



# Spherical micelle formation by mixed quaternary ammonium surfactants with long, and short, tails in ethanol/water solvent and micellar freezing upon solubilising styrene polymerisation



Jianxi Zhao\*, Hongbin Yu

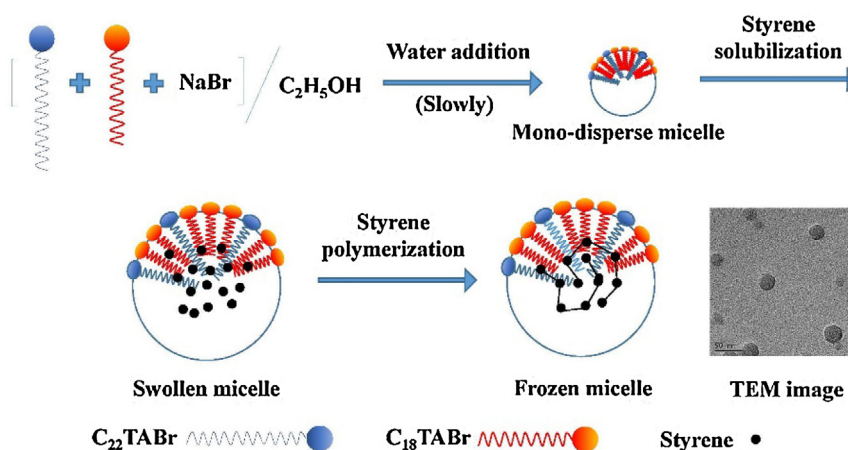
Institute of Colloid and Interface Chemistry, College of Chemistry and Chemical Engineering, Fuzhou University, Fuzhou, Fujian, 350108, PR China

## HIGHLIGHTS

- Mixed  $C_{22}TABr/C_{18}TABr$  micelles were prepared in ethanol/water (15/85 wt%) solvent.
- NaBr was used to inhibit secondary aggregation of the micelles.
- The micelles were fixed via the polymerisation of solubilised styrene monomers.

## GRAPHICAL ABSTRACT

$C_{22}TABr/C_{18}TABr$  formed mixed micelles in ethanol/water (15/85 wt%) with the assistance of NaBr and styrene were then solubilized and polymerized *in situ*, by which means the mono-disperse, spherical micelles were frozen.



## ARTICLE INFO

### Article history:

Received 26 July 2016

Received in revised form 21 October 2016

Accepted 27 October 2016

Available online 28 October 2016

### Keywords:

Mono-disperse  $C_{22}TABr/C_{18}TABr$  micelles

Styrene polymerisation

Frozen micelles

Spherical morphology

## ABSTRACT

The association of mixed docosyltrimethylammonium bromide and octadecyltrimethylammonium bromide,  $C_{22}TABr/C_{18}TABr$ , in ethanol (a common solvent favoured for both their alkyl tails and head-groups) induced by the addition of water (a non-solvent for the tails) has been studied using light-scattering measurements. Under the assistance of NaBr, which promoted the surfactant molecules to pack tightly in the micelles, mono-disperse spherical micelles composed of mixed  $C_{22}TABr/C_{18}TABr$  were obtained in ethanol/water (15/85 wt%). Styrene was solubilised into the templating  $C_{22}TABr/C_{18}TABr$  micelles ( $\beta_{surf}$ , the molar ratio of  $C_{18}TABr$  to  $C_{22}TABr$ , was 2.5) and then was polymerised *in situ*. To achieve a good freezing effect, the amount of styrene solubilised, represented as the molar ratio of styrene monomer to total surfactants,  $n_{st}/n_{surf}$ , was required to be greater than 4.87 for this templating micellar system. The diluting tests demonstrated that, after polymerisation, the styrene-containing micelles froze their microstructure well. Light-scattering measurements, and TEM observation, all indicated that these micelles were mono-dispersed, and retained their spherical shape. As swollen by polystyrene, the micelle had an average radius of 18 nm.

© 2016 Elsevier B.V. All rights reserved.

\* Corresponding author.

E-mail address: [jxzhao.colloid@fzu.edu.cn](mailto:jxzhao.colloid@fzu.edu.cn) (J. Zhao).

## 1. Introduction

Colloidal crystals of ordered microspheres are a new class of advanced materials [1,2]. A typical, and important, application is based on their novel light diffraction and photonic band gap properties by which photonic devices, sensors, selective membranes, and even microchips have been developed [3–6]. To date, traditional colloids such as silica spheres or polystyrene latex spheres have been used to obtain two- or three-dimensionally structured patterns and arrays. Such polymer colloids with self-assembling properties were thought to be a facile route to the creation of ordered colloidal crystals arrays [3,6,7]. Compared with polymer particles, the aggregates formed by surfactant self-association have a mono-disperse size and a clear, definite core-shell structure, which favours functional modification of the particle surface. Thereby these aggregate particles are new candidates for constructing colloidal crystals, in which the self-assembly between the aggregate particles can be expected to play its fullest extent. However, this approach has not been tested.

To this end, a key problem needs to be resolved in advance, *i.e.*, how to 'freeze' these aggregates because surfactant self-aggregation is controlled by thermodynamics [8], and changes in concentration, temperature, salinity, pH, *etc.*, will modify their microstructures. Two methods have been tried: one was to polymerise the monomers, such as styrene, that was previously solubilised in the aggregates, by which the micellar microstructures were expected to cohere [9–13], another was using polymerisable surfactants [14–16]. The former approach was convenient, and more common, than the latter.

