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Micelle-to-vesicle transition induced by β-cyclodextrin in mixed catanionic surfactant solutions

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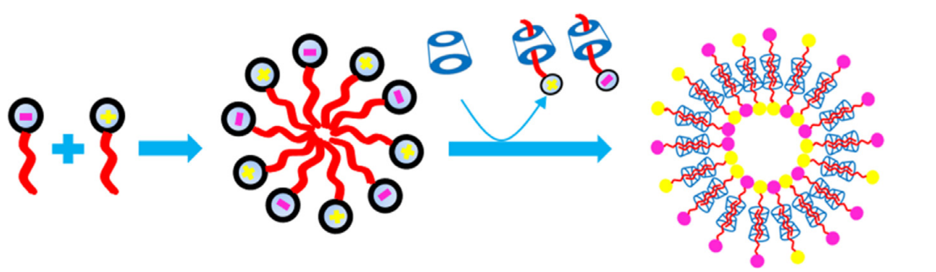
HIGHLIGHTS

- Aggregate transition was successfully achieved in catanionic surfactant solutions.
- Through the addition of β-CD, micelles can be transformed into vesicles.
- Association constants were investigated to show the ability of inclusion complexation of β-CD to surfactants.

GRAPHICAL ABSTRACT

Micelle-to-vesicle aggregate transition induced by β-CD in catanionic surfactant solutions is investigated in this work. At first, the solutions are transparent and water-like which are proved to be micelles in mixed systems. After the appropriate addition of β-CD, the hydrophobic chains of surfactants will be included in the cavity of β-CD which will increase the critical packing parameter. The association constant value of NaOle is larger than C_{16}mimCl. The NaOle is easier included by β-CD. Due to the formation of inclusion complexes and the increased critical packing parameter, the vesicles are formed.



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ABSTRACT

Micelle-to-vesicle aggregate transition is investigated in this work through the addition of β-cyclodextrin [1](β-CD) in mixed catanionic surfactant aqueous solutions. The catanionic system is composed of 1-hexadecyl-3-methylimidazolium chloride (C_{16}mimCl) and sodium oleate (NaOle) which are cationic surfactant and anionic surfactant, respectively. The mixed surfactant solutions can self –assemble into micelles, which are studied by dynamic light scattering measurements and the calculation of molecular interaction parameter. The inclusion complexation of β-CD to C_{16}mimCl-NaOle surfactants is studied by surface tension measurements and the calculation of association constants. The dynamic light scattering (DLS), rheological measurements, freeze-fracture transmission electron microscopy(FF-TEM)were conducted to indicate that micelles can transform into vesicles with the addition of β-CD. Finally, the transformation mechanism is proposed. The main reason for micelle-to-vesicle aggregate transition is the inclusion complexation of β-CD to surfactants and it will alter the composition of mixed C_{16}mimCl-NaOle surfactant systems which should be responsible for the phase behavior.

1. Introduction

Surfactants can self-assemble into multiple phase behaviors when the concentration is higher than the critical micelle concentration (CMC), [1] such as micelle, lamellae, vesicle, and liquid

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crystal. [2–6] Meanwhile, the above aggregate behaviors also occur in mixed cationic/anionic surfactant systems [7]. Usually, the aggregate polymorphism greatly depends on the electrostatic, van der Waals, hydrophobic, as well as the composition of catanionic surfactant systems [8,9]. It is believed that aggregate transition can happen among these aggregates. Many researches have focused on the aggregate transition because of their wide applications in petroleum engineering, medicinal chemistry, and fluid sensor etc [10–14]. Aggregate transition from micelle to vesicle can be applied on drug release carrier, for instance, that micelle loads substance into the cavity of vesicle. As a result, the stability of drug delivery system will be improved and it promotes membrane proteins reconstitution into vesicular membranes [15,16].

Generally, the aggregate transition should be achieved precisely with the help of some external stimuli [17], including salt addition, temperature, pH, light, as well as the organic additives in aqueous solutions [18–22]. Among these stimuli, cyclodextrins (CDs) have attracted increasing attention recently for its interesting property of forming host-guest complexes with surfactants. Commonly, methods to achieve structural transition need to be easily controlled and follow a general rule. CDs do provide such a host-guest approach to modulate aggregate transition process [23]. However, seldom studies were investigated on aggregate transition induced by CDs in catanionic systems. Huang et al. investigated regulating effects about CDs to surfactant aggregates [24]. Jiang reported that aggregate transition was achieved successfully by the addition of β-CD in catanionic surfactant aqueous solutions [25]. Further researches about the effects of CDs to phase behaviors in mixed catanionic systems are necessary. CDs can be divided into α-cyclodextrin (α-CD), β-cyclodextrin (β-CD), and γ-cyclodextrin (γ-CD) according to the number of glucose. CDs are oligosaccharides with hydrophobic cavities and hydrophilic outer surface, hydrophobic groups can be included into cavities and form inclusion compounds with high binding constants which property provides the possibility to achieve aggregate transition [26]. In single surfactant solutions, the addition of CDs will break the aggregate structure [27]. While for mixed catanionic surfactant systems, aggregate transition may happen by selective inclusion of surfactants into CDs. After this, the composition of cationic/anionic surfactant systems varies. The phase behavior greatly depends on the composition of the mixed systems in mixed catanionic surfactant solutions, the altered concentration of free surfactants and the ratio of cationic/anionic surfactants make the aggregates morphology different. Between the cationic surfactant and the anionic surfactant, one of them will be prior chosen to form inclusion compounds with CDs due to size matching or some other factors. The selective inclusion of surfactants into CDs has a direct impact on the composition of mixed catanionic surfactants systems and the aggregate transition may occur.

