

# SANS study of micellar aggregation of multi-headed surfactants

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**Abstract.** We report the aggregation properties of recently synthesised novel single-chain surfactants bearing one, two and three head groups. Small-angle neutron-scattering studies in aqueous solutions of these surfactants indicate that the extent of aggregate growth of these micelles dramatically decreases with the increase in the number of head groups. It is also seen that, unlike single-headed surfactants where the micelles grow on addition of salts (KBr and sodium salicylate), the sizes of the micelles of multi-head-group surfactants are independent of these additives. These studies show that the micellar properties of surfactants could be remarkably influenced by manipulation of the charge densities at the head groups.

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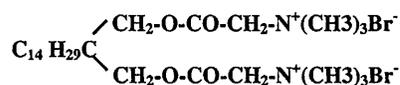
Surfactant molecules consist of two distinct segments that are opposite in character. One part is polar in character and is known as the head group, while the other part comprises one or more long hydrocarbon chains. These molecules tend to self-organise in water, often producing nearly spherical aggregates called micelles in the dilute range and lyotropic mesophases at higher concentrations. Polar head groups of these aggregates lie near the bulk aqueous medium, whereas the hydrocarbon chains extend inwardly to stay away from unfavourable water contact. Electrostatic interactions at the head-group level determine their relative positions and separations in an aggregate [1]. It is of interest to examine the role of charge densities at head groups on the micellar properties.

Surfactant molecules such as cetyltrimethylammonium bromide (CTAB) ionise in aqueous solution and the corresponding micelles are aggregates of CTA<sup>+</sup> ions. The micelle is charged and is called an ionic micelle. However, the ionisation is far from complete on a micellar surface. The Br<sup>-</sup> ions, known as counterions, tend to stay near the CTA<sup>+</sup> micellar surface. The shape, size and fractional charge of the micelle and the intermicellar interaction depend on the

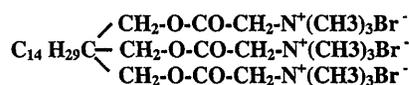
distribution and the nature of these counterions. This paper reports the aggregation of surfactant molecules when the charges or counterions on a surfactant are continuously increased. Small-angle neutron-scattering (SANS) experiments have been carried out on a recently synthesised novel class of surfactants with multi-head groups [2]. These surfactants consist of a single chain bearing one ( $h = 1$ ), two ( $h = 2$ ) and three ( $h = 3$ ) head groups (Fig. 1).



(a) Single headed surfactant



(b) Double headed surfactant



(c) Triple headed surfactant

**Fig. 1.** Chemical structures of multi-headed surfactants

## 1 Experiment

All the surfactants were synthesised and characterised as discussed in the earlier paper [2]. The micellar solutions were prepared by dissolving a known amount of surfactants in D<sub>2</sub>O, since it provides better contrast in neutron experiments than H<sub>2</sub>O. Small-angle neutron-scattering measurements were carried out using a SANS diffractometer at the Dhruva reactor, Trombay, India [3]. The mean wavelength of the neutrons used was 5.2 Å and the data were collected in the wave-vector transfer  $Q$  range of 0.02 to 0.2 Å<sup>-1</sup>. The samples were held in a quartz sample holder of thickness 2 mm and the temperature for all the samples was kept at 40 °C. The measured SANS data have been corrected and normalised to an absolute scale using standard procedures.

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## 2 SANS analysis

In a SANS experiment one measures the differential scattering cross section ( $d\Sigma/d\Omega$ ) per unit volume. For a system of monodisperse interacting micelles,  $d\Sigma/d\Omega$  can be expressed as