Recently, interest has arisen in the self-assembly of long-tailed surfactants. Due to poor dissolution of long hydrocarbon-tailed compounds in water, their aggregates, if formed, are expected to freeze kinetically to a great extent. If the polymerisation method for extrinsic styrene monomers is further applied, the freezing effect must be more perfect. Now, it is interesting to note how to prepare the aggregates of long-tail surfactants in water or in the mixed solvents of water-rich compounds.

Very recently, we reported a study on the aggregation of long-tailed ( $C_{22}$ ) surfactants in ethanol depending on the addition of water [17]. In this case, the surfactants were dissolved in ethanol (a common solvent favoured for both their alkyl tails and head-groups) in advance, and then water (a non-solvent for the tails) was slowly added to induce their aggregation. This method referenced the work of Eisenberg *et al.* [18–22]: in their study, the self-assembly of amphiphilic block copolymers (BCPs) was performed in a common solvent (such as DMF) upon an addition of a non-solvent (generally water), by which the kinetically frozen aggregates were obtained when the non-solvent was present in excess. Upon attempting the application of this method, we found that docosyltrimethylammonium bromide ( $C_{22}$ TABr) formed core-shell micelles but the micellar cores were swollen by ethanol, resulting in the exposure of the alkyl tails to the polar solvent. These micelles thus further associated into secondary aggregates with an average radius of greater than 100 nm so as to reduce the system energy [17]. In the present work, we tried to inhibit this secondary association. For this purpose, a quaternary ammonium surfactant with a slightly shorter tail, octadecyltrimethylammonium bromide ( $C_{18}$ TABr), was introduced to fill the gaps made by the swelling of the ethanol. In addition, a simple salt, NaBr, was also added to compress the gaps. As a result, mono-disperse core-shell micelles were successfully obtained in ethanol/water (80–85 wt%) solvents. Furthermore, we solubilised styrene monomers into the micelles and then polymerised them *in situ*. Finally, we obtained well-frozen micelles, as reported below.

## 2. Experimental work

### 2.1. Materials

$C_{22}$ TABr and  $C_{18}$ TABr were synthesised in our laboratory [17,23]. Ethanol (AR, Sinopharm) was used as received. The water used was of Milli-Q grade with a resistivity of 18.2 M $\Omega$  cm. Sodium bromide (NaBr, purity >99%) was purchased from Beijing Chemical Reagents Co. and used as received.

### 2.2. Sample preparation

The surfactants were dissolved in ethanol and the solution was filtered through a 0.22  $\mu$ m pore-size filter. The Milli-Q water was slowly added to the solution at 30 °C using a drop-rate auto-controllable micro-syringe (LongerPump TJ-1A) at a flow rate of 20  $\mu$ L min<sup>-1</sup> until the desired water content was reached. The solution was stirred for 24 h at 30 °C before the test.

### 2.3. Styrene solubilisation and polymerisation

Reagent grade styrene (AR, Sinopharm) was washed with 10 wt% NaOH several times and then washed with water until the solution pH reached 7 to remove the inhibitor and any polymeric residue. Desired amounts of styrene were put into test tubes containing  $C_{22}$ TABr/ $C_{18}$ TABr micelles in ethanol/water solvent. The test tubes were vibrated for 48 h at constant 30  $\pm$  0.1 °C to ensure the solubilisation equilibrium of styrene in the micelles.

The UV absorption spectrum of each styrene-containing solution was recorded on a Hitachi U-3010 (Japan) UV-vis spectrophotometer using a quartz cell with a 10 mm path length.

Polymerisation was carried out in a 250 mL glass reactor with a solution of  $C_{22}$ TABr/ $C_{18}$ TABr micelles solubilised by styrene. The glass reactor was equipped with a temperature controller, and was stirred using a magnetic stirrer.  $K_2S_2O_8$  to 1 wt% with respect to the monomer was added and the solution was heated to 70 °C while being stirred. The reaction was performed for 8 h, after which the temperature was rapidly decreased to room temperature.

### 2.4. Light-scattering measurements

The light-scattering ability of the solutions was measured with a Brookhaven Instrument which was composed of a BI-200SM goniometer, a BI-9000AT digital correlator (522 channels), and a photomultiplier detector. A green laser with 200 mW output power and 532 nm wavelength was used as the light source. The measurement temperature was controlled by a thermostatic circulator (Poly-Science, USA) with an accuracy  $\pm$ 0.01 °C.

For dynamic light-scattering (DLS), the experimental data were analysed by the CONTIN program to obtain the intensity-fraction distributions around each characteristic aggregate size. For those double distributions of scattering intensity, a double-exponential model (Dblexp) was also used to analyse the data to a greater precision [24,25].

For static light-scattering (SLS), the reduced scattering intensity  $KC/R_\theta$  was measured at different concentrations. Here,  $R_\theta$  is the Rayleigh ratio obtained by calibration measurements with benzene:  $R_\theta = 8.51 \times 10^{-6}$  at 25 °C [26],  $C$  is the surfactant concentration, and  $K$  is the optical constant which is given by

$$K = 4\pi^2 n_0^2 (dn/dc)^2 / (\lambda_0^4 N_A) \quad (1)$$

where  $n_0$  is the solvent refractive index, and  $dn/dc$  the refractive index increment measured by BI-DNDC.

Download English Version:

<https://daneshyari.com/en/article/4982558>

Download Persian Version:

<https://daneshyari.com/article/4982558>

[Daneshyari.com](https://daneshyari.com)