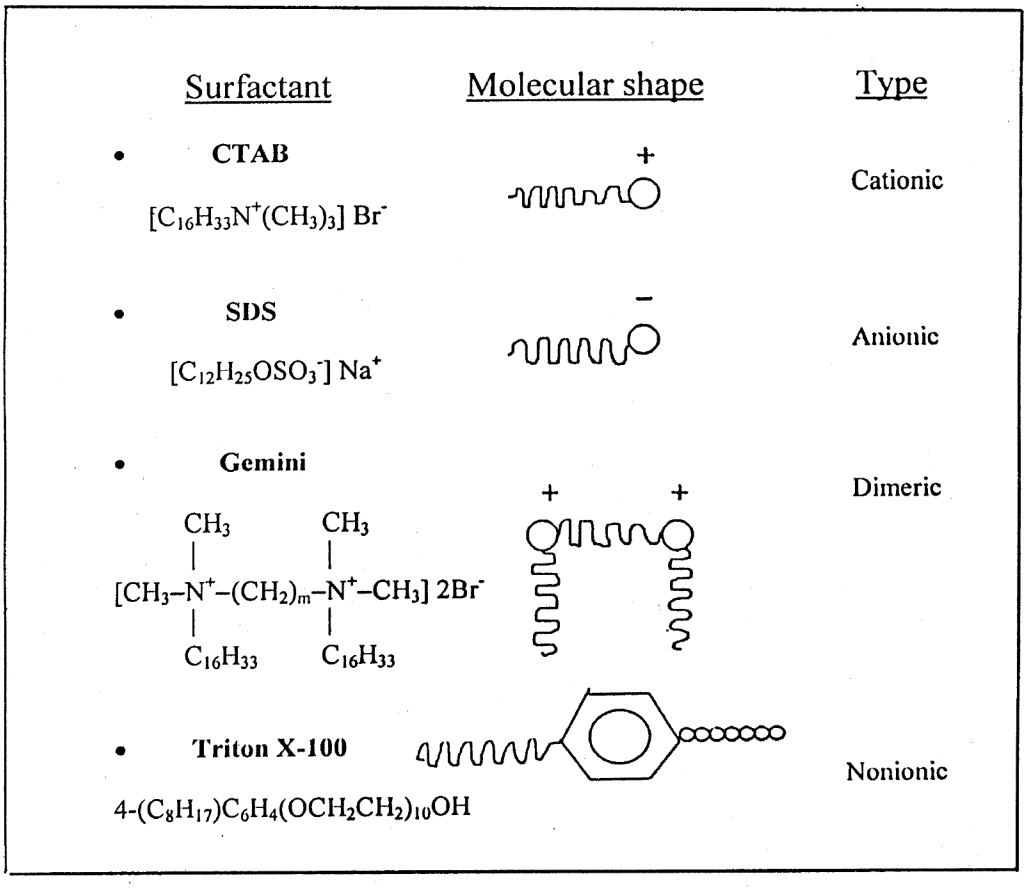

Figure 2. Some of the commonly used surfactants.

triblock (PEO-PPO-PEO) copolymers are the other examples of non-ionic surfactants. There is another class of surfactants, called zwitterionic surfactants, which tend to make long thread-like micelles. Alkyl dimethyl betaines are an example of zwitterionic surfactants[15]. Thus we see there are a variety of surfactants; their micellar solutions, in general, could have different structures or inter-particle interactions.

3. Parameters controlling the micellar structure and the inter-micellar interactions

Micelles are formed by the 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 a micelle can attain. The architecture of the molecule and the head group charge thus play important roles in deciding the micellar shape. It can be shown that micellar shape depends on the relative values of tail length (l), head group area (a) and the molecular volume (v) of the molecule. Israelachvili *et al.*[16] have argued that depending on the value of packing parameter p ($= v/al$), the surfactant aggregates could acquire different shapes (Figure 3). They showed that, in general, micelles are spherical for $p < 1/3$ and ellipsoidal and cylidrical for $1/3 < p < 1/2$. The surfactant aggregates tend to be bilayers for $p > 1/2$ and in suitable cases this results in formation of vesicles. It may be mentioned that the effective head group area a can be altered by addition of salt to the micellar solution or by changing the solution temperature and this results in changes in micellar shape[17–20]. The addition of an electrolyte to the ionic micellar solution, for example, screens the Coulombic repulsion between head groups and this modifies the value of a. The value of a for non-ionic surfactants changes on heating because of dehydration of hydrophilic tails. SANS experiments have shown that micellar structures change on addition of salt or with a change in temperature[6–10].

