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Aggregation behavior and interface properties of mixed surfactant systems gemini 14-*s*-14/CTABr

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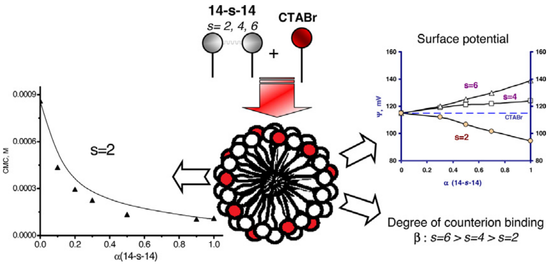
HIGHLIGHTS

- Micelle structure of mixed systems gemini 14-*s*-14/CTABr were experimentally studied.
- Negative deviation from ideal behavior is found for mixed micelles 14-2-14/CTABr.
- Surface potential decreases if molar fraction of gemini surfactant in mixture ≥0.3.
- Degree of counterion binding follows the series 14-6-14 > 14-4-14 > 14-2-14.

GRAPHICAL ABSTRACT



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ABSTRACT

Mixed micellar systems of cationic gemini 14-*s*-14 (*s* = 2, 4, 6) and cationic conventional surfactant cetyltrimethylammonium bromide (CTABr) were investigated. The critical micelle concentrations of mixed micelles measured by surface tension, ion selective probe, and conductivity techniques reveal a synergism in the case of 14-2-14/CTABr mixture. Microenvironment and interface properties were studied using bromide selective electrode and by solubilization of a hydrophobic dye Orange OT, solvatochromic dyes Reichardt's betaine and Methyl Orange. Surface potential values, Ψ, for mixed micelles are calculated using *p*-nitrophenol, and are found to be remarkably low for 14-2-14/CTABr systems. These results provide new information for understanding the effect of gemini surfactant structure on the properties of mixed micelles of dicationic/monocationic surfactants.

1. Introduction

Micellar systems consisting of surfactant mixtures of variable structures are of a high theoretical and industrial interest [1]. Interaction between surfactant molecules in the solution have been widely investigated due to strong interest toward cooperative interaction attributed to the effect of nonideal mixing [2,3]. The synergism results in critical micelle concentrations (*cmc*), which are

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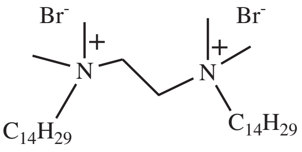
substantially lower than it would be expected from the properties of a single surfactant alone. Nonconventional surfactants may play a crucial role in designing mixed micellar systems with variable aggregation and interfacial properties.

Gemini surfactants form a remarkable class of surfactants possessing a number of unusual properties, namely, abnormally low *cmc*, micellar polymorphism, and propensity to the mesophase formation [4,5]. Studies of mixed micellar systems of gemini with conventional cationic [6–9], anionic [10,11], non-ionic [10], and zwitter-ionic [12] surfactants have been recently reported. A nonideality have been observed for the mixture of dicationic gemini with various nonionic and found to be sensitive to the components structure and pH value for zwitter-ionic amphiphiles [13]. Dicationic dimeric surfactants, alkanediyl-α,ω-bis(dimethylalkylammonium salts (*n*-*s*-*n*, where *n* is number of carbon atoms in each chain, and *s* is number of methylene groups in the spacer), are being widely studied in their mixtures with conventional trimethylammonium analogs. Mixed micellization of 12-2-12 gemini with alkyltrimetylammonium bromide surfactants have been studied by conductivity [8,14], surface tension [15], turbidity [16], fluorometry [17] and cryo-TEM [5] methods. The spacer and surfactant chain length [6,18,19] as well as counterion effects [20] affect micellization of both cationic gemini and their mixed micelles. Synergistic interactions in micelles of 14-*s*-14 gemini with cetylpyridinium bromide are shown to be sensitive to the spacer length [21] and counterion [22] effects. Mixed micelles of cationic gemini with tetraalkylammonium and phosphonium surfactants were investigated to analyze the head group and hydrophobic tail contributions [16].

