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Self-assembled Gemini surfactant film-mediated dispersion stability

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Abstract

The force–distance curves of 12-2-12 and 12-4-12 Gemini quaternary ammonium bromide surfactants on mica and silica surfaces obtained by atomic force microscopy (AFM) were correlated with the structure of the adsorption layer. The critical micelle concentration was measured in the presence or absence of electrolyte. The electrolyte effect (the decrease of CMC) is significantly more pronounced for Gemini than for single-chain surfactants. The maximum compressive force, F_{max}, of the adsorbed surfactant aggregates was determined. On the mica surface in the presence of 0.1 M NaCl, the Gemini micelles and strong repulsive barrier appear at surfactant concentrations 0.02–0.05 mM, which is significantly lower than that for the single C_{12}TAB (5–10 mM). This difference between single and Gemini surfactants can be explained by a stronger adsorption energy of Gemini surfactants. The low concentration of Gemini at which this surfactant forms the strong micellar layer on the solid/solution interface proves that Gemini aggregates (micelles) potentially act as dispersing agent in processes such as chemical mechanical polishing or collector in flotation. The AFM force–distance results obtained for the Gemini surfactants were used along with turbidity measurements to determine how adsorption of Gemini surfactants affects dispersion stability. It has been shown that Gemini (or two-chain) surfactants are more effective dispersing agents, and that in the presence of electrolyte, the silica dispersion stability at pH 4.0 can also be achieved at very low surfactant concentrations (∼0.02 mM).

Keywords: Atomic force microscopy; Surface forces; Micelles; Gemini surfactants; Surface tension; Suspension stability

1. Introduction

Surfactant adsorption onto solid surfaces is a phenomenon of vital importance to various industrial processes ranging from ore flotation, lubrication, and paint technology to enhanced oil recovery [1]. At interfaces, the self-assembly process is influenced by surfactant–surfactant, surfactant–surface, surfactant–solvent, and solvent–surface interactions. These interactions include the free energy of adsorption, roughness, surface heterogeneities, charge, and crystallinity [1].

Atomic force microscopy (AFM) has been used in the past to directly image and measure forces resulting from surfactant adsorption at the solid/liquid interface [2–8]. Adsorbed surfactant molecules can form bilayers, semi-cylinders, full cylinders, semi-spheres and full spheres (see Fig. 1), and it has been found that the surface has an important influence in controlling the aggregate structure [2–4, 7,8]. For example, in quaternary ammonium surfactant systems, mica leads to the formation of full cylindrical micelles while amorphous silica leads to full spheres [7,9]. Force–

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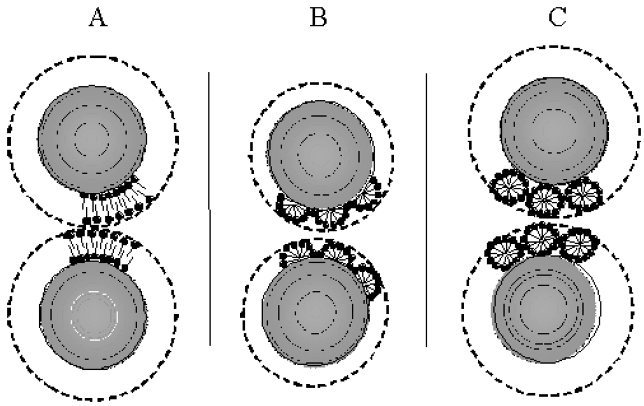

Fig. 1. Schematic diagram showing the possible structures of surfactants adsorbed at the solid/liquid interface. (A) Bilayer formation, (B) semi-cylindrical micelles or semi-spheres, (C) full cylinders or spheres.

distance curves of C_nTAB samples were measured in a fluid cell using AFM contact mode. It was proposed by Patist [10] and Adler et al. [2] that the maximum compressive force of the adsorbed surfactant aggregates, F_{max}, is directly related to the stability of solid/liquid dispersions. It is clearly demonstrated that as the C_{12}TAB surfactant concentration increases from 8 to 10 mM, the interaction (repulsive) force between the AFM tip and the silica substrate increases significantly and concurrently with the onset of suspension stability [2,3].