The statistical description of the micellar solution employs a single component fluid model with micelles as the constituents[21]. The presence of water, the electrolyte and the counterions (in ionic micelles) is taken into account via an effective inter-micellar potential energy $U(r)$. There are, in general, three contributions to $U(r)$: (i) the hard sphere potential $U_{hs}(r)$, (ii) the van der Waals attractive potential $U_{vw}(r)$ and (iii) the water-mediated interaction $U_{wm}(r)$. In case of ionic micelles, there is an additional contribution $U_c(r)$ arising from Coulombic repulsion between the micelles as modified by the presence of counterions, etc. SANS has been successfully used to obtain information about interaction potential $U(r)$ for micellar solutions when inter-micellar distance is ~ 100 Å (refs 10 and 22, also see ref. 28).

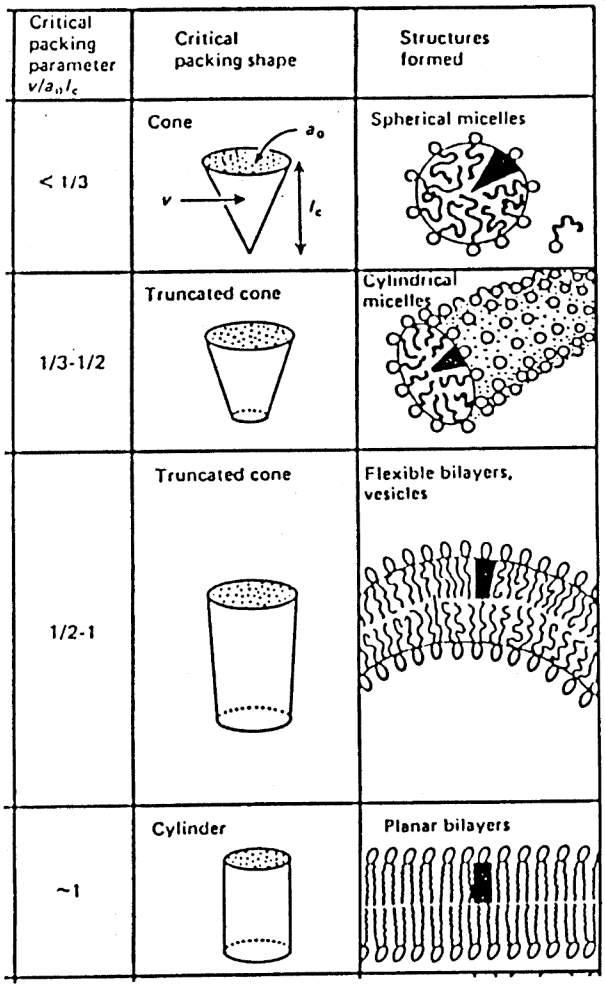

Figure 3. The packing parameter of a surfactant molecule and the various structures they form in aqueous solutions.

4. Small angle neutron scattering

The technique of SANS is used for studying the structure of a material on length scale of 10–1000 Å (refs 23–26). In particular, it is used to study the shapes and sizes of the particles dispersed in a homogeneous medium. The particle could be a macromolecule (biological molecule, polymer, micelle, etc.) in a solvent, a precipitate of material A in a matrix of another material B, a microvoid in certain metal or a magnetic inhomogeneity in a nonmagnetic matrix. The spatial distribution of particles in a medium can also be studied using SANS and thus, this technique provides information about inter-particle interactions also.

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 (Figure 4). The wave vector transfer Q ($= 4\pi\sin\theta/\lambda$, where λ is the incident neutron wavelength and 2θ is the scattering

