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Effect of spacer rigidity on the aggregations of ester containing Gemini surfactants in aqueous solutions: A study of density and fluorescence

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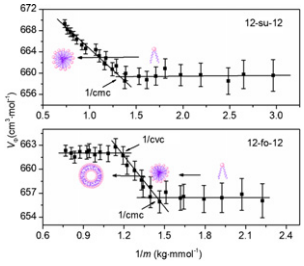
HIGHLIGHTS

- New volumetric method was proposed to detect the second aggregation point.
- The vesicle formation of the surfactant with rigid spacer was confirmed.
- The rigidity of the spacer affects the microenviromental properties greatly.
- Gemini surfactant has larger surface area at micelle interface than at water surface.

GRAPHICAL ABSTRACT



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ABSTRACT

The two Gemini surfactants (1-Dodecanaminium,N,N′-[[(2E)-1,4-dioxo-2-butene-1,4-diyl]bis(oxy-2,1-ethanediyl)]bis[N,N-dimethyl-,bromide)(12-fo-12) and (1-dodecanaminium,N,N′-[(1,4-dioxo-1,4-butanediyl)bis(oxy-2,1-ethanediyl)] bis[N,N-dimethyl-, bromide) (12-su-12), which have very similar structure but bearing rigid and flexible spacers respectively, and their monomeric counterpart 1-dodecanaminium, N-[2-(acetyloxy)ethyl]-N,N-dimethyl-, bromide (DTAAB) were synthesized and their aggregation behaviors in aqueous solutions were studied by measurements of the density and fluorescence. From the density measurements, the vesicle formation of 12-fo-12 was confirmed and the volumetric properties of the aggregates were obtained. By using fluorescence methods, the micropolarity, the steady-state anisotropy and the aggregation number in the micelles were measured. It was found that the rigidity of the spacer affected the microenvironmental properties significantly. The aggregation numbers were used to compare with those calculated from the geometric properties of the micelles by a simple geometry model, which showed good consistence with each other except for the calculations involving the surface area of the headgroup for the 12-su-12 system. It indicated that the surface area of 12-su-12 at the water–micelle interface was significantly larger than that at the water–air interface.

1. Introduction

It has been generally recognized that the thermodynamic studies of properties of surfactants in aqueous solutions, such as the activity, the enthalpy change, the volume property and the electrical conductivity, etc are important to understand their behaviors in aqueous solutions. These quantities are indispensable to test various theories and models of surfactant systems and are the guidelines for their practical applications. The volumetric properties such as the apparent molar volume V_Φ or the partial volume of surfactant in the aqueous solution is one of the most important physicochemical quantities; however compared to other properties, the studies on the volume property of the surfactant solutions are rather limited.

The volumetric property is supposed to be sensitive to the structure change of the surfactants in solutions, because the structure

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change must alter the parking parameter resulting in the change of the average volume occupied by a surfactant molecule/ion in the aggregate [1,2]. This sensitivity seems to be more general for various surfactant systems and it has been used to determine the critical micelle concentration (cmc) and the second critical aggregation concentration (scac) by examining the variation of the apparent molar volume or the partial molar volume of the surfactant with the concentration; however the scac was seldom detected with reliable precision [3,4]. Rosenholm [5] proposed a formulism for determination of the cmc by the measured apparent molar volumetric data (V_Φ) for surfactant solutions based on a pseudo-phase separation model:

$$V_\Phi = V_\Phi^{mic} + \frac{cmc}{m}(V_\Phi^{mon} - V_\Phi^{mic}) \quad (1)$$

for $m \geq$ cmc, where $V_\Phi^{mon}$and $V_\Phi^{mic}$are the apparent molar volumes of the monomer surfactant and the surfactant in the micelle respectively; m is the molality of the surfactant; for $m \leq$ cmc,

$$V_\Phi = V_\Phi^{mon} \quad (2)$$

and V_Φ keeps almost unchanged. This method has been successfully used in determination of the first cmc of some surfactant systems [6–8] and has an additional advantage to provide the volumetric properties of the monomer and the micelle for surfactants. However, to our best knowledge, this method has not been used to detect the second aggregate formation. As it is well known that the density of solutions may be measured by a vibrating tube density meter with a precision of 10^{-6} g ml^{-1}, which is capable to give an apparent molar volume or a partial molar volume of a solute in a surfactant solution with an accuracy about 0.3% at diluted concentration, thus it is possibly to be a more advantageous technique in detection of the second aggregation in the surfactant systems.

The microenvironment of the aggregates formed by surfactants is another important physicochemical property of the aggregates which plays a crucial role in practical applications such as functional materials [9–11], drug delivery [12] and micelle catalysis [13]. In the past decades, the microenvironmental properties of different aggregates have received much attention due to the development of the fluorescence technique, which is a powerful tool to study microheterogeneous systems.

