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Report:

The solid-liquid extraction method with which we are working on, consists in selectively precipitate metal ions from a bulk mixture using cationic surfactant below their Krafft point. This technique has been shown to be very efficient for separation of actinides and lanthanides using long chain ammoniums or pyridiniums (CP). *A particular point of this process is the recognition of cationic metal ions by cationic surfactants.* The original proposed mechanism was the formation of a complex ion involving anionic counter-ions of the metal salt, in order to ensure electric neutrality.

We aim at understand these attractive interactions between positively charged polar head groups of the surfactants and metal cations before and after precipitation. Main concerns are about the effect of metal polarisability on its adsorption at the micelle surface, the role of counter-ions and further the structure of precipitated solid (amorphous, crystalline or mesoporous).

As required within this proposal SC2975 an ASAXS study at different adsorption threshold was carried out.

For the CP-Cl system (Chloride form) with addition of the copper salt and for which we did not observe any change in the Krafft temperature the different SAXS spectra recorded around the Cu^{2+} K-edge are all superimposed after transmission and background corrections.

This means that the copper ions are dispersed homogeneously in the surrounding media of the micelles and the correlation in term of scattering length density distribution is equivalent and thus independent of the energy of the incident X-rays. The same experiment is now carried out at the zinc K-edge for the CP-Cl / Zn^{2+} system, still at high ionic strength (1 M HCl). Some selected scattering curves, just below the K-edge of zinc, i.e. 9.66 keV, are then presented in figure left. Contrary to the copper system, we can clearly see that the scattering curves differ as a function of the incident energies after normalisation. Furthermore, these

differences are more pronounced and visible at low scattering angles than at large Q. We can state that the scattering curves with the increase of intensity at low Q show the signatures of elongated micellar aggregates as for cylindrical micelles of CP-N presented before. In the previous paragraph, this effect was explained by a change of the interaction area per polar head, due to an adsorption of the nitrate counterions within the head-group corona of the micelles.
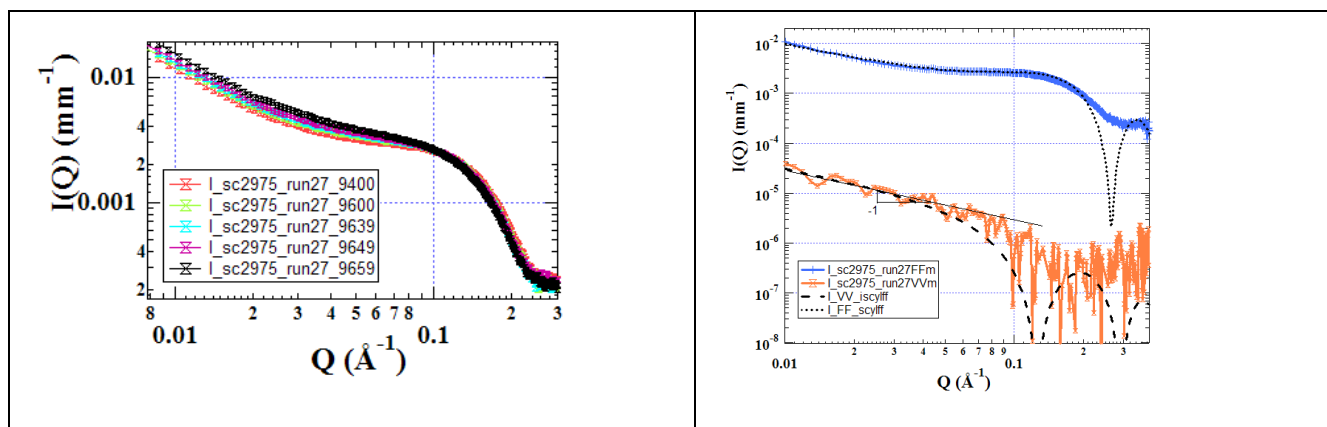
Left- Selected SAXS curves recorded at different energies around the K-edge of zinc for CPC 50mM with 10mM of ZnCl$_2$ and 1M of HCl (T > 40°C). right) Contributions to the ASAXS curves: the classical (non-resonant, blue) SAXS curve far away from the absorption edge fitted by a core–shell cylinder model (dotted black line) and the Fourier Transform of the Zn^{2+} ion-ion spatial correlation (resonant curve, orange) together with its fit.

Moreover, two qualitative remarks can be pointed out relative to the ion distribution: First, when looking at the Porod region ($Q > 0.15$ Å^{-1}), the differences between the scattering curves are rather weak. When considering an adsorption of the Zn^{2+} cations at the micellar interface the local concentration of Zn^{2+} is weak (Zn^{2+} ions are less localised) and the contrast is weak. This might be understood as a homogeneous dispersion of the metal ions within the polar head group region. Second, the contrast effect is more pronounced at lower Q, that is to say the scattering window through which the scattering intensities are more related to the 1D shape of the aggregation. That means that even if the inhomogeneous distribution of the Zn^{2+} ions in the solvent is weak it exists and it is visible. A quantitative analysis of the ASAXS curves in order to separate the various contributions, i.e. the Fourier Transform of the zinc ion-ion spatial correlation from the other elements is shown in figure 9b with split intensity for the resonant (orange) and the non-resonant (blue) curve. The latter represents the classical SAXS curve similar to those obtained far away from the absorption edge. A core–shell model (dotted curve) is used to adjust the scattering data considering here a monodisperse dispersion of very long cylindrical aggregates with a core radius of 1.7 nm (with SLD 280 e/nm^3) and a headgroup corona thickness of 0.3 nm (with SLD 420 e/nm^3) in an aqueous solution (with SLD 330 e/ nm^3). These values in size are comparable with those observed for CPN system in 1 M HNO$_3$. The difference concerns the SLD of the micellar shell which is higher than those estimated for the pyridinium polar head only.

This difference can be explained by considering one [Zn(Cl)$_4$]$^{2-}$ complex for four polar pyridinium heads within the corona. This is close to the molar ratio between the metal ion and CP (1:5).

This work will be published in JPC quite soon!