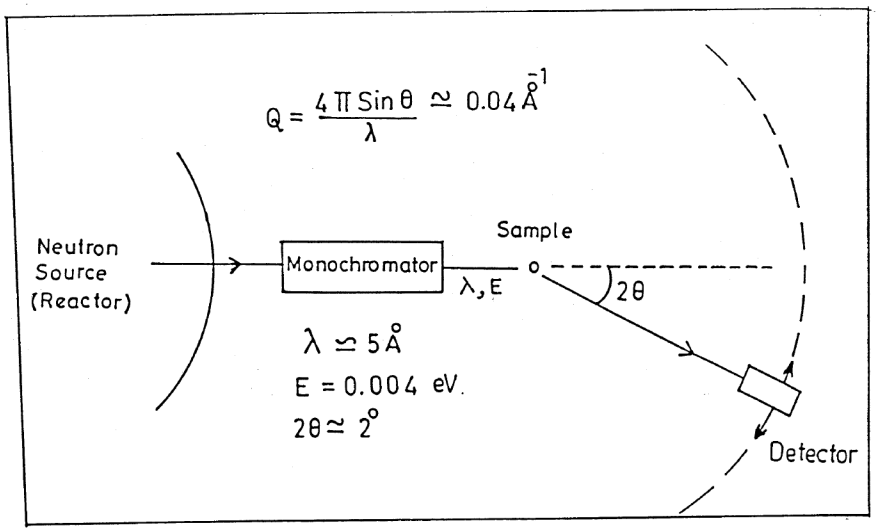

Figure 4. Schematic details of SANS experiment.

angle) in these experiments is small, typically in the range of 10^{-3} to 1.0 $Å^{-1}$, the wavelength of neutrons used for these experiments usually being 4–10 Å. Since the smallest Q values occur at small scattering angles (~ 1°), the technique is called as small angle neutron scattering.

SANS experiment measures the coherent differential cross-section ($d\Sigma/d\Omega$) as a function of wave vector transfer Q. For a system of monodisperse particles, it is given by ref. 26,

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

where n is the number density of the particles, ρ_p and ρ_s are, respectively, the scattering length densities of the particles and the solvent and V is the volume of the particle. $P(Q)$ is the intra-particle structure factor and is decided by the shape and size of the particle. Expressions for $P(Q)$ for some standard geometries are available. $S(Q)$ is the inter-particle structure factor, which depends on the spatial arrangement of particles and is thereby sensitive to inter-particle interactions.

In case of dilute solutions, inter-particle interference effects are negligible and $S(Q) = 1$. Thus measured SANS distribution from a dilute micellar solution depends on particle form factor $P(Q)$ and is ideally suited for studying micellar structure. This is especially so as it is known that in a suitable Q range, $P(Q)$ varies as $1/Q^2$ for disc-like particles and as $1/Q$ for rod-like particles. That is, the information on the shape of micelle is extracted from the Q dependence of $P(Q)$. The information about inter-micellar interaction potential $U(r)$ is obtained from the experimentally measured $S(Q)$. This involves carrying out SANS experiments on the concentrated micellar solutions, where inter-micellar distances are comparable to the particle diameter.

Neutron is a neutral particle and its scattering from a material arises because of a nuclear interaction (characterized by scattering length b) between the neutron and the atomic nuclei present in the sample. The scattering length densities ρ_p and ρ_s in eq. (1) are the sums of the scattering lengths of all the nuclei present in the unit volume of the particle and the solvent, respectively. It is seen that 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. $(\rho_p - \rho_s)^2$ is referred to as contract 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 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. The contrast between the particle and the solvent can be easily changed by deuterating either the particle or the solvent.

Figure 5 shows a SANS diffractometer installed at the guide laboratory of Dhruva reactor at Trombay[27]. Neutron beam from the guide is monochromatized by the BeO filter. The average wavelength of the monochromated beam is 5.2 Å. This beam passes through two slits S_1 (2 cm × 3 cm) and S_2 (1 cm × 1.5 cm) before it is incident on the sample. Distance between S_1 and S_2 is 2 m and this gives an angular divergence of ± 0.5°. The angular distribution of neutrons scattered by the sample is recorded using a one-dimensional position sensitive detector. The sample to detector distance is 1.85 m. The

