Self-assembly of some long-tail surfactants driven by water addition in ethanol

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HIGHLIGHTS

- We developed a new insight to prepare homogenous solution of long-tailed surfactants.
- Long-tailed surfactant can self-associate into micelles in ethanol upon water addition.
- Water induced secondary aggregation of long-tailed surfactant micelles in ethanol.
- Dispersed core–shell micelles can be obtained when both SBzs and C_8OH added.

GRAPHICAL ABSTRACT

The added water induced the self-assembly of long-tail surfactants in ethanol, primary micelles, with their incomplete coronal structure, were formed due to the core swelling under the influence of ethanol and thus they further associated into large aggregates.
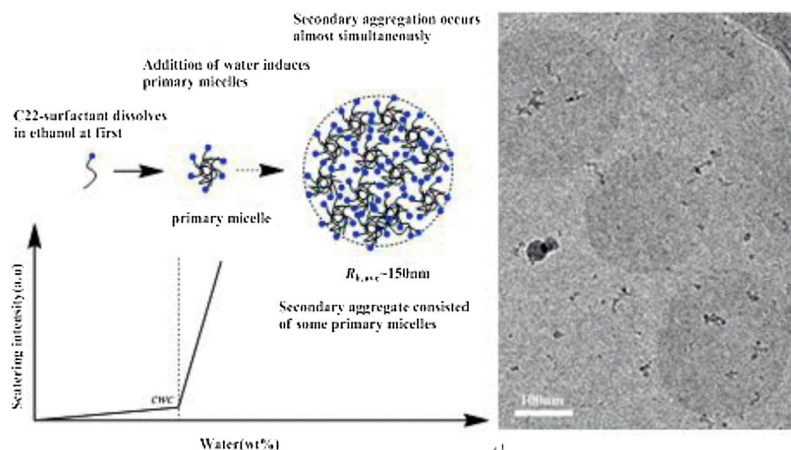
ABSTRACT

The self-assembly of C_{22}-tailed surfactants in ethanol (a common solvent favoured for both the alkyl tail and the head-group) induced by the addition of water (a non-solvent for the tail) has been studied using light-scattering measurements. These surfactants self-associated into core–shell micelles in ethanol upon the addition of water. However, the coronas of the micelles cannot envelop the cores particularly well since the cores were swollen by the solvent: these micelles were thereby further associated into secondary aggregates with an average radius of greater than 100 nm. Upon an increase in water content, the core contracted and the exposure of the alkyl tails was lessened: this reduced the extent of secondary aggregation. The surfactant with a more hydrophilic head-group promised the addition of more water. If the water content was relatively high, secondary aggregation may be avoided and complete core–shell micelles could be obtained upon the addition of some additives that filled the gaps in the corona. The results represented the development of a new self-assembly approach to traditional surfactants, by which the solubility thereof was enhanced owing to the use of a common solvent. Therefore, the self-assembly of those surfactants insoluble in water could be examined by this method.

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1. Introduction

The self-assembly of amphiphilic molecules in aqueous solution has been an oft-researched topic since this behaviour resulted in a variety of remarkable structures of different shapes and sizes [1]. In aqueous solution, the driving force to form aggregates comes mainly from the hydrophobic effect between the alkyl tails of these molecules [2]. Therefore, the study of long-tailed surfactants has aroused interest over recent decades. Due to surfactants with a long tail being generally insoluble in water, the realisation of a homogeneous solution was the first key step to achieve the aims of these studies. General ways of overcoming this difficulty were to increase the hydrophilicity of headgroups, such as carrying double or triple quaternary ammonium headgroups on a supra-long chain [3,4], or to adopt an unsaturated tail such as an erucyl chain [5–8]: this eliminated the more popular surfactants.

To overcome this problem, the method used by Eisenberg et al. in their study of the self-assembly of amphiphilic block copolymers (BCPs) in solution may be a good reference [9]. There, the preparation of solutions was rather special: typically, BCP was dissolved in a common solvent, such as DMF, dioxane, or THF, which are good solvents for all blocks. Then a selective solvent, such as water, that is a non-solvent for the hydrophobic block, was slowly added to the solution. When the water content reached a certain value, BCP self-assembly began to form aggregates with a core consisting of insoluble blocks and a corona of soluble blocks [9][9a]. Finally, the addition of water can be excessive, by which the processes of association and the morphologies of the aggregates were kinetically frozen.

