INTERPRETATION OF COMPLEX SANS SPECTRA : CONTRIBUTION OF NUMERICAL SIMULATIONS

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It is well known that the intensity I(q) measured in a SANS experiment does not contain all the structural information of the sample. This is mainly due to the loss of the phase and the incomplete knowledge of I(q) in all q-space. Therefore, data analysis focuses often on prominent features of the intensity, like correlation peaks, power laws, or the Guinier regime. Sometimes, data fitting with analytical expressions can be done, which exist only for simple geometries (spheres, rods, etc.).

Here, we discuss two cases of data recently measured on small angle spectrometers (PAXE at LLB and D11 at ILL) for which specific models of more complex geometries have been developed and successfully applied. The <u>first</u> study investigates the phase behaviour of a mixture of charged-neutral hydrophilic diblock copolymers and surfactant of opposite charge in aqueous solution.
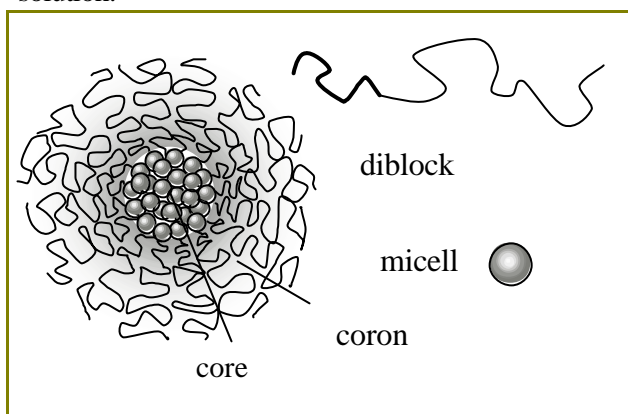

Figure 1. Complex aggregate formed by charged micelles and neutral-charged copolymers.

The data presented here has been obtained in the DTAB/PANa-b-PAM/D_2O system, but very similar features have been found in other systems, e.g. charge-inversed ones. The surfactant forms micelles which attract each other under the influence of the copolymer (bridging), and seem to build a micelle-containing aggregate of well-defined aggregation number [1,2]. This is schematically represented in Fig. 1.

To check the consistency of this picture with the data, we have set up a simple model of micelles in thermal motion inside a sphere, which represents the confinement of the micelles within the aggregate core. This confinement is due to the intermicellar attraction mediated by the charged part of the copolymer. The hairy outer layer of the aggregates, which is made up of the uncharged, hydrophilic part of the copolymer, is thought to prevent the aggregates from infinite growth. An example of experimental and theoretical SANS intensities is shown in Fig. 2 [3].
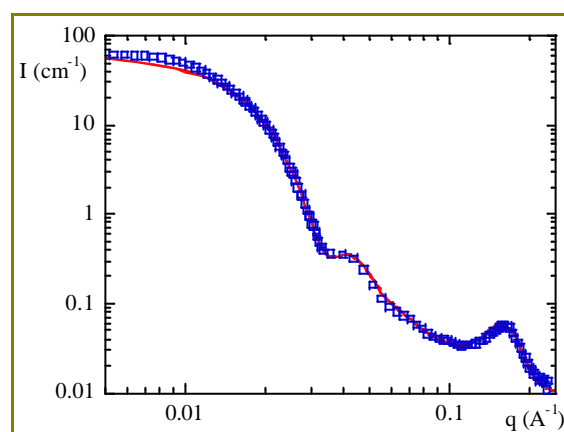

Figure 2. Scattered intensity of a mixture of ionic surfactant (DTAB) and a hydrophilic copolymer (PANa-b-PAM). The solid line is our model calculation (internal volume fraction 50%, hard sphere repulsion between micelles, core radius = 120 Å, Gaussian polydispersity 25 Å). The low-q deviation is due to the interaggregate structure factor, which is not described here.

Note that the size, polydispersity and internal concentration of the aggregate are directly related to the small- and intermediate-angle scattering (signal height and oscillations). The interaction peak at 0.16 Å^{-1} is due to the internal structure of the aggregates. The rather good agreement between model and experiment is a strong hint in favour of our understanding of the aggregate structure at all length scales accessible in SANS.

A <u>second</u> study deals with the fragmented structure of non ionic surfactant (like Triton X-100, or C_nE_m) adsorbed onto colloidal silica beads in water at high pH. It is well-known that build-up of complete bilayers is favored at low pH, due to the possible hydrogen-bonding of the oxy-ethylene headgroups with the surface silanols. At higher pH, the adsorption isotherms indicate reduced adsorption. Up to now, the incomplete layer has always been described in structural studies as a complete layer of lower density [4], although early dynamical results (fluorescence-decay) indicate micellar-type aggregates at the surface [5].

The result of a calculation of a complete layer structure (cf. lower inset) is compared to an experimental SANS-intensity in Fig. 3. In this experiment, the silica has been matched by the solvent [6]. The scattering from the adsorbed layer (dotted line) is predicted to be very high, and has to be reduced by a factor of 5 to fit the experimental data in the intermediate q-range. Then, the high-q scattering is far too low. The reason for its failure at high q is the presence of a lateral organization in the layer. We have studied a simple model (cf. upper inset) which reproduces the scattered intensity quite nicely (solid line) [6]. It is based on the geometrical description of adsorbed micelles, taking the hard-core repulsion between micelles into acount. Given the relatively high volume fraction of silica (some percent), the bead-bead interference term was also included (by RMSA) in this work. As a result, we are able to

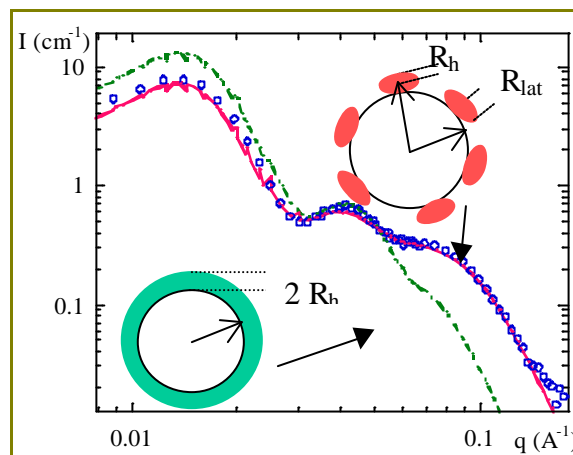quantify the shape and degree of ordering of the aggregates adsorbed on the surface.

Figure 3. Intensity scattered by a matched silica bead with adsorbed surfactant. The continuous layer model (dotted line, thickness 40 Å) predicts a wrong Porod decay. The solid line is the prediction of our decorated bead model with excluded volume interactions between beads (R_h = 25 Å, R_{lat} = 30 Å, N_{mic}^{av} = 14).

The two examples discussed here show that under certain circumstances (for instance, low polydispersity) structures can be shown to be consistent with experimental data, or on the contrary, be ruled out, by relatively easy and straightforward modelling. If modelling is successful, additional information on sizes, aggregation numbers or polydispersities can be obtained.

References

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