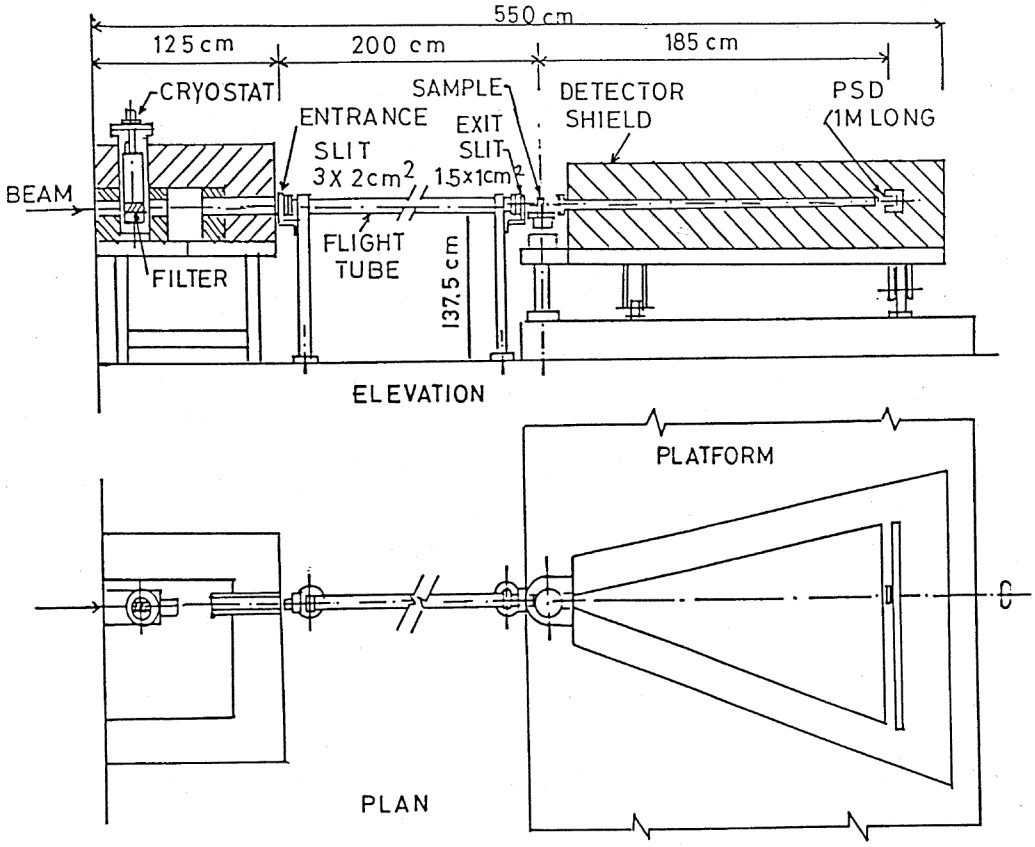

Figure 5. The schematic of SANS diffractometer at Dhruva reactor.

Q range of the diffractometer is 0.018–0.30 Å^{-1} and it is suitable for the study of the particle sizes in the range 10–150 Å (i.e. π/Q).

5. Typical results

5.1. *Role of molecular architecture on micellar structure*

The structures of micelles (sizes and shapes) in a variety of micellar systems have been studied using SANS[11,12]. It is known that the sizes and shapes of micelles in micellar solutions depend on the architecture of the surfactant molecule, the surfactant concentration and the solution temperature[2–4]. In the following, we show results of SANS experiments on micellar solutions of CTAB surfactant and 16-m-16 Gemini surfactants to bring out the role of molecular architecture on the micellar shape. The architecture of CTAB and 16-m-16 molecules are shown schematically in Figure 2. While CTAB is a single tail/single head group molecule, the gemini surfactant 16-m-16 consists of two tails and two head groups connected by a spacer. The spacer of 16-m-16 molecule consists of a hydrocarbon chain with m carbon atoms and the two tails of this molecule have the same length (16 carbon atoms) as that of the CTAB molecule. SANS experiments have shown that CTAB micelles in 0.1 M solution are nearly spherical[28]. Similar experiments on gemini surfactants show that micelles are disc-like for $m = 3$, rod-like for $m = 4$ and nearly spherical for $m = 10$ (ref. 29). The fact that micellar shapes are different for $m = 3$ and 4 is nicely brought out in Figures 6 and 7, where the variation of SANS cross-section with Q are shown on a log-log scale. It is seen that $d\Sigma/d\Omega$ varies as $1/Q^2$ for $m = 3$ and as $1/Q$ for $m = 4$. Further, it was seen that micelles are ellipsoidal for $m \geq 5$ and become nearly spherical for $m = 10$.

The above results are consistent with the packing considerations as discussed in §3. The average distance between CTAB head groups on the micellar surface is about 8 Å. This distance is different for different spacer lengths in a Gemini surfactant. A change in value of m results in a change in effective head group area and the packing parameter p. This is the reason for the change in the micellar shapes with the change in spacer length[29].

