

Salt effect on the interactions between gemini surfactant and oppositely charged polyelectrolyte in aqueous solution

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Received 17 July 2006; accepted 10 October 2006

Available online 20 November 2006

Abstract

The effect of alkali halides (NaBr, NaCl, KCl) on the interactions between the cationic gemini surfactant hexylene-1,6-bis(dodecyldimethylammonium bromide) (12-6-12) and the anionic polyelectrolyte sodium polyacrylate (NaPAA) in aqueous solution has been investigated by fluorescence emission spectroscopy, UV transmittance, zeta potential, and transmission electron microscopy (TEM). With increased addition of NaBr, a counterbalancing salt effect on the critical aggregation concentration (CAC) is observed. At low concentrations, NaBr facilitates the formation of micelle-like structures between surfactant and polyelectrolyte and results in a smaller CAC. At high concentrations, NaBr screens the electrostatic attraction between surfactant and polyelectrolyte and leads to a larger CAC. Upon the formation of micelle-like structures at high surfactant concentrations, the addition of NaBr is favorable for larger aggregates. The microstructure detected by TEM show that a global structure is generally formed in the presence of NaBr. The interactions also depend on ion species. Compared to NaBr, the addition of NaCl or KCl yields a smaller CAC. © 2006 Elsevier Inc. All rights reserved.

Keywords: Gemini surfactant; Polyelectrolyte; Interactions; Salt; Alkali halide

1. Introduction

Currently the interactions of ionic surfactants with polyelectrolytes are the subject of extensive investigation due to their wide applications in many industrially important processes and products, such as water treatment, detergency, and oil recovery [1]. Ionic surfactants can strongly interact with oppositely charged polyelectrolytes to form micelle-like structures 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 [2–6]. This is attributed to the electrostatic attraction between the surfactant and the polyelectrolyte, as well as to the hydrophobic interaction between the surfactant tails. In a surfactant/polyelectrolyte solution, the addition of salt is expected to have a significant effect on their interactions.

It has been shown that the addition of salt reduces the strength of electrostatic interaction between surfactants and polyelectrolytes, which results in a larger CAC [7–12]. Moreover, the addition of a sufficiently large amount of salt can completely screen the electrostatic interaction and prevent the formation of polyelectrolyte/surfactant complexes [13–16]. Nevertheless, the effect of added salt in the surfactant/polyelectrolyte solution is rather complicated. In addition to the reduction of electrostatic interaction, stabilization of surfactant aggregates was reported [6]. As a consequence, a decrease of CAC in the surfactant/polyelectrolyte solution can be expected by adding salt, e.g., in sodium carboxymethylcellulose and dodecyltrimethylammonium bromide with the addition of NaBr [17].

While many studies have been devoted to salt effects on interactions between single-chain surfactants and oppositely charged polyelectrolytes, salt effects on interactions of gemini surfactants with polyelectrolyte are less understood. Only recently was a study reported on the effect of NaBr on complex formation between a cationic gemini surfactant and an anionic

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polyelectrolyte, and the CAC was found to be insensitive to the added NaBr [18]. A gemini is a dimeric surfactant consisting of two identical amphiphilic moieties (twins) covalently joined by a spacer group at or close to the ionic head groups [19]. As a new family of amphiphilic molecules, gemini surfactants have stimulated extensive interest with stronger surface activity and better solubilizing, wetting, foaming, and lime–soap dispersing capability than conventional surfactants [20]. Due to the unique features of gemini surfactants, the effect of salt is expected to be different from that on traditional surfactants. More systematic investigations are needed to further understand complex formation between gemini surfactants and polyelectrolytes.

We have recently examined the interactions between the gemini surfactant alkanediyl- α,ω -bis(dodecyldimethylammonium bromide) (12- n -12, $n = 3, 4, 6$) and the anionic polyelectrolyte sodium polyacrylate (NaPAA) [26]. In this work we further examine the effect of added alkali halides (NaBr, NaCl, KCl) on the interactions between 12-6-12 and NaPAA in aqueous solution at 25 °C. Fluorescence emission spectroscopy and UV transmittance were measured. The effect of salt on the microstructure change of the 12-6-12/NaPAA complex induced by increasing surfactant concentration with zeta potential was determined. The microstructure of mixtures in the presence of NaBr was detected by negative-staining and transmission electron microscopy. The interactions for different salt concentrations and ion species were also studied.

