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^{1}H NMR study of micelles formed by mixture of nonionic *n*-dodecyl-*β*-D-maltoside and cationic gemini surfactants

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ABSTRACT

The relative arrangement and interaction of the cationic butane-1,4 bis(dodecyl dimethyl ammonium chloride) gemini (12–4–12) with nonionic sugar-based surfactant *n*-dodecyl-*β*-D-maltoside (DM) was studied by NMR techniques. It is shown that the methylene group next to the ammonium head in the gemini is close to the penultimate sugar ring of DM in their mixed micelles, and the hydrophobic chain of DM molecule and the two hydrophobic chains of 12–4–12 gemini are side by side in the interior of the micellar core. The size of the mixed micelles is largely dependent on the DM composition at fixed total surfactant concentrations. At fixed DM concentration, the interaction between DM and 12–4–12 gemini increases gradually with decrease in DM/12–4–12 ratio from 1:1 to 1:4. At higher 12–4–12 gemini ratios of 1:6 and 1:8.5, the intermolecular interaction starts to decrease gradually, implying the intramolecular interaction is more dominant than intermolecular interactions in the mixed micelles. NMR results suggest that relatively strongest intermolecular interactions in the mixed micelles of DM and 12–4–12 gemini exist at DM/12–4–12 mixing ratio of 1:4.

1. Introduction

Many mixed systems of nonionic–ionic are widely used in many biological and industrial processes, because of their synergistic performance [1–4]. Properties of mixed surfactant micelles in aqueous solutions have been studied in the past by various spectroscopic methods, including proton nuclear magnetic resonance (^{1}H NMR) [5–8], for both theoretical and practical reasons. In our previous work, non-ideal mixing behavior of mixed systems of *n*-dodecyl-*β*-D-maltoside (DM) with other anionic, cationic and nonionic surfactants has been observed and the effects of surfactant interaction on mixed micellization have been studied [9–11]. The micellar size, shape, and aggregation number of dodecyl maltoside have been studied by small-angle neutron scattering (SANS) technique [12–14] and nuclear magnetic resonance [15]. The interactions between DM and some cationic surfactants have been reported before [16–18], and it was suggested that there is stronger surfactant interactions between cationic gemini and alkylmaltoside, alkylglucoside surfactants than the comparable conventional cationic surfactants. The mixed systems mostly resulted in negative interaction parameters (β), indicating attractive interaction between surfactant molecules in mixed micelles. However the relative arrangement, interaction sites and optimum mixing ratios of the molecules of the two surfactants in the mixed micelles has not been reported. Here, we present results for mixed micelles of DM and cationic 12–4–12 gemini, and the effects of mixing ratio on micellar structure using NMR technique. The results give important information at molecular level on surfactant interactions and mixed micellization behavior, as well as the relative arrangement of different surfactants in their mixed micelles.

2. Materials and methods

Cationic gemini surfactant, butane-1,4 bis(dodecyl dimethyl ammonium chloride), represented here as 12–4–12, was synthesized by the reaction of 1,4-dichlorobutane with corresponding alkyl dimethyl amine [19,20]. After solvent evaporation, crude product was purified by repeated recrystallization in ethanol/ethyl acetate solvent. The final product was stored in a desiccator under vacuum for the complete removal of the solvent. Besides NMR, the purity of 12–4–12 gemini was also confirmed by the absence of a minimum in its surface tension curve, see Fig. 1. Surface tension results yielded a value of 1.5 mM for the critical micelle concentration of cationic 12–4–12 gemini.

Nonionic sugar-based surfactant *n*-dodecyl-*β*-D-maltoside (DM), >95% purity by TLC, was purchased from Calbiochem. D_2O of 99.9% deuterated was obtained from Cambridge Isotope Laboratories Inc. They were used as received without any purification. The critical micellar concentration of DM measured by surface tension experiments is 0.18 mM.

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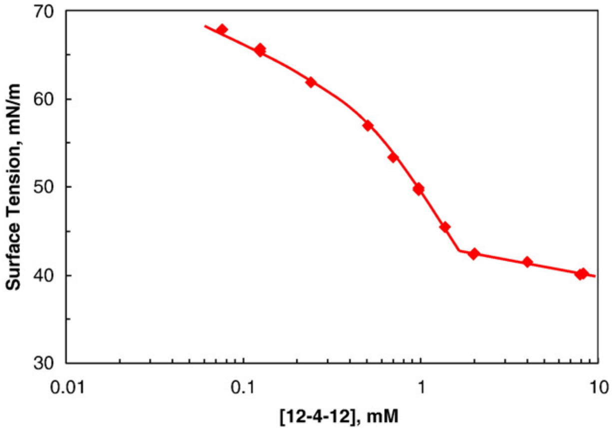

Fig. 1. Surface tension vs. log C plot of 12–4–12 cationic gemini in H_2O (without salt) at neutral pH and 25 °C.

All ^1H NMR measurements were performed in D_2O solutions on a Bruker DMX-500 NMR spectrometer with a ^1H proton frequency of 500.13 MHz at 25 °C. The peaks were referenced with respect to DOH ($\delta = 4.79$ ppm) in D_2O. The NMR self-diffusion experiment is performed with Diffusion Ordered Spectroscopy (DOSY). Inversion recovery and Carr-Purcell-Meiboom-Gill (CPMG) pulse sequences were used for the measurements of spin–lattice relaxation time (T_1) and spin–spin relaxation time (T_2) respectively. 2D NOESY experiments were performed with the standard three-pulse sequence [21]. Mixing time of 30, 50 and 100 ms was chosen. The tested concentrations of DM, 12–4–12 gemini and their mixtures are well above the cmc to ensure formation of surfactant micelles.