5.2. *Role of additives on the micellar structure*

Spherical micelles in ionic micellar solutions transform to ellipsoidal and cylindrical micelles on addition of

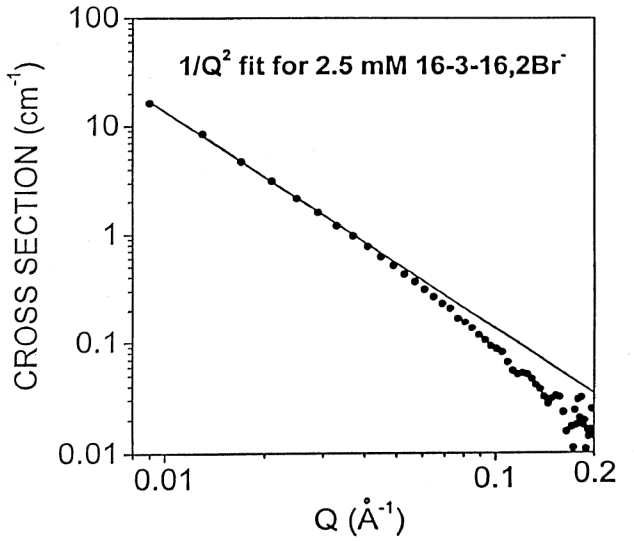

Figure 6. A log–log plot of SANS data for 16-3-16 gemini micellar system. The cross section varies as $1/Q^2$ for $0.009 < Q < 0.07$ Å^{-1}.

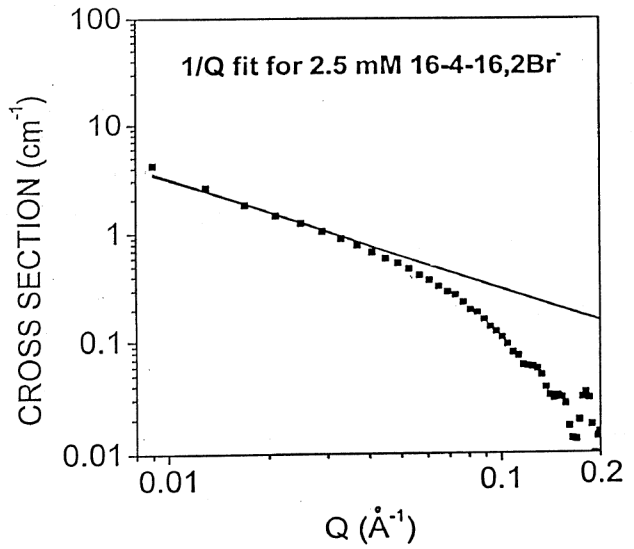

Figure 7. A log–log plot of SANS data for 16-4-16 gemini micellar system. The cross section varies as $1/Q$ for $0.009 < Q < 0.04$ Å^{-1}.

additives such as salts, alcohols and amines – and this results in an increase in viscosity of the solution[30,31]. It is seen that while the minor axis (~ length of the surfactant molecule) of the micelle is independent of the additive concentration, the length of the major axis increases with the additive concentration. The growth rate of the major axis is, however, different for different additives. The reasons for different growth rates for different additives are not fully understood though several different possibilities have been considered in the literature[32]. Aswal and Goyal[33] have carried out systematic studies on several different micellar systems and have shown that the ionic sizes of the additives play an important role in deciding the growth rate of the micelle. Figure 8 shows the results of their SANS studies on 0.3 M sodium dodecyl sulphate (SDS) solutions in presence of different alkali halides of the type ABr (A = Na, K, Cs) (ref. 33). The salt concentration was kept fixed (= 0.1 M) in these studies. It is seen that peak in the SANS distribution shifts to lower Q values on addition of NaBr, KBr and CsBr and the shift is different for different salts. It may be recalled that the peak in SANS distribution arises from a corresponding peak in the inter-particle structure factor $S(Q)$ the position of which at Q_m (= $2\pi/d$) depends on the inter-particle distance d. The growth of a micelle at a fixed surfactant concentration results in a decrease in number of micelles or an increase in d. That is, a larger shift in the peak position in a SANS distribution implies a larger growth in micelle[18]. The values of the major axis of SDS micelles in SDS/CsBr, SDS/KBr and SDS/NaBr as obtained from the above SANS data are 55.8, 49.7 and 42.4 Å, respectively. This indicates that there is a definite correlation between the ionic sizes of the counterions (Na^+, K^+ and Cs^+) and the micellar growth.