Herein, special effect of CDs on phase behaviors in mixed catanionic surfactant solutions is studied in this work. The 1-hexadecyl-3-methylimidazolium chloride (C_{16}mimCl) and sodium oleate (NaOle) are used in this work, which are cationic surfactant and anionic surfactant respectively. We expect that the aggregate transition will be observed in C_{16}mimCl-NaOle mixed solutions by the effect of β-CD, which provides further comprehension of aggregate transition induced by external stimulus and widen their applications.

2. Experimental

2.1. Materials

C_{16}mimCl was synthesized in our laboratory. The synthesis and purification process were described previously [28]. The compounds of 1-methylimidazole and 1-chlorohexadecane were mixed in tetrahydrofuran with a flask, and then refluxed under nitrogen at approximately 75–80 °Cfor 48 h. After that, tetrahydrofuran was removed by rotary evaporator. The target products were cooled to the room temperature and then recrystallized in ethyl acetate at least four times. Finally, C_{16}mimCl products were dried in vacuum dryer for 24 h. NaOle (> 99%) and β-cyclodextrin(β-CD) were purchased from Aladdin Chemistry Co. Ltd. and used as received.

Ultrapure water was used throughout the work.

2.2. Sample preparation and phase behavior transition

About 20 mmol/L C_{16}mimCl and 5 mmol/L NaOle mixed surfactant solutions were first prepared (20 ml). The mixtures were transparent solutions and placed in thermotank at the temperature of 25 °C for 48 h to reach equilibrium. And then, β-CDs with various concentration (1–15 mmol/L) were added into mixed C_{16}mimCl-NaOle surfactant systems gradually. The mixtures were stirred until β-CD was completely dissolved. At first, when the concentration of β-CD was low, the mixed solutions kept intact. With the increase of concentration, slightly bluish solution was observed when the concentration of mixed surfactant solutions reached to 12 mmol/L. Afterwards, the phenomenon became more obvious and the solutions presented bluish. The entire process indicates that the aggregate transition happened which will be demonstrated by a series of experiments.

2.3. Methods

2.3.1. Dynamic light scattering (DLS)

DLS is often employed to characterize the size distribution in solutions. Measurements were carried out with ALV/DLS/SLS-5000 conducting at the temperature of 25 °C. And the scattering angle was fixed at 90 .

2.3.2. Inclusion complex constant measurements

Association constants for β-CD/surfactant inclusion complexes were derived from surface tension measurements. β-CD has an impact on surface tensions of surfactants, C_{16}mimCl and NaOle, at the air/water interface at the room temperature. The association constant is deduced by the following formula [29]

$$\frac{[H]_0}{{}^{b}S_i} = \frac{1}{nK_n} \times \frac{1}{{}^{o}S_i} + \frac{1}{n} \tag{1}$$

where, $[H]_0$ is the concentration of β-CD; ${}^0S_i$ is the concentration of surfactant and ${}^bS_i$ is the concentration difference between surfactant solutions in the presence and the absence of β-CD when they have the same surface tensions; n is the ratio of host: guest complexes; Kn is the association constants that we need to calculate.

In the Eq. (1), $\frac{[H]_0}{{}^{b}S_i}$ varies linearly with $\frac{1}{{}^{0}S_i}$, and the slope of the straight line ($\frac{1}{nK_n}$) and the ratio of host: guest complexes (n) are deduced through linear match method. Herein, the association constant Kn can be calculated.

2.3.3. Cryogenic transmission electron microscopy (Cryo-TEM)

The sample was embedded in a vitreous system at 25 °C on a TEM copper grid by blotting the grids with two pieces of filter paper. And then plunging the sample into a reservoir of liquid ethane which was cooled by liquid nitrogen. The frozen hydrated specimen was stored in liquid nitrogen until it was transferred to a cryogenic sample holder. After that the sample was examined with the equipment of JEOL JEM-1400 TEM at 120 kv and the temperature was about −174 °C. Images were recorded on a Gatan multiscan CCD and processed with Digital Micrograph.