Experimental report

20/04/2016

Proposal: **9-12-365** **Council:** 4/2014

Title: SELF-ASSEMBLY OF SURFACTANTS IN THE PRESENCE OF SILVER NANOPARTICLES

Research area: Chemistry

This proposal is a new proposal

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Samples: Ag
dodecyltrimethyl ammoniumchloride (DTAC) / C15H34ClN
berol 266 (alcohol ethoxylate with chain length C9-11 and 4-7 ethylene oxide groups)
sodium dodecylbenzenesulfonate (LAS) / C12H25C6H4SO3Na
Hexadecyltrimethylammonium bromide (CTAB) / C16H33N(CH3)3Br

Instrument	Requested days	Allocated days	From	To
D22	3	0		
D33	3	0		
D11	3	2	27/04/2015	29/04/2015

Abstract:

The use of silver nanoparticles (Ag NPs) in consumer products, such as sportswear, washing machines and medical devices, has rapidly increased on the market due to their antibacterial properties. An important source of Ag NPs to the environment is from cleaning of Ag NP impregnated textile, where they come in contact with surfactants in the laundry circle (notably anionic sodium dodecylbenzenesulfonate (LAS), cationic dodecyltrimethylammoniumchloride (DTAC) and nonionic Berol 266 (Berol)). We have previously studied the surfactant–Ag NP interactions by means of dynamic light scattering, Raman spectroscopy, zeta potential, and
Quartz Crystal Microbalanceby, and the results indicate formation of self-assembled surfactant structures in the proximity of Ag NPs. Our interest in using small-angle neutron scattering is to characterize the structure of those self-assembled aggregates formed in presence of differently charged Ag NPs.

Introduction

Nanoparticles and surfactants frequently come into contact in many applications. Silver nanoparticles (Ag NPs), which are often incorporated in sport clothing, have for example been shown to be released during the laundry cycle and interact with surfactants in the washing powder[1-4]. Surface interactions between the Ag NPs and the surfactants influence their speciation and stability in solution. This may influence their subsequent transport through different chemical transients, and influence their potential bioavailability and toxicity[4-7]. A deeper understanding of such interactions between surfactants and nanoparticles is consequently of high importance. The interaction between both positively and negatively charged silver nanoparticles (Ag NPs) with oppositely charged surfactants was therefore investigated by means of SANS using the D11 instrument at ILL. By applying a model based on the sticky hard sphere model to account for cluster formation of micelles, we were able to fit our SANS data with good agreement between experiments and modelled data. Based on these results we are able to propose a novel mechanism for the stabilization of charged nanoparticles in a solution of oppositely charged surfactants, where cluster formation of micelles in the vicinity of the particles prevents particle agglomeration.

Experimental

Sample preparation

The negatively charged Ag NPs were synthesized based on a procedure developed by Creighton *et al.* [8] and for the positively charged Ag NPs we optimized the synthesis procedure presented by Sui *et al*[9]. The final Ag concentration in solution (*i.e.* not sedimented particles and complexes) was determined by means of atomic absorption spectroscopy (AAS) to approximately 50 mg/L. The particles were then mixed with stock solutions of the oppositely charged surfactants, to concentrations both above and below the CMC of the surfactant. The surfactants used comprise the positively charged surfactants cetyltrimethylammonium bromide (CTAB) and dodecyltrimethylammonium chloride (DTAC), and the negatively charged surfactant sodium dodecyl benzene sulfonate (LAS).

Experimental setup

The SANS experiments were carried out at the D11 SANS instrument. A range of scattering vectors, q, from 0.001 to 0.5 $Å^{-1}$, was covered by three sample-to-detector distances ($d = 1.2$, 8, and 20 m) at the neutron wavelength λ of 6.0 Å. The settings ($d = 8$ m, $\lambda = 6.0$ Å) and ($d = 20$ m, $\lambda = 6.0$ Å), respectively, were used as reference settings for the absolute scale. The wavelength resolution was 10% (full width at half-maximum value).

Data analysis

The SANS data were analyzed with a model for ellipsoidal micelles that form clusters, based on the Baxter sticky hard sphere model[10], in the vicinity of the Ag NPs. More details about the fitting models will be presented in two scientific papers that are under preparation and will be submitted to peer-reviewed scientific journals during the spring of 2016.

Results and discussion

The authors have in a previous paper speculated that the stabilization effect between negatively charged Ag NPs and the positively charged CTAB surfactant derives from a bilayer type formation on the particles,[3] as schematically illustrated in Figure 1a. This hypothesis was investigated using SANS. However, such a model could not fit the SANS data in a satisfactory way. On the other hand, by instead assuming that the surfactants form micelles in the vicinity of the charged particles, schematically illustrated in Figure 1b, we were able to obtain excellent fits to our SANS data as presented below.

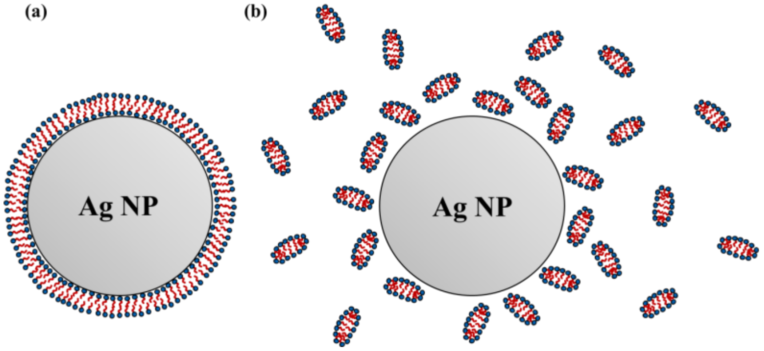

Figure 1: Schematic representations of two possible mechanisms of stabilization of the Ag NPs by surfactants, showing (a) the bilayer type formation on the particles and (b) the micelle formation in the particles vicinity. The latter is believed to be most realistic based on the fitting of our data.