It may be mentioned that the counterions (e.g. Na^+, K^+, etc.) decrease the effective head group area of the surfactant molecule (increase in the packing parameter p) by neutralizing the charge on the micellar surface and this results in transformation of spherical micelles to cylindrical ones. The effectiveness of the counterions in charge neutralization depends on the relative affinity of these ions to the micelle or the water. It seems that the affinity of alkali ions to water decreases as we go from Na to Cs. The sizes of the hydrated counter ions are 3.6, 3.3 and 3.3 Å for Na^+, K^+, Cs^+, respectively. This explains why a smaller hydrated counterion results in a larger micellar growth. It may be noted that though the sizes of the hydrated K^+ and Cs^+ ions are similar,

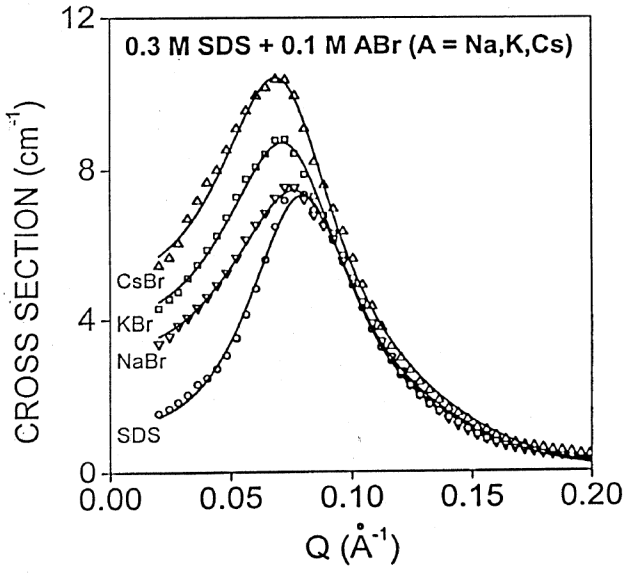

Figure 8. SANS distributions from 0.3 M SDS and in presence of 0.1 M NaBr, 0.1 M KBr and 0.1 M CsBr.

the water of hydration is more in K^+ as the bare ionic size of K^+ is smaller than that of Cs^+.

5.3. *Effect of additives on inter-micellar interactions*

The inter-micellar interaction potential $U(r)$ has several contributions as discussed in §3. In the case of ionic micelles, $U(r)$ is largely decided by the Coulombic repulsion between the micelles. When one adds an electrolyte to these solutions, the Coulombic forces between micelles are screened out, and at high salt concentrations repulsive Coulombic forces become comparable to the attractive van der Waals interactions. Goyal *et al.*[28] have successfully used SANS to study the relative roles of Coulombic and van der Waal's interactions between CTAB micelles in the CTAB/KCl solutions. CTAB/KCl was chosen as it is known that sizes of CTAB micelles are independent of KCl concentration up to high salt concentrations.

Figure 9 shows the measured SANS distributions for 0.1 M CTAB solution with the varying concentration of KCl. The well-defined peak at $Q \sim 0.05$ Å^{-1} in the SANS distribution from pure CTAB solution indicates the presence of strong electrostatic interaction between CTAB micelles. When the KCl concentration is increased, this above peak broadens without any significant shift in the peak position. The broadening of the peak is a result of the reduction in the Coulomb interaction between the micelles. It was seen that at high salt concentrations, where the Coulomb interaction has been screened out, SANS distributions were very similar to those obtained from non-ionic micellar solutions. These studies showed that the van der Waal's term of the interaction potential $U(r)$ is characterized by the Hamaker constant $H = 14.7\ k_BT$ and is independent of KCl concentration. The Coulomb term varies with KCl concentration and is characterized with the variation in the fractional charge on the CTAB micelle.

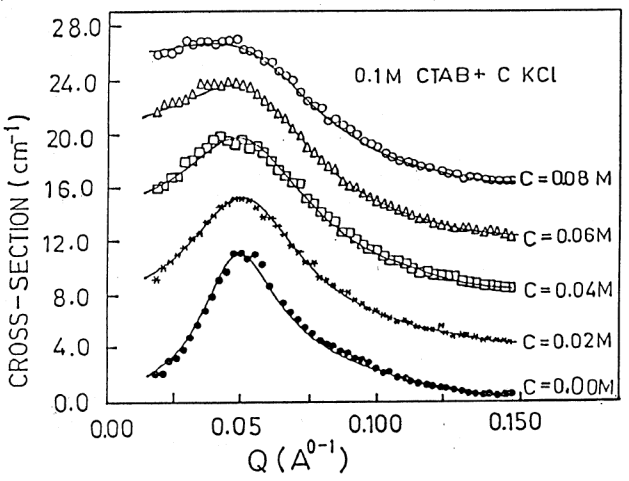

Figure 9. SANS distributions from 0.1 M CTAB with varying concentrations of KCl.

