Experimental Report

27/05/2014

Proposal: **9-12-339** **Council:** 10/2012

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

This proposal is a new proposal

Researh Area: Chemistry

Main proposer: **SKOGLUND Sara**

Experimental Team: BERGSTROM Magnus
SKOGLUND Sara

Local Contact: GRILLO Isabelle

Samples: berol 266 (alcohol ethoxylate with chain length C9-11 and 4-7 ethylene oxide groups)
sodium dodecylbenzenesulfonate (LAS) / $C_{12}H_{25}C_6H_4SO_3Na$
dodecyltrimethyl ammoniumchloride (DTAC) / $C_{15}H_{34}ClN$
Hexadecyltrimethylammonium bromide (CTAB) / $C_{16}H_{33}N(CH_3)_3Br$

Instrument	Req. Days	All. Days	From	To
D33	3	3	24/05/2013	27/05/2013

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

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The self-assembly of laundry-relevant surfactants in proximity of differently charged silver nanoparticles (Ag NPs) was investigated with small angle neutron scattering (SANS) on the D33 instrument. The use of Ag NPs in consumer products, such as sportswear, washing machines and medical devices, has rapidly increased on the market due to their antibacterial properties[1]. An important source of Ag NPs to the environment is from cleaning Ag NP-impregnated textiles. A thorough understanding of the interaction between Ag NPs and silver ions with surfactants present in washing powder and softeners is hence of great importance to assess potential environmental risks.

We have recently investigated how Ag NPs of different charge interact with surfactants relevant to the laundry cycle[2],[3]. The surfactants used comprise the negatively charged sodium dodecylbenzenesulfonate (LAS), the positively charged dodecyltrimethylammoniumchloride (DTAC) and a nonionic surfactant represented by an alcohol ethoxylathe (berol). Also the positively charged cetyrltrimetylammonium bromide (CTAB) was examined, as a model system, since SANS analysis on this surfactant have already been performed and evaluated to some extent by the authors [4, 5]. Changes in surface composition of the Ag NPs and the adsorption of the surfactants on them were studied using Surface Enhanced Raman Spectroscopy (SERS). The size distribution of the Ag NPs in solution was examined using dynamic light scattering (DLS), and their surface charge by means of zeta potential measurements. The morphology of the pure Ag NP dispersions samples have been investigated by means of transmission electron microscopy (TEM) [2].

The earlier performed Raman measurements indicated adsorption of cationic CTAB via electrostatic interaction with the head group oriented towards the negative Ag NP surface. The positive surface charge density of CTAB-modified Ag NPs is a result of adsorption exceeding monolayer coverage due to the electrostatic interaction between the cationic head-group of the surfactant and the negatively charged nanoparticle, combined with hydrophobic interactions between the hydrophobic tails of the surfactants. Due to this effect the surfactants are assumed to form some kind of bilayer on the surface. However no obvious increase in size was observed with DLS [3].The lack of growth in size after interaction with the surfactants indicates that the surfactant molecules do not pack completely as suggested by Sui *et al*[6]. The aim with these SANS experiments was hence to see if the surfactants self-assemble into adsorbed bilayers or some other structure, for instance, micelles or patches of bilayers at the silver particle/water interface.

A q-range of about 0.002 to 0.5 $Å^{-1}$ have been studied, covering both the large angles, middle angles and in some cases were the samples scattered a lot of the neutrons, also the small angles. The SANS data is at the present being analysed by means of least-square model fitting using different geometrical models[7].

The scattering length density of Ag NPs is about $3.5 \cdot 10^{10}$ cm^{-2}/molecule which means that they are matched out in SANS by a solvent with a water-to-deuterium oxide ratio equal to about H_2O/D_2O = 40/60. To start with each sample was measured in pure D_2O as well as in mixtures of H_2O/D_2O, but since also in pure D_2O the Ag NPs didn’t scatter notably (Figure 1), and since pure D_20 samples showed less noise and lower deviation in the scattered intensity (I) versus scattering vector (q) plot and thus more reliable results, onlypure D_2O-samples were finally analyzed.

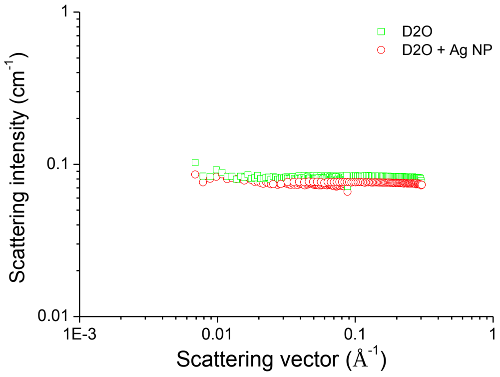

Figure 1. Symbols represent SANS data obtained, where squares corresponds to D_2O without added Ag NPs, and circles to D_2O containing 10 mM silver.

In order to identify the structure dependency on surfactant concentration, several concentrations below as well as above the critical micelle concentration (CMC) for the various surfactant solutions were investigated (ranging 0.01*CMC up to 10*CMC). In general the scattering from the samples with surfactant concentrations below CMC did not scatter sufficiently and could thus not be evaluated.

The structure of the self-assembled CTAB both without and in presence of the positively charged Ag NPs was examined, and the data was fitted using a model for triaxial ellipsoids, Figure 2. This corresponds well with previous findings on similar systems. [4],[5]. When adding the Ag NPs to the system the curve did not change significantly, which indicates that the silver concentration (10 mM) was not high enough to have any impact.