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

where  $n$  denotes the number density of the micelles,  $\rho_m$  and  $\rho_s$  are, respectively, the scattering length densities of the micelle and the solvent and  $V$  is the volume of the micelle.  $P(Q)$  is the intraparticle structure factor and  $S(Q)$  is the interparticle structure factor.  $B$  is a constant term that represents the incoherent scattering background, which is mainly due to hydrogen in the sample. We have used  $P(Q)$  for ellipsoidal micelles and  $S(Q)$  has been calculated using the method of Hayter and Penfold, which assumes the screened Coulomb interaction between the charged micelles [4]. The dimensions of the micelle, aggregation number and the fractional charge have been determined from the analysis [5]. The semimajor axis ( $a$ ), the semiminor axis ( $b = c$ ) and the fractional charge ( $\alpha = z/N$ , where  $z$  is the micellar charge) are the parameters in analysing the SANS data. The aggregation number ( $N$ ) is calculated by the relation  $N = 4\pi ab^2/3v$ , where  $v$  is the volume of the surfactant monomer.

## 3 Results and discussion

SANS distributions from micellar solutions of multi-head-group surfactants at fixed concentration ( $C = 50$  mM) and temperature ( $T = 40$  °C) are shown in Fig. 2. All the distributions show well-defined peaks characteristic of suspensions of charged particles. The peaks arise because of corresponding peaks in the interparticle structure factor  $S(Q)$ . The micellar parameters in these systems are given in Table 1. It is seen that micelles are formed from all the surfactants irrespective of the number of head groups. The micelles are prolate ellipsoidal ( $a \neq b = c$ ) in these systems. The aggregation number ( $N$ ) decreases with an increase in the  $h$  value. Fractional charge is a measure of the dissociation of the counterion of the surfactant molecules present in the micelle. It is seen that the fractional charge ( $\alpha$ ) on the micelle increases with the number of head groups on the surfactants. The dramatic drop in the  $N$  value with an increase in the number of head groups (244 for  $h = 1$  to 20 for  $h = 3$ ) can be understood, since with every rise in the number of cationic head groups the charge repulsion at the head-group level among the proximal surfactant become more and more pronounced. To mitigate these unfavourable electrostatic consequences, the semiminor axis of the micelle decreases with an increase in the number of head groups, and the hydrophobic chains in the micelles of multi-headed surfactants take up severely bent conformations, leading to the formation of an increasingly disorganised collection of surfactant molecules in the resulting micellar aggregate. However, in micelles of surfactants bearing a single charge on the head group, the hydrocarbon chains could be fully extended.

It is known that additives such as KBr and sodium salicylate (NaSal) induce pronounced micellar growth of CTAB

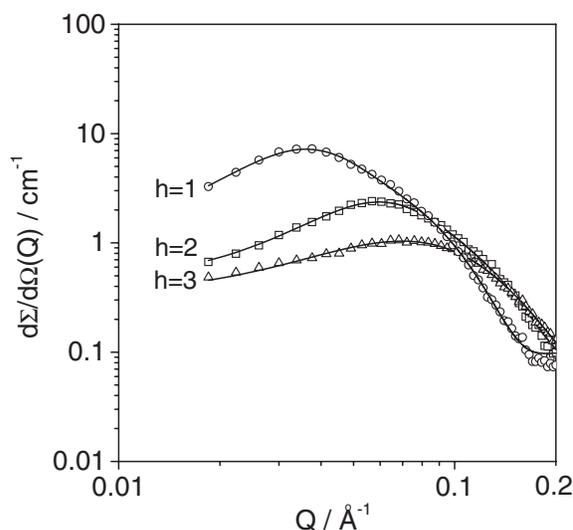


Fig. 2. SANS distributions from 50-mM micellar solutions of multi-head-group surfactants

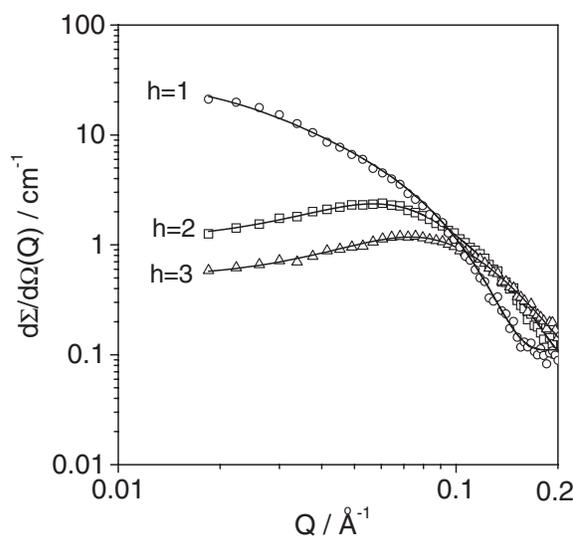


Fig. 3. SANS distributions from 50-mM micellar solutions of multi-head-group surfactants with the addition of 10-mM NaSal

