



Moderate the adsorption of cationic surfactant on gold surface by mixing with sparingly soluble anionic surfactant



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ABSTRACT

Surfactants with amine groups are often used in the nanoparticle synthesis due to the high affinity with Au atoms. The match of charges of a capping reagent with Au has significant influence on structures in nanoparticle synthesis. Thus we studied the adsorption of a catanionic surfactant system on Au surface. The surfactants used in the study are bis[[amidoethyl]carbamoyl]ethyl]octadecylamine (C18N3) and arachidic acid. Three combinations of the surfactants were studied with regard to the protonation state of the amine groups and the match of charges of the surfactant headgroup. The morphology of the surfactant mixtures changes from high-curvature aggregates to low-curvature with increasing the molar ratio of arachidic acid in the mixtures or the pH of the surfactant solutions. The adsorption of the mixed surfactant systems was studied by means of scanning electron microscopy (SEM), quartz crystal microbalance (QCM) and cyclic voltammetry (CV). The results revealed that the homogeneity and the compactness of the adsorbed layer on a gold surface were increased with the molar ratio of arachidic acid in the complexes. Furthermore, we may obtain the construction of the film of the mixed surfactant on gold surface using the result obtained by QCM.

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1. Introduction

Surfactant adsorption at an air–liquid or liquid–solid interface, along with the resulting lowering of the surface tension, plays a central role in controlling the desired behavior in many practical applications involving surfactants. In many practical applications, better properties can be attained by using mixed surfactant systems comparing to using an individual surfactant [1]. Mixtures of cationic and anionic surfactant represent interesting models for understanding structure formation in two-dimensional (2D) and three-dimensional (3D) structures. One of their interesting features is the competitive interaction between the cationic part and the anionic part leading to a richness of phases and special aggregation structures. This calls for systematic variations of these interactions and one of the conventional methods is to vary the charge of the hydrophilic headgroups. For the mixed systems of fatty acid and fatty amine as the most frequently studied system, this is possible via variation of the hydrophilic part.

Multihead surfactants have drawn the attention of researchers due to its unique properties and applications in nanotechnology [2]. With regard to the increase of steric repulsion and the decrease of hydrophobicity, multihead surfactants exhibit a higher critical micellar concentration (CMC) comparing to conventional surfactants with the alkyl chain of an equal length. The aggregates formed by multihead surfactants in an aqueous solution are generally micelles with a low aggregation number, although it is possible to form other types of aggregates by balancing the hydrophilic part with a longer alkyl chain [3]. This may be understood by the molecular packing parameter (p). The molecular packing parameter is defined as $p = v/a \cdot l$ where a is the area of the surfactant headgroup, l equals to the length of the alkyl chain at a stretched configuration, and v is the volume of the surfactant molecule [4]. Due to the large area of the headgroup for a multihead surfactant, the packing parameter is commonly smaller than 1/3, which indicates a large spontaneous curvature of the aggregates [5].

In the previous studies from our group, we have synthesized a multihead surfactant with a dendritic headgroup, bis[[amidoethyl]carbamoyl]ethyl]octadecylamine (abbreviated as C18N3), which exhibited many interesting features as a capping reagent in nanocrystal synthesis and nanoparticle self-assembling [6–16]. C18N3

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is a surfactant with an eighteen-carbon chain and a dendritic head-group analogy to the dendritic unit of poly(amidoamine) (PAMAM) [17]. The dendritic headgroup is composed of two primary amines and a tertiary one. The three-amine groups are protonated at low pH, and maintain uncharged at high pH. Thus the area of the headgroup changes corresponding to the pH of the solution. It also resulted in different aggregation morphology at different pHs, such as micelles at pH 2 and lamellar structures at pH 10.5. Due to the multiple-amine groups, the surfactant shows a strong interaction with metal elements, such as aurum, silver and copper [8,9,12]. For example, the surfactant interacted with silver ions and the aggregates of the surfactant transferred from micelles to vesicles at low pH [12]. The vesicles were used as a template to assemble AgCl nanoparticles on the vesicle surface and synthesize hollow nanostructures. The diameter of the hollow nanostructure increases with a controlled growth rate due to the competitive interaction with silver ions between the surfactant and the chloride ions [12].

