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Interactions between gemini surfactant alkanediyl-α,ω-bis(dodecyldimethylammonium bromide) and polyelectrolyte NaPAA

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Abstract

Interactions between cationic gemini surfactant alkanediyl-α,ω-bis(dodecyldimethylammonium bromide) (12-n-12, $n = 3, 4, 6$) and oppositely charged polyelectrolyte sodium polyacrylate (NaPAA) in aqueous solution have been investigated by measuring fluorescence, conductivity, UV–vis transmittance, dynamic lighting scattering, and transmission electron microscopy. Micelle-like structure and 12-n-12/NaPAA complex are observed to form due to the electrostatic and hydrophobic interactions, and the effective diameter of the complex reduces with increasing 12-n-12 concentration. The microstructures of 12-n-12/NaPAA solution determined from fluorescence and electron microscopy measurements are in good agreement. The spacer length is found to play an important role in the interactions of 12-n-12 with NaPAA.

Keywords: Gemini surfactant; Polyelectrolyte; Interaction; Microstructure; Spacer length

1. Introduction

In many industrial processes and products, such as water treatment, detergency and oil recovery, ionic surfactant/polyelectrolyte solutions are widely used [1]. Upon mixing with an oppositely charged polyelectrolyte, ionic surfactant aggregates into micelle-like structure in the vicinity of polyion, and forms complex intimately associated with polyion [2] at a very low critical aggregation concentration (CAC), which is usually a few orders of magnitude lower than the critical micellization concentration (CMC) of the free surfactant. This is attributed primarily to the strong electrostatic interaction between surfactant and polyelectrolyte, as well as to the hydrophobic interaction between surfactant tails. The participation of polyelectrolyte in aggregation reduces the repulsive interaction between the ionic head groups of surfactant, and consequently, the polyelectrolyte-induced micelle is more stable and densely packed than the free micelle [3,4]. The formation of complex leads to marked changes in various properties of the surfactant/polyelectrolyte solution, which can be measured using a variety of techniques such as surface tension [5,6], dye solubilizate [5,7], binding isotherm [8,9], rheology [10,11], fluorescence [3,4,10,12], NMR [13,14], and SANS [15]. A large number of factors have been found to be important in the interactions between ionic surfactant and polyelectrolyte, including the hydrocarbon chain length of surfactant [3], the chain flexibility of polyelectrolyte [16], the concentration [16], temperature [16], pH [17], and the addition of salt [3].

Gemini surfactants are a new family of amphiphilic molecules and have stimulated extensive interest with stronger surface activity, better solubilizing, wetting, foaming, and lime-soap dispersing capability than the conventional surfactants [18]. A gemini is a dimeric surfactant consisting of two identical amphiphilic moieties (twin) covalently joined by a spacer group at or close to the ionic head groups [19]. The spacer group increases the hydrophobicity of the gemini sur-

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factant, and results in a CMC far below that of the monomeric analogue. The spacer group also governs the separation distance between the head groups, and influences the packing geometry and mobility of the surfactant. Several experimental studies have demonstrated that the spacer group plays a key role in the properties of gemini surfactants [20–24].

Compared to the conventional monoquaternary ammonium counterpart, the interactions of gemini surfactant with polyelectrolyte are less understood. Only recently have there been a few such experimental studies, notably by Pisárčik et al. [25–27]. They investigated the properties of cationic gemini surfactant with sodium hyaluronate (NaHA) using different techniques including viscosity and surface tension measurement, static and dynamic light scattering. Their results showed a nonlinear behavior of viscosity, a decrease in surface tension, and an increase in the molecular weight and aggregate size with increasing surfactant concentration. Zana and Benrraou [28] demonstrated that a dimeric gemini surfactant interacts with a polyanion much more strongly than the corresponding conventional monomeric surfactant. Wang et al. [29] revealed the addition of NaBr has little effect on the CAC between cationic gemini surfactant and polyelectrolyte. The interactions of DNA as a biologically relevant polyelectrolyte with gemini surfactants have been also investigated. Upon addition of gemini surfactant, DNA was found to undergo a transition from random coil to globule [30]. In the presence of synthetic dilauroylophosphatidylcholine, DNA and gemini surfactant were observed to form a condensed lamellar phase with ordered DNA monolayers intercalated between lipid bilayers [31]. The size and structure of DNA/gemini surfactant aggregates were measured, and an anomaly in the growth of aggregate was found [32].

