Selective Counterion Condensation in Ionic Micelles

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SANS and SAXS measurements have been carried out on the micellar solutions of cationic surfactants CTABr and CTACl in presence KCl and KBr, respectively. The results show that, while the condensed Br- counterions are retained around the micelles in CTABr solution in presence of KCl, the condensed Cl- counterions in CTACl micellar solution are replaced by the Br- on the addition of KBr.

It is known that the effect of addition of salts KBr and KCl to the ionic micellar solutions of cationic surfactant (e.g. CTABr or CTACl) is quite different [1]. In terms of counterion condensation, this suggests the differences in condensation of Br- and Cl- ions that takes place on the charged micelles. We compare the structure in the equimolar surfactant to salt micellar solutions of CTABr/KCl and CTACl/KBr systems and explain the results in terms of selective counterion condensation. In particular, we show that CTACl/KBr micellar solution behaves like CTABr/KCl due to the selectivity of counterion condensation:

A combined study of SANS and SAXS has been used to characterize the counterion condensation. While neutron scattering in micellar solutions arises 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 counterions is negligible in comparison to that from the core. Thus neutrons 'see' the core of the micelle and x-rays, in combination with neutron studies, give the information related to the counterion condensation around the micelle [2]. Figure 1 shows the SANS data from equimolar surfactant to salt CTABr/KCl and CTACl/KBr micellar solutions. These systems have the same number of surfactant CTA^+ ions as well as Br^- and Cl^- counterions in common. For comparison, the data from 100 mM CTABr and CTACl micellar solutions without salt are also shown in Figure 1. It is observed that the counterion condensation is more effective in CTACl/KBr than in CTABr/KCl. We believe that this is due to selective condensation of the counterions around the micelles [3]. In CTABr/KCl, Br^- counterions from the dissociated CTABr molecules are condensed on the CTA^+ charged micelles. The condensation of Cl^- ions of the salt KCl takes place around the condensed Br^- ions. However, in CTACl/KBr, Cl^- counterions of the CTACl molecules are replaced by Br^- ions of the KBr in the micelle. This is expected since Cl^- ions are less effective than Br^- to neutralize the charge on the micelles. The condensation of Br^- ions around the condensed Cl^- counterions does not seem possible in CTACl/KBr as this, in contrary to the experimental results, would make the counterion condensation less effective in CTACl/KBr than CTABr/KCl to neutralize the charge on the micelles.

The above SANS results are confirmed by the SAXS experiments (Figure 2), where the scattering data depending on the condensed counterions is expected to be different. Figure 2 shows that, while the SAXS data of CTABr and CTACl are very different, the data for CTABr/KCl and CTACl/KBr are quite similar. The small differences in the SANS or SAXS data of CTABr/KCl and CTACl/KBr can be explained in terms of a small fraction of undissociated CTACl molecules in the micelles of CTACl/KBr solutions. This provides slightly higher condensation of Cl^- counterions on the micelles of CTACl/KBr than CTABr/KCl, otherwise these two systems have similar counterion condensation of Br^- and Cl^- ions around them.

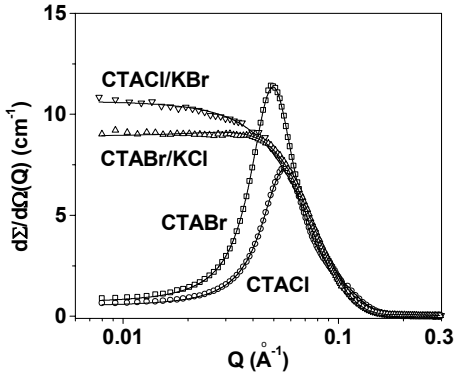

Figure 1: SANS data from 100 mM equimolar surfactant to salt micellar solutions of CTABr/KCl and CTACl/KBr. The data from 100 mm CTABr and CTACl micellar solutions without salt are shown also.

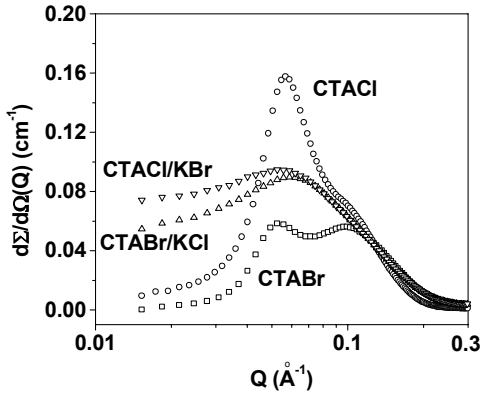

Figure 2: SAXS data from 100 mM equimolar surfactant to salt micellar solutions of CTABr/KCl and CTACl/KBr. The data from 100 mm CTABr and CTACl micellar solutions without salt are shown also.

[1] V.K. Aswal, P.S. Goyal, Phys. Rev. E 61, 2947 (2000).
[2] V.K. Aswal et al. Chem. Phys. Lett. 329, 336 (2000).
[3] V.K. Aswal, P.S. Goyal, Phys. Rev. E (submitted).