Recently we reported the aggregation behaviors of two Gemini surfactants that differ only at the rigidity of the spacers [14], namely (1-dodecanaminium,N,N′-[(1,4-dioxo-1,4-butanediyl)bis(oxy-2,1-ethanediyl)] bis[N,N-dimethyl-, bromide) (12-su-12) and (1-Dodecanaminium,N,N′-[[(2E)-1,4-dioxo-2-butene-1,4-diyl]bis(oxy-2,1-ethanediyl)]bis[N,N-dimethyl-,bromide)(12-fo-12), and their monomeric counterpart 1-Dodecanaminium, N-[2-(acetyloxy)ethyl]-N,N-dimethyl-, bromide (DTAAB), the structures of which are shown in Fig. 1. We measured the cmc by various methods and determined the size and the morphology of the aggregates in the surfactant aqueous solutions by DLS and transmission electron microscopy for each of the above systems and found that 12-su-12 only formed spherical micelles in the concentration range studied, while 12-fo-12 formed micelles first and then the micelles quickly grew up to form vesicles; however none of the measurement of the surface tension, the measurement of the conductivity, or isothermal titration calorimetry (ITC) was capable of indentifying the difference between the critical vesicle concentration (cvc) and the cmc. From our previous experimental results we also deduced that the surface area occupied by a 12-su-12 molecule at the water–micelle interface is significantly larger than that at the water–air interface [10].

In the present paper, we propose a volumetric method and use the fluorescence techniques to get more insights into the differences of the aggregation behaviors of the above surfactants in their aqueous solutions and to confirm previous findings.

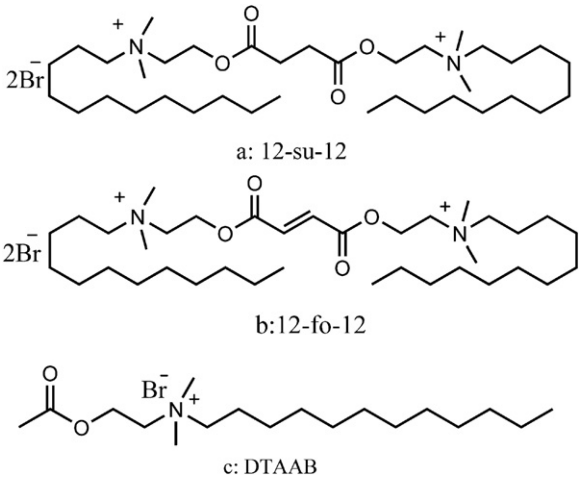

Fig. 1. Chemical structures of 12-su-12 (a), 12-fo-12 (b) and DTAAB (c).

2. Experimental

2.1. Materials

The surfactants were synthesized and purified as previously reported [10]. Dodecyltrimethylamonium bromide (DTAB, mass purity >99%) and cetyltrimethylammonium bromide (CTAB, mass purity >99%) were purchased from J&K Chemical Ltd. and Sinopharm Chemical Reagent Co. Ltd., respectively; sodium bis(2-ethylhexyl)sulfosuccinate (AOT, mass purity >99%), pyrene (mass purity >98%), 1-dodecylpyridinium chloride (DPC, mass purity >98%) and 1,6-diphenyl-1,3,5-hexatriene (DPH, mass purity >98%) were purchased from Sigma–Aldrich. All chemicals were used as received except for AOT, which was kept over phosphorus pentoxide under vacuum for a week before use. Double distilled water was used in preparations of all surfactant solutions.

2.2. Density measurement

The densities of the surfactant solutions were measured using a vibrating tube density meter supplied by Anton Paar (Model DMA-5000 M) with automatic viscosity correction. The temperature in the sample cell was regulated to ±0.001 K by a Peltier unit and measured by the built-in platinum resistance thermometer with an accuracy of ±0.01 K and a repeatability of ±0.001 K. The accuracy and the repeatability in the density measurement were $\pm 5 \times 10^{-6}$ g ml^{-1} and $\pm 1 \times 10^{-6}$ g ml^{-1}, respectively. The more detail description of the apparatus and the procedure for density measurement was reported previously [15]. The precision in determination of the density was checked by repeating the measurements of the densities of freshly prepared solutions and found to be about $\pm 2 \times 10^{-6}$ g ml^{-1}.

The apparent molar volume V_Φ was calculated from the density data by [16]

$$V_\Phi = \frac{M}{\rho} + \frac{10^3(\rho_0 - \rho)}{m\rho_0\rho} \quad (3)$$

where M is the molecular weight of the surfactant, ρ and ρ_0 (g ml^{-1}) are the densities of the solution and the water respectively, m (mol kg^{-1}) is the molality of the surfactant.

2.3. Steady-state fluorescence

The steady-state fluorescence measurements were taken using a fluorimeter (Model FLS 920) supplied by Edinburgh Instrument. The fluorimeter was equipped with a 450 mW Xe arc lamp and a