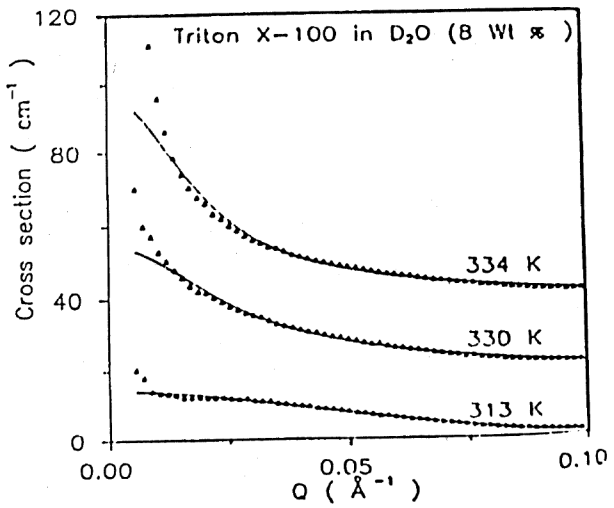

Figure 10. SANS distributions from 8 wt% Triton X-100 solution at different temperatures.

5.4. *Effect of temperature on inter-micellar interactions*

The interaction potential $U(r)$ between two non-ionic micelles is dominated by attractive van der Waal's forces. These attractive interactions are, however, screened by the water of hydration which is attached to the hydrophilic part of the micelle. It may be recalled that unlike ionic surfactants where head group is small in size, the non-ionic surfactants have a bulky hydrophilic chain. The non-ionic micelle thus has a significant amount of water attached to its outer surface. When one increases the solution temperature, the amount of water of hydration decreases and this results in a decrease in screening of van der Waal's interactions. That is, the interaction potential $U(r)$ between non-ionic micelles becomes more attractive with an increase in temperature. SANS has been used to study the interaction potentials in non-ionic micellar solutions and in the following we give results of such studies on Triton X-100 (ref. 10).

Micellar solutions of non-ionic surfactant Triton X-100 become cloudy on heating at a well defined temperature T_{cp}, called cloud point[9]. Above cloud point, the solution separates in two phases – one rich and the other poor in micellar concentration. The effect of temperature on SANS distribution from Triton X-100 solutions is shown in Figure 10. It is seen that scattered neutron intensity at low Q values diverges as one approaches the cloud point. The changes in the measured distributions

are connected with the changes in the interaction potential $U(r)$ with the temperature. The parameters of the potential have been obtained by analysing the SANS data in terms of Sticky Hard Sphere model, which assumes a narrow square well potential for the attractive part. The depth U_o/k_BT of the square well potential at 295, 328 and 334 K has been found to be 0.9, 2.6 and 2.9, respectively for 8 wt% Triton X-100 micellar solution[10].

6. Summary

Small angle neutron scattering is a neutron diffraction experiment involving small wave vector transfers and is used for studying the structures of materials on a length scale of 10–1000 Å. In particular, this technique is used to study the sizes and shapes of particles dispersed in a homogeneous medium. SANS is ideally suited for studying the structures of hydrogenous materials where the contrast between the particle and the solvent can be varied by deuterating either the particle or the solvent.

This paper deals with use of SANS in study of structure and inter-micellar interactions in micellar solutions. The fact that micelles are made up of organic material and have a typical size of ~ 50 Å, SANS has been fruitfully used for studying micellar solutions. Results of SANS studies both on the micellar structure and the inter-micellar interactions are given in the paper.