[6–8]. This leads to a marked increase in viscosity of the micellar solution due to a spherical to rod-like morphological transition. It is found that while  $h = 1$  also shows a similar behaviour in the presence of KBr and NaSal, such changes in viscosity cannot be brought about on the micelles of either  $h = 2$  or  $h = 3$  with the above additives [2]. Figure 3 shows the SANS distributions from 50-mM micellar solutions of surfactants of  $h = 1$ ,  $h = 2$  and  $h = 3$  with the addition of 10-mM NaSal. For  $h = 1$  the scattering cross section becomes quite large and the correlation peak in the SANS data disappears with the addition of NaSal. This is due to a large growth of micelles in this surfactant/salt system. From SANS data for  $h = 2$  and  $h = 3$ , it is observed that, unlike the single-headed surfactant, the peak positions of the distributions do not change with the addition of the salt. This is an indication of the almost the same size of the micelles with and without the addition of the salts in these systems. The micellar parameters in these systems are given in Table 1. The param-

**Table 1.** Micellar parameters of 50-mM multi-headed surfactants and in presence of 10-mM NaSal

Surfactant	Aggregation number $N$	Fractional charge $\alpha$	Seminor axis $b = c(\text{\AA})$	Semimajor axis $a(\text{\AA})$
50 mM $h = 1$	$244 \pm 9$	$0.08 \pm 0.01$	$24.5 \pm 0.5$	$66.9 \pm 1.4$
50 mM $h = 2$	$48 \pm 2$	$0.23 \pm 0.02$	$17.3 \pm 0.5$	$36.2 \pm 1.1$
50 mM $h = 3$	$20 \pm 1$	$0.27 \pm 0.02$	$14.5 \pm 0.5$	$27.3 \pm 1.0$
50 mM $h = 2 + 10$ mM NaSal	$51 \pm 2$	$0.25 \pm 0.02$	$17.3 \pm 0.5$	$37.8 \pm 1.2$
50 mM $h = 3 + 10$ mM NaSal	$22 \pm 1$	$0.36 \pm 0.03$	$14.5 \pm 0.5$	$29.2 \pm 1.1$

eters for  $h = 1$  with salt are not included in Table 1, as the length of the micelles in this system is expected to be too large to be resolved by the limited  $Q_{\min}$  of the data. It has also been observed that the micellar structures for these surfactants are the same even when the concentration of NaSal is increased to 100 mM. These results about the stability of their structure against the very strong charge-neutralising salt for new cationic multi-headed surfactants are striking. The conventional single-headed surfactants for the above salt concentrations of NaSal are known to form large micellar structures where they are entangled one over the other and exhibit viscoelastic behaviour [6, 8]. The differences between the single- and multi-head-group surfactants arise because of differences in the counterion distribution around the micelles. Small-angle X-ray-scattering (SAXS) experiments to examine the counterion distribution in the above systems are planned.

In summary, we have seen some unusual effects associated with micellar aggregation properties of multi-head-group surfactants. It has been found that micelles become dramatically smaller in size with the increase in the number of head groups. To accommodate the increase in the number of head groups at the surface of a micelle results in a smaller aggre-

gation number, and in turn gives rise to the folding of the hydrocarbon chains and a decrease in micellar size. While the micellar solution of conventional single-head-group surfactants shows a large growth of micelles in the presence of salts such as NaSal, it has been found that the structure of multi-headed surfactants is largely unchanged in the presence of these salts. These studies thus show that the micellar aggregation properties could be altered remarkably by the number of head groups on the surfactant.

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