In this work, with fluorescence emission spectroscopy, UV-transmittance, and conductivity measurements, we have studied the interactions between cationic gemini surfactant alkanediyl-α,ω-bis(dodecyldimethylammonium bromide) [$C_{12}H_{25}$-$(CH_3)_2N^+$–$(CH_2)_n$–$N^+(CH_3)_2C_{12}H_{25}$]$2Br^-$ (12-n-12) and anionic polyelectrolyte sodium polyacrylate [–CH_2–CH(CO-ONa)–] (NaPAA) in aqueous solution at 25 °C. In addition, dynamic light scattering and transmission electron microscopy measurements were carried out to detect the microstructures of the 12-n-12/NaPAA solution with various 12-n-12 concentrations. By changing n from 3, 4 to 6, the effect of spacer length for a homologous series of 12-n-12 on the interaction with NaPAA was examined.

2. Experimental materials and methods

2.1. Materials

Gemini surfactants 12-n-12 ($n = 3, 4, 6$) were prepared in our lab by a reaction of α,ω-dibromoalkanes with N,N-dodecyldimethylamine [33]. Polyelectrolyte NaPAA ($\bar{M}_w = 5100$) and pyrene as the fluorescence probe were purchased from Aldrich Chemicals, and used as received. Deionized H_2O was treated with $KMnO_4$ to remove oxidable impurities and redistilled. The surface tension of H_2O is 71.81 mN m^{-1}, and the electrical conductivity is 1.1 ± 0.1 μS cm^{-1}.

2.2. Methods

We first prepared 10^{-4} and 0.1 M 12-n-12 aqueous solution, and 10^{-3} M NaPAA aqueous solution, and then mixed them with pure H_2O to obtain various 12-n-12/NaPAA samples with a constant NaPAA concentration as of 10^{-4} M.

2.2.1. Fluorescence emission spectroscopy

Samples for fluorescence emission spectroscopy were prepared by mixing pyrene stock solution with surfactant/polyelectrolyte solution, and allowed to stand for 3 day to equilibrate. Samples with precipitates appeared were centrifuged at 12,000 rpm for 20 min to remove the precipitates. The pyrene stock solution was prepared by dissolving pyrene in hot water up to saturation, cooled to 25 °C, and filtered. The concentration of pyrene in the solution was determined to be 6.53×10^{-7} M [27]. Emission spectrum ($\lambda_{EX} = 335$ nm) of the mixed solution was recorded with recorded with F4500 (HITACHI) at 25 °C. A typical emission spectrum has five peaks at 373, 379, 384, 390, and 397 nm, respectively. The ratio of the first to the third vibronic peaks I_1/I_3 is sensitive to the local environment of pyrene [34–36].

2.2.2. Conductivity

The electrical conductivity of 12-n-12 solution in the absence or presence of 10^{-4} M NaPAA was measured using a conductivity meter (DDS-307, China) at 25 °C in a thermostated water bath.

2.2.3. UV–vis transmittance

Transmittance of 12-n-12/NaPAA solution and 10^{-4} M pure NaPAA solution was recorded using a UV-spectrophotometer (UV-2450, SHIMADZU) at room temperature about 22–25 °C. All measurements were made in a quartz cuvette (1 cm width) in the wavelength range 190–800 nm using water as a reference.

2.2.4. Dynamic light scattering

Samples for scattering were prepared with surfactant concentration c_s in the range of $2–30 \times 10^{-5}$ M in the presence of 10^{-4} M NaPAA. The temperature of scattering cell was controlled at 25 °C. Nano-ZS (MALVERN) using backscatter detection was used for scattering measurements with a detecting angle of 173°, and the data were analyzed with the software supplied for the instrument.

2.2.5. Transmission electron microscopy

Samples were prepared by freeze-etching technique (Balzers BAF-400D, Liechtenstein) and negative-staining with uranyl acetate. The microstructure of mixing solution was determined using a transmission electron microscope (JEM-100CX, Japan).

3. Results and discussion

3.1. Micropolarity

I_1/I_3 in the fluorescence spectrum reflects the intensity of micropolarity around pyrene, and the change in I_1/I_3 can be