2. Experimental materials and methods

2.1. Materials

The gemini surfactant 12-6-12 was prepared in our lab by a reaction of 1,6-dibromohexane with N,N -dodecyldimethylamine [21]. Polyelectrolyte NaPAA ($\bar{M}_w = 5100$) and pyrene as the fluorescence probe were purchased from Aldrich Chemicals and used as received. Sodium bromide (NaBr), sodium chloride (NaCl), and potassium chloride (KCl) were analytical grade without further treatment before use. Deionized H₂O was treated with KMnO₄ and redistilled.

2.2. Methods

2.2.1. Fluorescence emission spectroscopy

Samples were prepared by mixing a pyrene stock solution with 12-6-12/NaPAA in the absence or presence of salt and allowed to stand for 3 days to equilibrate. 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 was determined to be 6.53×10^{-7} M [22]. The emission spectrum ($\lambda_{EX} = 335$ nm) of the mixed solution was recorded by F4500 (HITACHI) at wavelengths between 350 and 450 nm at a room temperature of about 24–26 °C. The slit width of excitation is 5 nm, and the slit width of emission is 2.5 nm. 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 peak I_1/I_3 is sensitive to the local environment of pyrene [23–25].

2.2.2. UV-vis transmittance

Transmittance of 10^{-4} M pure NaPAA solution, 12-6-12/NaPAA, and 12-6-12/NaPAA/salt solution was recorded using a UV spectrophotometer (UV-2450, Shimadzu) at room temperature of about 24–26 °C. The slit width is 2 nm.

2.2.3. Zeta potential

Nano-ZS (MALVERN) using laser Doppler velocimetry and phase analysis light scattering was used for zeta potential measurement. The temperature of the scattering cell was controlled at 25 °C. A light scattering angle of 17° was combined with the reference beam, and the data were analyzed with the software supplied for the instrument.

2.2.4. Transmission electron microscopy

Samples were prepared by negative staining with uranyl acetate. The microstructure of the mixture was determined using a transmission electron microscope (JEM-100CX, Japan).

3. Results and discussion

3.1. Effect of NaBr

The I_1/I_3 in the fluorescence spectrum reflects the intensity of the micropolarity around pyrene, and a change in I_1/I_3 can be used to detect the formation of micelles and aggregates. Fig. 1 shows I_1/I_3 as a function of surfactant concentration c_s in 12-6-12/NaPAA/NaBr solution at various NaBr concentrations. At a low c_s , I_1/I_3 is nearly a constant, which implies that no hydrophobic microdomain is formed in the solution. A later sharp decrease in I_1/I_3 reflects the CAC, the onset for the formation of micelle-like structures near the binding site of the polyion chain. Due to the strong attraction between the oppositely charged surfactant and polyion, the CAC is much lower than the CMC in the absence of polyelectrolyte, as we observed previously [26]. Apparently, in the presence of 0.002 M NaBr, the CAC becomes smaller. The decrease in the CAC is much

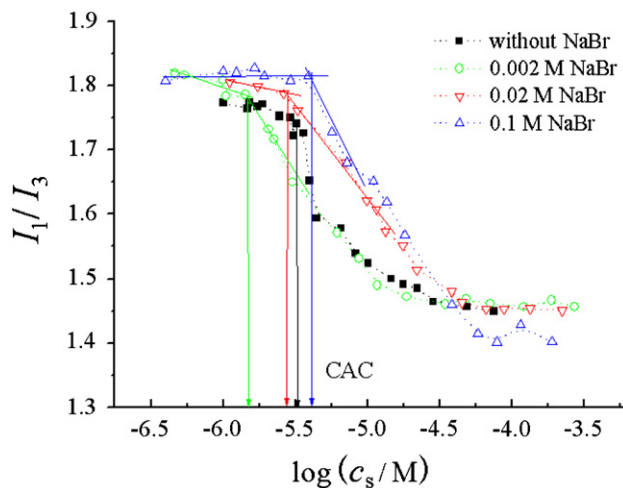


Fig. 1. Surfactant concentration dependence of the micropolarity in 12-6-12/NaPAA/NaBr solution at various NaBr concentrations ($c_{\text{NaPAA}} = 10^{-4}$ M). The curves are drawn to guide the eye.

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