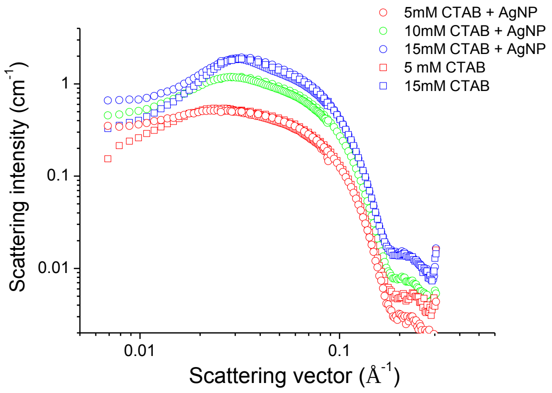

Figure 2. Symbols represent SANS data obtained, where squares corresponds to samples without added Ag NPs, and circles to samples containing 10 mM silver.

The interactions between positively charged CTAB modified particles and anionic LAS at different LAS concentrationswere then examined. As visualized in Figure 3a, the intensity at different concentrations is rather similar at low q angles, and is continuously decreasing with increasing scattering vector q, until around 0.03 Å^{-1} where they show a small plateau, a tendency which is more pronounced the higher the concentration of LAS. The increase in intensity at low scattering vectors is most likely coming from impurities in the surfactant, which makes these samples uninterpretable.

The interaction between negatively charged Ag NPs and nonionic Berol was studied for a concentration series of Berol, and as shown in Figure 3bthe intensity is decreasing with increasing scattering vector. It is difficult to draw any conclusions also from these samples, since the increase in intensity at low angles could be the result of either impurities in the surfactant, or even because it is a commercial surfactant which is rather polydisperse, being an alcohol ethoxylate with a chain length of C9−11 and 4−7 ethylene oxide groups (molecular weight range of 320–480 g/mol)[2]. Impurities seem to be a likely explanation since the appearance of curve changes considerably upon filtration, Figure 3b.

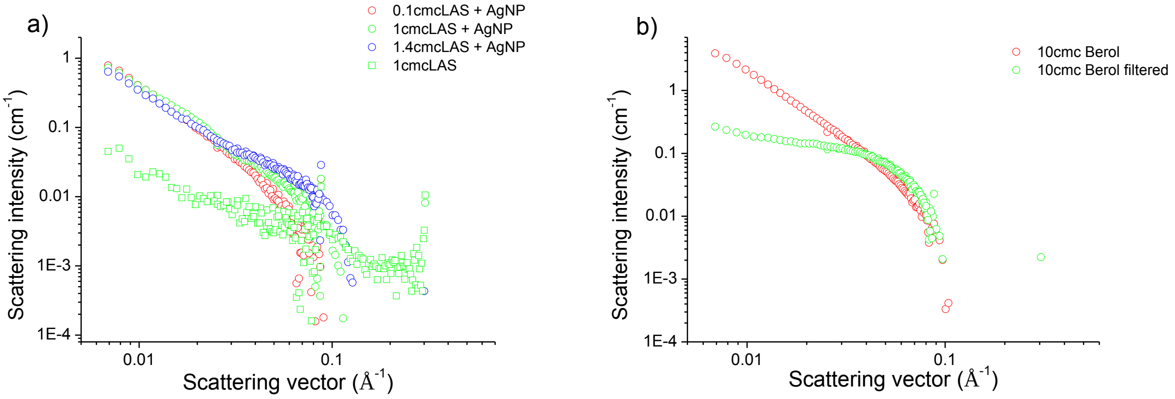

Figure 3. Symbols represent SANS data obtained, where squares corresponds to samples without added Ag NPs in a) LAS and b) Berol, and circles to samples containing 10 mM silver.

Further investigations involved studies of the interaction between negatively charged Ag NPs and positively charged DTAC using a concentration series of DTAC. These results, shown in Figure 4, demonstrate similar findings as for the case with CTAB and negatively charged Ag NPs, ie that the intensity increases with increasing surfactant concentration, but that no difference between samples with and without 10 nM silver can be seen.

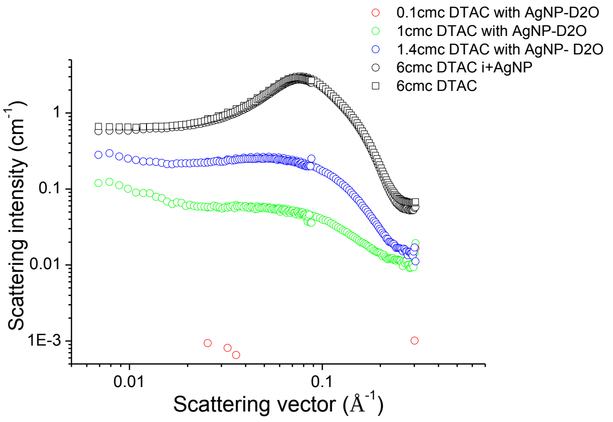

Figure 4. Symbols represent SANS data obtained, where squares corresponds to samples without added Ag NPs, and circles to samples containing 10 mM silver.

The general conclusion from these experiments was that the concentration of Ag NPs was too low to generate sufficient data. It should also be noted that one problem could be that the samples are polydisperse which would be in accordance with previous findings by the authors [2]. Therefore, complementary studies are planned with SANS of samples with higher Ag NP concentrations, as well as SAXS studies where the Ag NPs particles are visualized.

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