The formation of features larger than single surfactants was observed with SANS far below the CMC of the surfactants, indicative of the formation of self-assembled aggregates on, or close to, the particle surface. It is thus evident that the surfactants are affected by the presence of the Ag NPs and that micellar aggregates are formed already at concentrations far below the CMC.

For the negatively charged particles in positively charged surfactants CTAB and DTAC this is seen in the SANS spectrum in Fig 2a and b respectively, on the characteristic scattering behavior of surfactant micelles at about 0.1 Å^{-1}. This is not an effect of the Ag NPs, which is apparent when looking at SANS data from a sample containing only negatively charged Ag NPs (no surfactants) since the increase in scattering intensity of this sample is significantly smaller than for solutions containing both Ag NPs and surfactants.

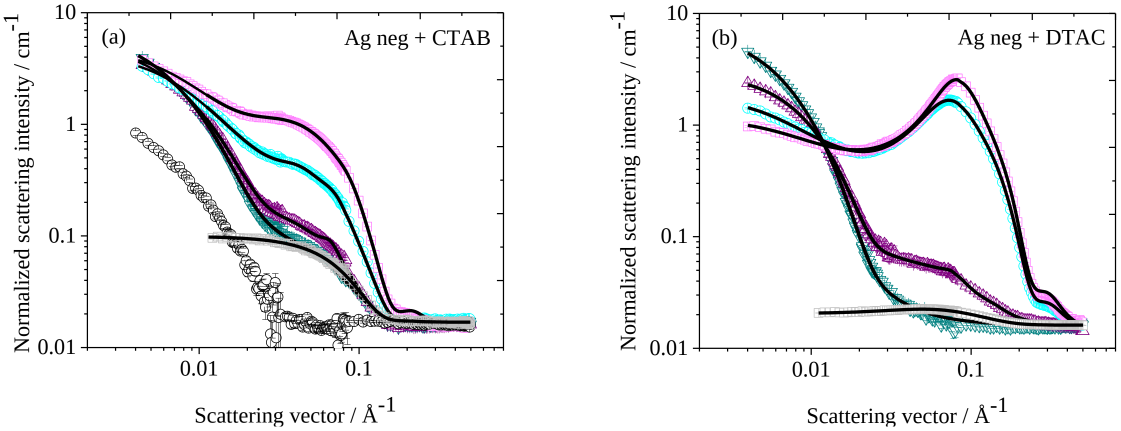

Figure 2: Normalized scattering cross section as a function of the scattering vector q for mixtures of negatively charged Ag NPs and varying surfactant concentration (10×CMC (□), 5×CMC (○), 1×CMC (△) 0.8×CMC (▽)) of the positively charged surfactants CTAB (a) and DTAC (b). Additional data for 2×CMC of pure surfactant (□) is presented, and (a) furthermore displays data for a solution of pure negatively charged Ag NPs (○). The symbols represent SANS data, and the solid lines represent the best available fit with a model for micelle clusters in the vicinity of the particles.

The interaction between positively charged Ag NPs and the negatively charged surfactant LAS gave rise to large mixed structures consisting of both the positive surfactant CTAB that was used as a stabilizer during the synthesis, and the negatively charged LAS. The large structures are indicated by the appearance of the SANS spectrum presented in Figure 3, where the high intensities at low q-values are likely related to these structures.

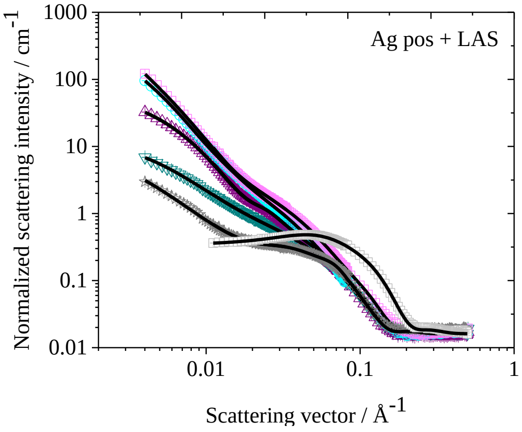

Figure 3: Normalized scattering cross section as a function of the scattering vector q for mixtures of positively charged Ag NPs and varying surfactant concentration (10×CMC (□), 5×CMC (○), 1×CMC (△) and 0.8×CMC (▽)) of the positively charged surfactant LAS. Data for 20×CMC of pure LAS (□) as well as data for a solution of pure positively charged Ag NPs (*) are also presented. The symbols represent SANS data, and the solid lines represent the best available fit with a model for micelle clusters in the vicinity of the particles.

In order to further test the validity of the cluster model, a least-square model fitting analysis was performed of the SANS data. The agreement between the model and the observed data is very good [*cf.* Figs. 2 and 3]. Detailed information about the fitting model as well as the results of the fitting parameters will be presented in the scientific papers that are under preparation.

Concluding remarks

The results from the SANS measurements at D11 that was performed for the beam-time proposal 9-12-365 have strongly contributed to the assessment of a mechanism for particle stabilization of charged Ag NPs in contact with surfactants of opposite charge. These very novel and interesting results will, together with complementing results from SAXS and DLS measurements on the same samples, be presented in full in two scientific publications, papers currently in preparation and planned to be submitted during the spring 2016. The authors highly appreciate the possibility for performing the SANS measurements at D11 and gratefully acknowledge the expertize and help from Dr. Isabelle Grillo, Institut Laue Langevin, DS/LSS, Grenoble, France.

References

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