

Counterion distribution around the micelles of multi-headed surfactants

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Conventional surfactants usually consist of a hydrophilic head group and a hydrophobic tail. These molecules above critical micelle concentration in aqueous solution self-aggregate and the aggregates are called as micelles [1]. The hydrophobic tails of the surfactant molecules constitute the central core of the micelle and the hydrophilic head groups reside on the outer surface of the micelle. In the case of ionic surfactants, such as cetyltrimethylammonium bromide (CTABr), the surfactant molecules ionize in aqueous solution and the micelle largely consists of CTA⁺ ions. The Br⁻ ions, referred to as counterions, tend to stay near the surface of the micelle. The shape and size of the micelles and the intermicellar interactions depend on the distribution of these counterions.

We have recently synthesized a novel class of surfactants consisting of multiple charged head groups [2,3]. Unlike CTABr surfactant, the multi-headed surfactants are a single-chain surfactants bearing higher number of charged head groups. SANS experiments show the dramatic decrease in the micelle size with an increase in the number of head groups. This is because of the fact that an effective larger head group area requires greater micellar surface and thus a smaller number of surfactant molecules are available to pack into a micellar aggregate. More importantly, it is seen that unlike the single-headed surfactants where the micelles grow on the addition of salts [e.g. NaBr and sodium salicylate (NaSal)], the sizes of micelles of multi-headed surfactants are independent of these additives. The single-headed surfactants for the above salts are known to form worm-like micelles and the system exhibits viscoelastic behavior [4-6]. The present SAXS experiments show that the differences in the above properties of the micellar solutions of single- and multi-head group surfactants arise because of differences in the counterion distribution around the micelles.

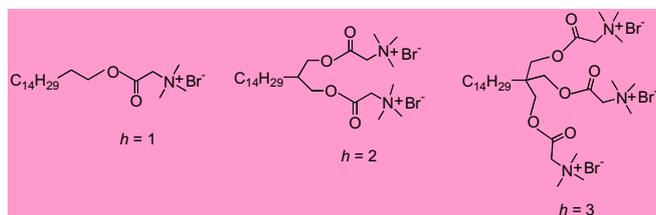


Fig. 1. Chemical structure of multi-headed surfactants.

The scattering techniques SANS and SAXS in combination provide a direct method to study the counterion distribution in ionic micelles. While neutron scattering in micellar solutions is from the core of the micelle, x-rays are largely scattered by counterions especially when the counterion has a large atomic number (e.g. Br⁻). The neutron scattering intensity from the counterion distribution is negligible in

comparison to that from the core. Thus neutrons see the core of the micelle and x-rays give information relating to the counterion distribution around the micelle [7-10].

SAXS experiments were carried out from the multi-headed surfactant bearing one, two and three head groups. The chemical structure of these surfactants is shown in Fig. 1. The measurements were made for the surfactant concentration of 50 mM and at the different concentrations of the salts NaBr and NaSal in the range of 0 – 100 mM.

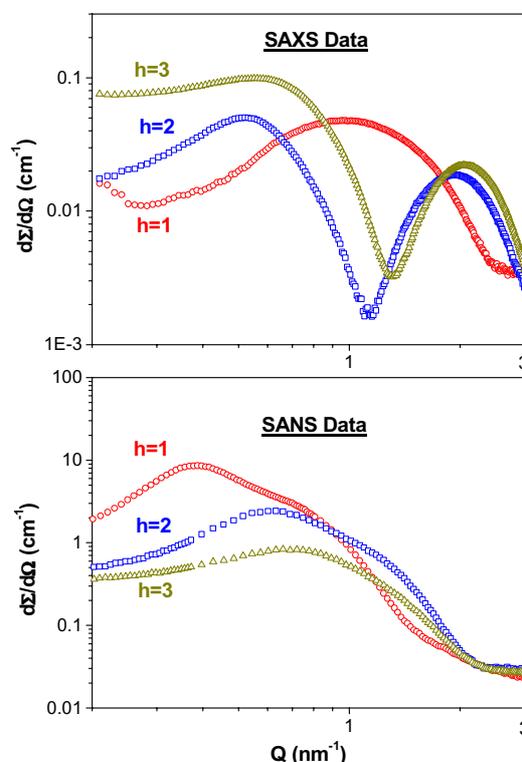


Fig. 2. SAXS and SANS data from 50 mM micellar solutions of multi-headed surfactants.

Fig. 2 shows the comparison of SAXS and SANS data on 50 mM micellar solutions of multi-headed surfactants. All the SAXS data show two peaks. The first peak towards the low Q values which is also present in the SANS data is the correlation peak due to the contribution of the interparticle structure factor $S(Q)$. The second peak in the SAXS data arises from the scattering of shell-like structure of the counterions around the micelles. The differences in the position and the width of the second peaks in SAXS data for different multi-headed surfactants suggest the differences in counterion distribution around these micelles. It is found that the counterions are distributed over much larger shell thickness when the numbers of head groups are increased.