1. Tanford, C., *The Hydrophobic Effect: Formation of Micelles and Biological Membranes*, Wiley, New York, 1973.
2. Degiorgio, V. and Corti, M., (eds), *Physics of Amphiphiles: Micelles, Vesicles and Microemulsion*, North Holland, Amsterdam, 1985.
3. Zana, R., *Surfactant Solutions: New Methods of Investigation*, Dekker, New York, 1987.
4. Chevalier, Y. and Zemb, T., *Rep. Prog. Phys.*, 1990, **53**, 279.
5. Moulik, S. P., *Curr. Sci.*, 1996, **71**, 368.
6. Rao, U. R. K., Manohar, C., Valaulikar, B. S. and Iyer, R. M., *J. Phys. Chem.*, 1987, **91**, 3286.
7. Menon, S. V. G., Goyal, P. S., Dasannacharya, B. A., Paranjpe, S. K., Mehta, R. V. and Upadhyay, R. V., *Phys. B*, 1995, **213**, 604.
8. Aswal, V. K., Goyal, P. S. and Thiyagarajan, P., *J. Phys. Chem.*, 1998, **102**, 2469.
9. Degiorgio, V., in *Physics of Amphiphiles: Micelles, Vesicles and Microemulsions* (eds Degiorgio, V. and Corti, M.), North-Holland, Amsterdam, 1985.
10. Goyal, P. S., Menon, S. V. G., Dasannacharya, B. A. and Thiyagarajan, P., *Phys. Rev. E*, 1995, **51**, 2308.
11. Chen, S. H., *Annu. Rev. Phys. Chem.*, 1986, **37**, 351.
12. Goyal, P. S., *Phase Transitions*, 1994, **50**, 143.
13. Zana, R. and Talmon, Y., *Nature*, 1993, **362**, 228.
14. De, S., Aswal, V. K., Goyal, P. S. and Bhattacharya, S., *J. Phys. Chem.*, 1996, **100**, 11664.
15. Bhatia, A. and Qutubuddin, S., *Colloids and Surfaces*, 1993, **69**, 277.
16. Israelachvili, J. N.,. Mitchell, D. J. and Ninham, B. W., *J. Chem. Soc., Faraday Trans. 1*, 1996, **72**, 1525.
17. Berr, S. S., *J. Phys. Chem.*, 1987, **91**, 4760.
18. Goyal, P. S., Dasannacharya, B. A., Kelkar, V. K., Manohar, C., Rao, K. S. and Valaulikar, B. S., *Phys. B*, 1991, **174**, 196.
19. Sheu, E. U., Wu, C. F. and Chen, S. H., *J. Phys. Chem.*, 1986, **90**, 4179.
20. Kumar, S., Aswal, V. K., Goyal, P. S. and Kabir-ud-Din, *J. Chem. Soc., Faraday Trans.*, 1998, **94**, 761.
21. Reatto, L. and Tau, M., *Chem. Phys. Lett.*, 1984, **108**, 292.
22. Chen, S. H., Sheu, E. U., Kalus, J. and Hoffmann, H., *J. Appl. Cryst.*, 1988, **21**, 751.
23. Feigin, L. A. and Svergun, D. I., *Structure Analysis by Small-Angle Neutron X-ray and Neutron Scattering*, Plenum Press, New York, 1987.
24. Linder, P. and Zemb, T. (eds), *Neutron, X-Ray and Light Scattering*, North Holland, Amsterdam, 1991.
25. Hayter, J. B. and Penfold, J., *Colloid Polym. Sci.*, 1983, **261**, 1022.
26. Chen, S. H. and Lin, T. L., in *Methods of Experimental Physics* (eds Price, D. L. and Skold, K.), Academic Press, New York, vol. 23B, 1987, p. 489.
27. Aswal, V. K. and Goyal, P. S., *Curr. Sci.*, 2000, **79**, 947.
28. Goyal, P. S., Menon, S. V. G., Dasannacharya, B. A. and Rajagopalan, V., *Chem. Phys. Lett.*, 1993, **211**, 559.
29. Aswal, V. K., De, S., Goyal, P. S., Bhattacharya, S. and Heenan, R. K., *Phys. Rev. E*, 1998, **57**, 776.
30. Cates, M. E. and Candau, S. J., *J. Phys. Condens. Matter*, 1990, **2**, 6869.
31. Rehage, H. and Hoffmann, H., *Mol. Phys.*, 1991, **74**, 933.
32. Aswal, V. K., Goyal, P. S., Menon, S. V. G. and Dasannacharya, B. A., *Phys. B*, 1995, **213**, 607.
33. Aswal, V. K. and Goyal, P. S., *Phys. Rev. E*, 2000, **61**, 2947.

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