This method was introduced in the present work to study the self-assembly of C_{22}-tailed surfactants, where ethanol was used as a common solvent and water was a non-solvent for their C_{22}-tails. At first glance, this seems to be a simple system for the self-assembly of a surfactant in mixed solvent. Indeed, water/ethanol is a popular mixed solvent and was often used to provide information about surfactant–solvent interactions [10]. However, the present consideration is completely different from those in the literature whether considering the procedure for preparing the solution, or the attempt introduced this method. First, it did not prescribe a limiting mixed solvent ratio and directly dissolved the long-tailed surfactant in ethanol, which meant that the surfactant carrying a longer tail due to increased solubility in ethanol could be used. Water was later added to induce the association in the surfactant. This made it possible to exhibit a successive picture of water content and its influence on the structure of aggregates, which favours better understanding of surfactant–solvent interactions. Second, the addition of water can be excessive, which results in a kinetically frozen state of the micelles formed by the water-insoluble surfactant, similar to those BCP aggregates observed by Eisenberg et al. [9]. In those particles frozen kinetically, their mono-disperse feature may be useful in new material applications such as the construction of colloidal crystals.

Colloidal crystals of ordered microspheres are a new class of advanced materials [11,12]. A typical, and important, application is based on their novel light diffraction and photonic band gap property, by which photonic devices, sensors, selective membranes, and even microchips have been developed [13–16]. To obtain three-dimensional (3-d) periodic arrays of colloids, many techniques were used, among which polymer colloids with self-assembling properties were thought to be a facile route for this purpose [13,16,17]. Compared with polymer particles, the aggregates formed by surfactant association have not only a mono-disperse colloidal size but also a clear and definite core–shell structure, the latter favours functional modification of their surface and thereby these aggregate particles are good candidates for constructing colloidal crystals, in which the self-assembly between the
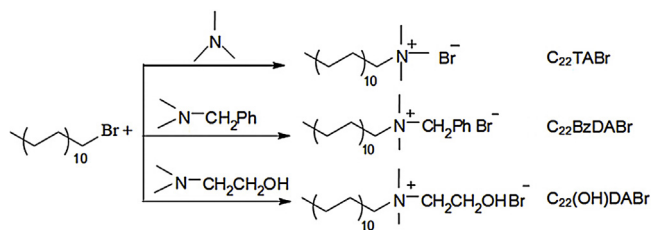
Scheme 1. The synthetic route to C_{22}TABr, C_{22}BzDABr and C_{22}(OH)DABr.

aggregate particles is expected to play to the fullest extent. However, this approach has not been tested. In the present work, the shape and morphology of the aggregates formed by long-tailed surfactants can be frozen kinetically, which becomes a basis to develop new colloidal crystals using surfactant aggregates. Different from the particles formed by polymers, the surfactant aggregates are small in size and thereby their periodic arrays may be interesting in property.

Here, a detailed study of this method, using the three C_{22}-tailed surfactants as representative of popular surfactants, was undertaken. In addition, some basic details were also discussed such as the choice of common solvent and the preparation conditions. All these were required to establish a good basis for the expansion of this method to the self-assembly of long-tail surfactants.

2. Experimental work

2.1. Materials

Docosyltrimethylammobium bromide (C_{22}TABr), docosylethoxyldimethylammobium bromide (C_{22}(OH)DABr), and docosylbenzyl-dimethylammobium bromide (C_{22}BzDABr) were synthesised and purified according to the method of Palouana et al. [18]. The synthesis route of the C_{22}-tailed surfactants is represented by Scheme 1. All of these compounds were confirmed by ^{1}H NMR and elemental analyses.

Ethanol (AR, Sinopharm) was used as received. The water used was of Milli-Q grade with a resistivity of $18.2\,M\Omega\,cm$; n-octanol (99.5%) was purchased from Aladdin Co., and sodium benzenesulfonate (SBzs, 98%) was a Sigma–Aldrich product.

2.2. Sample preparation

The surfactant was dissolved in ethanol and the solution was filtered through a 0.22 μm pore size filter. The Milli-Q water was slowly added to the solution using a drop-rate auto-controllable micro-syringe (LongerPump TJ-1A) at a flow rate of $20\,\mu L\,min^{-1}$, except in those experiments about the conditions themselves, until the desired water content was reached and the solution was stirred for 24 h before the test. All experiments were performed at 30 °C expect those involving the conditions themselves.

2.3. Methods

2.3.1. 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 ±0.01 °C.

For dynamic light-scattering (DLS), the experimental data were analysed by program CONTIN to get the intensity–fraction