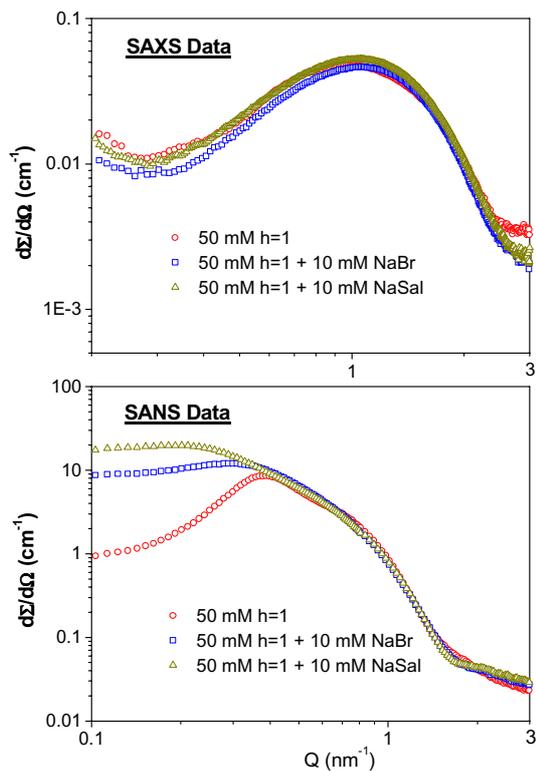


Fig. 3. SAXS and SANS data from 50 mM micellar solution of h=1 with 10 mM NaBr and NaSal.

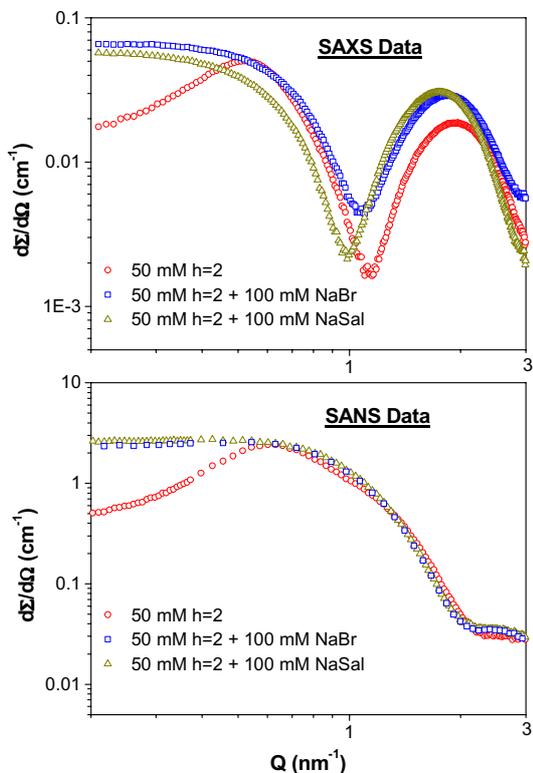


Fig. 4. SAXS and SANS data from 50 mM micellar solution of h=2 with 100 mM NaBr and NaSal.

Figs. 3-5 show the SAXS and SANS data on the salt effect in multi-headed surfactants. SANS data for h=1 suggest the strong growth of the micelles with the addition of small

amount of salts NaBr and NaSal. However, the SAXS data in the higher Q values, which corresponds to the scattering from counterions remain almost same. This is expected as the micelle size increases with the increase in the counterion condensation and the thickness over which the counterions are distributed remains same. The very different results are observed with the h=2 and h=3 multi-headed surfactants. While SANS data show that micelle size remains almost same, the SAXS data suggest the increase in the thickness of the counterion distribution around the micelles. We have also carried out ASAXS experiments on above systems from which one directly obtains the counterion distribution around the micelles.

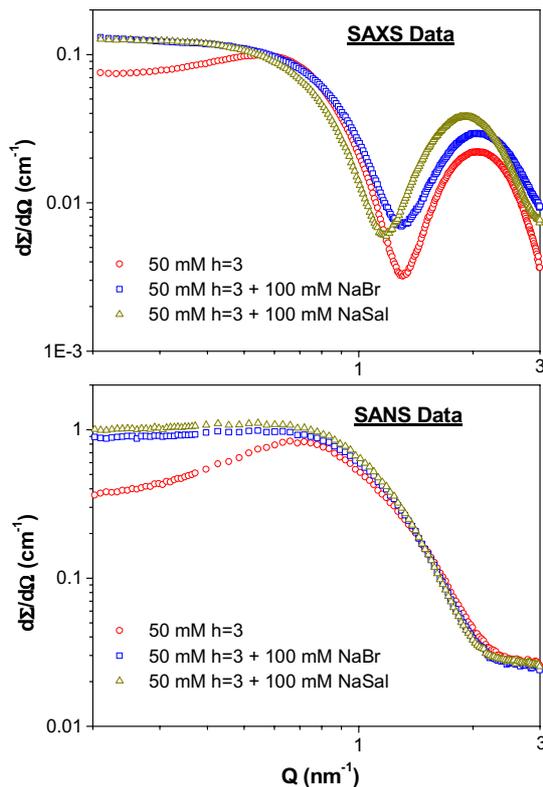


Fig. 5. SAXS and SANS data from 50 mM micellar solution of h=3 with 100 mM NaBr and NaSal.

References

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