3. Results and discussion

^1H NMR spectra of DM and 12–4–12 gemini as well as their mixtures in D_2O are shown in Fig. 2. According to their chemical shifts, protons in DM molecule are differentiated and assigned from numbers 1 to 16, and protons in 12–4–12 gemini from letter *a* to *h*. The corresponding ^1H chemical shifts are illustrated in Fig. 2 and are confirmed by their ^1H COSY spectrum. The ascriptions of proton signals of DM accord with literature [15]. Protons of 13H ($-CH_2$) in DM present two different chemical shift peaks because of its magnetic non-equivalence, which are shown as 13′H and 13″H in 2D NOESY maps. Due to proton exchange with D_2O, no NMR signal from hydroxyl groups in DM is observed. NMR signals of 15H protons in DM and *b*H protons in 12–4–12 from their mixtures overlap each other, due to this obvious overlap of NMR signals, we cannot discuss in details the interactions involving hydrophobic groups, even though hydrophobic chain–chain interactions play an important role in surfactant interactions and micellization.

3.1. The self-diffusion coefficients of the mixtures

Micellar self-diffusion offers a unique way to monitor the size of surfactant micelles [22,23]. NMR self-diffusion measurements of DM, 12–4–12 gemini and their mixtures have been performed to compare the size of their micelles. It should be noted that the observed NMR self-diffusion values are the average of self-diffusion coefficients of all protons in both the two surfactant monomers and micelles, with lower self-diffusion values from surfactant micelles than monomers. As we know, in aqueous solution chemical exchange of molecules between the monomeric surfactant and its micelle is rapid on the NMR time scale. Applying phase-separation model of micelle formation, at concentrations above solution cmc, the monomer concentration is nearly constant, and the calculation of the experimental

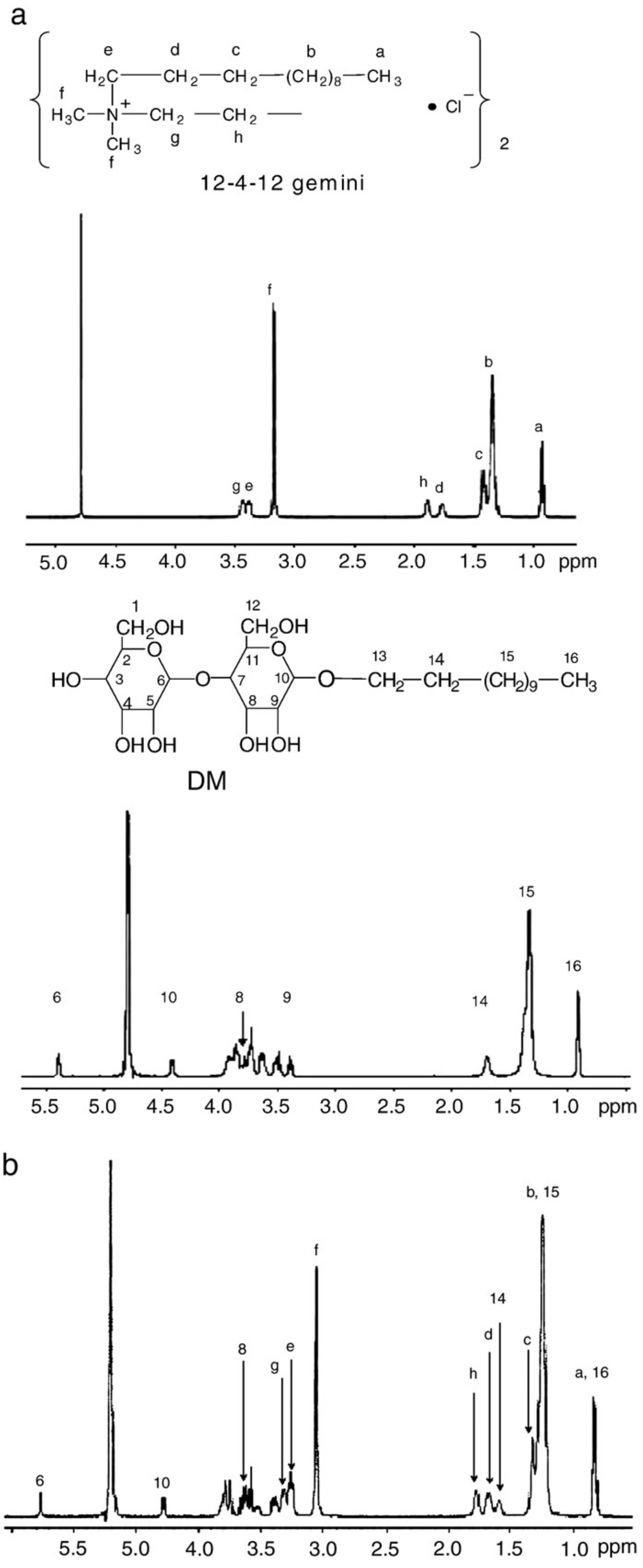

Fig. 2. a. Molecular structures of *n*-dodecyl-β-D-maltoside (DM) and cationic 12–4–12 gemini surfactants, their ^1H NMR spectra in D_2O and the corresponding proton assignments. b. ^1H NMR spectra of mixed system of DM and 12–4–12 in D_2O.