It was found that the maximum repulsive force, F_{max}, increases with the surfactant alkyl chain length. Adler et al. [2] also found additional factors influencing the magnitude of the maximum repulsive force, F_{max}, including the type of substrate used as well as the presence of added co-surfactant. For example, the repulsive forces are higher and observed at lower concentrations for mica as compared to silica. This is possibly due to the crystalline nature of the mica substrate. Moreover, the addition of small amounts of SDS to a C_{12}TAB solution significantly increases the maximum repulsive force [2]. Similarly to the increased stabilization of bulk micelles caused by charge repulsion, addition of SDS to a C_{12}TAB solution can greatly enhance stability of surfactant film at the solid/liquid interface due to the Coulombic interactions.

Each of the above methods increases the maximum repulsive force, F_{max}, between the AFM tip and the solid substrate via the surfactant–surfactant, surfactant–surface, surfactant–solvent, and solvent–surface interactions mentioned previously. Another way to increase the maximum repulsive force between particles with adsorbed surfactants is by changing the nature of the surfactant itself, such as in the case of Gemini surfactants. A Gemini (or two-chain) surfactant is a molecule composed of two identical hydrophilic head groups and two hydrophobic tail groups (Fig. 2). It is very similar to two single-chain surfactants linked covalently by a spacer group. The spacer group can vary in length and chemical structure, be flexible or rigid, and be hydrophilic or hydrophobic [11]. Gemini surfactants have three unusual

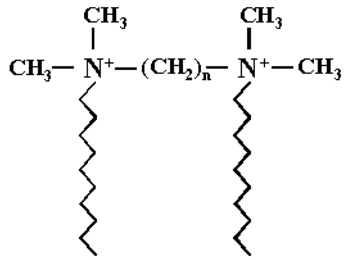

Fig. 2. Molecular schema of Gemini surfactants.

solution and interfacial properties. First, Gemini surfactants have critical micelle concentration (CMC) values one to two orders of magnitude lower than that of corresponding single-chain surfactants [12]. Second, they are much more efficient than their corresponding monomeric surfactants at decreasing the surface tension of water [13,14]. For example, the C_{20} (i.e., surfactant concentration required for lowering the surface tension of water by 20 mN/m) for 12-2-12 Gemini is 0.0083 wt%, while that for C_{12}TAB is 0.25 wt% [15]. Finally, Gemini surfactants with short spacers form large, threadlike aggregates, while the single-chain equivalent forms only small spherical micelles. For example, 12-2-12 Gemini has been shown to form long wormlike micelles at a concentration as low as 1.5 wt% (about 25 mM) [16]. As a result, aqueous solutions of these Gemini surfactants have a very high viscosity at relatively low surfactant concentration and show shear-induced viscoelastic behavior at concentrations as low as 0.7 wt% [17].

Along with the properties mentioned above, Gemini surfactants have been shown to have better solubilizing, wetting, and foaming properties compared to conventional surfactants [12]. Furthermore, the Krafft temperatures of Gemini surfactants with hydrophilic spacers are very low [12], allowing these surfactants to be used in cold water. Finally, Gemini surfactants have been shown to have interesting biological effects. For example, the alkyltrimethylammonium bromide-based Gemini surfactants induce various biological effects such as an inhibition of bacterial activity [18–20] and of photosynthesis [21].

The unusual characteristics listed above make Gemini surfactants a very interesting topic of study. Force/distance curves for 12-n-12 Gemini surfactant on the mica and silica surfaces have been reported in Ref. [22] for two concentrations of Gemini without additional electrolyte. Analysis of obtained results [22] is given only for relatively long distances. The authors drew a conclusion that the measured forces can be attributed to the ion-electrostatic force. However, to reach this conclusion the authors had to assume a tip radius to be of 1000 nm in calculations, while the actual tip radius used was near 20 nm. Therefore, a further investigation of mechanical characteristics of the surface layer of Gemini micelles should be continued. In the present paper, we investigated the aggregation behavior of selected quaternary ammonium Gemini surfactants as dispersants. The results were compared to their single-chain counterparts onto