Many interesting self-assembling structures have been achieved by applying the surfactant as a capping reagent in synthesizing gold nanoparticles. Recently C18N3 was used to self-assemble high-aspect-ratio gold nanorods and resulted in a highly ordered 2D structure on a micrometer scale, which is by far the largest 2D self-assembling structure of nanoparticles by using bottom-up methodology [13]. These results suggest that the increase of hydrophobic interaction by elongating the surfactant chain may benefit the self-assembling; while the liquid property of the alkyl chain has to be retained. Therefore in this study, an anionic surfactant, arachidic acid (AA) was introduced to the C18N3 system. Arachidic acid is an amphiphilic molecule, however sparingly soluble in water due to a long alkyl chain. Mixing with arachidic acid will maintain the strong hydrophobic interaction, and in the meantime moderate the charge density of the aggregates. The adsorption of the aggregates on gold surface was studied by means of scanning electron microscope (SEM), quartz crystal microbalance (QCM), and electrochemistry. Since C18N3 mostly has three protonated sites, three molar combinations of arachidic acid and C18N3 were thus studied concerning the match of the charges in the headgroups of the surfactants.

2. Materials and methods

2.1. Materials

Arachidic acid (99.5%), hydrochloric acid (37%), and sodium hydroxide (99.5%) were purchased from Aldrich–Sigma, and they were used without further purification. Chloroauric acid, methylene blue (MB) and trisodium citrate were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. Milli-Q water with a resistivity of 18 M ohm cm was used in all experiments.

Bis[[amidoethyl]carbamoyl]ethyl]octadecylamine (C18N3) was synthesized according to the method described in a previously published paper, and the structure is shown in Fig. 1 [17].

2.2. Au nanoparticles preparation

13 nm Au nanoparticles were prepared by reduction of chloroauric acid in an aqueous trisodium citrate solution. 2% chloroauric acid (0.3 ml) and 2% trisodium citrate (0.9 mL) were mixed with 60 mL water. The solution was then heated to the boiling temperature under rigorous agitation for 30 min. After cooling to room temperature, the Au nanoparticles solution was stored at 4 °C. The TEM image of the nanoparticles is shown in the supporting information (Fig. S2).

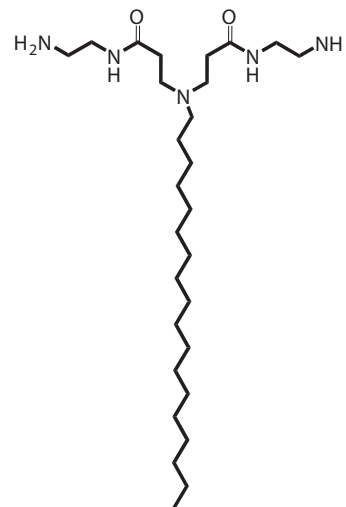


Fig. 1. The chemical structure of bis[[amidoethyl]carbamoyl]ethyl]octadecylamine (C18N3).

2.3. Transmitted electron microscope (TEM)

C18N3 and arachidic acid were dissolved in chloroform with the concentration of 1 mmol/L. The solution of C18N3 and arachidic acid at different molar ratio was mixed in a flask and the solvent was evaporated using rotary evaporator. The film of the mixtures was dried in a nitrogen atmosphere, and then rehydrated with pure water. In each sample, the final concentration of the total mixtures was 1 mmol/L. The pH of solution was then adjusted by 1 mol/L HCl or NaOH solution, and measured by a HI 8314 pH-meter (HANNA instrument) with a HI 1200B glass electrode. The solutions were placed in a thermal room of 25 °C to reach equilibrium.

One drop of the solution was placed on a carbon film supported by copper grids and maintained for 5 min in a sealed environment. Then the residuals were removed using a filter paper. TEM analysis was carried out with a negative-staining method on JEOL (JEM-2011).

2.4. Scanning electron microscope (SEM)

A silica substrate covered with a layer of gold film was immersed in a pre-mixed surfactant solution. After the adsorption of the sample on the substrate for half an hour, the substrate was removed from the solution, and rinsed with pure water. The substrate was then dried in a nitrogen environment. SEM images were taken on a HITACHI S4300.

2.5. Quartz crystal microbalance (QCM)

The gravimetric measurements were performed on a QCM. An AT-cut quartz crystal with a fundamental frequency of 9 MHz coated with gold layers on both sides, was purchased from Seiko EG&G (Tokyo, Japan). The effective adsorbing area on the quartz was 0.196 cm². The gold surface of the quartz resonator was pre-cleaned by detergents. Then the piranha solution (H₂SO₄:30%H₂O₂ = 3:1) was dropped on the gold surface and the surface was heated up to 50 °C for 2 min. The surface of the quartz was then rinsed by pure water and dried with a stream of nitrogen. However the glue between the gold layer and the quartz could not stand in an acidic solution, so the experiments were only performed for the samples without the addition of HCl and NaOH solution.

The resonators were immersed in the solution of the mixed surfactants for 30 min. Then the quartz was removed from the

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