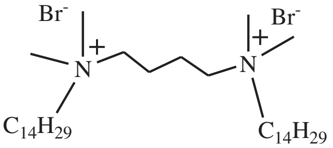
Some applied aspects, including study of the effect of gemini-conventional mixed micelles on solubilization of polycyclic aromatic hydrocarbons [23] and gene delivery [24] have been recently investigated. Micellar effects on acyl transfer processes are shown to be sufficiently affected by the functionalized (zwitter-ionic) monomeric/conventional cationic mixed micelle composition [25–27] whereas much less attention was paid to the deacylation (dephosphorylation) in the mixed gemini-conventional micelles [28–32].

NMR self-diffusion experiment and relaxation time measurements demonstrated that cationic conventional surfactants barely changed the molecule arrangement and thus barely influenced the exchange rate of 14-*s*-14, in contrast to the oppositely charged conventional anionic and non-ionic surfactants [33]. At the same time, those cationic gemini surfactant having tendency to form elongated aggregates at low concentrations (namely, *n*-2-*n* type surfactants) can undergo micellar transformation in the mixed micelles [5], and changing in the micelle morphology follows by changing of the microenvironment of the aggregate. The estimation of the intimate changes occurring in the mixed micelle variation of the added conventional surfactant fraction required comprehensive analysis of the aggregation behavior of the micellar system as well as an insight into the changes at the nanoaggregate interface.

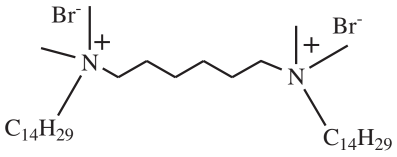
In the present study, we (i) characterize the formation of the mixed micelles of gemini surfactant type 14-*s*-14 (*s* = 2, 4, 6, see structures below) with conventional monocationic surfactant cetyltrimethylammonium bromide (CTABr) with different content of gemini cationic surfactant in mixture, and (ii) analyze the micropolarity and interfacial properties of mixed micelles to demonstrate that the spacer length and surfactant ratio in the system play important role in the properties of the mixed micelle.



14-2-14



14-4-14



14-6-14

2. Experimental

2.1. Materials

Commercially available CTABr, Reichardt's dye, Methyl Orange, *p*-nitrophenol, and Orange OT (all from Sigma–Aldrich) were used without additional purification. Gemini surfactant 14-2-14 was synthesized as described elsewhere [20,34]. The cationic gemini surfactants butanediyl-α,ω-bis(dimethylcetylammonium bromide (14-4-14) and hexanediyl-α,ω-bis(dimethylcetylammonium bromide (14-6-14) were obtained similarly to described by Zana [18]: 1-bromotetradecane was refluxed with *N*,*N*,*N*′,*N*′-tetramethyl-1,4-tetramethylenediamine in acetonitrile (14-4-14), and with *N*,*N*,*N*′,*N*′-tetramethyl-1,6-hexamethylenediamine in dry ethanol (14-6-14). After further purification, the structures of the resulting compounds were identified by elemental analysis and ^{1}H NMR spectroscopy. ^{1}H NMR spectra were recorded by using Bruker AVANCE 600 and Bruker AVANCE II 400 instruments. Surfactant solutions were prepared with doubly distilled water which surface tension has been confirmed to be of 72.0 ± 0.3 mN m^{-1}.

2.2. Instruments and methods

2.2.1. UV–vis spectroscopy

Absorption UV–vis spectra of studied samples were recorded in 10 mm quartz cells using Genesys 10S UV–vis (Thermo Electron) and Specord UV–vis (Analytik Jena) spectrophotometers equipped with a thermostated cell unit. Dyes Reichardt's betaine (RB) and Methyl Orange (MO) were prepared as 1–10 mM stock solutions, added by microsyringe, and used at the concentrations 0.05 mM and 0.01 mM, correspondingly. Surface potential measurements were based on the technique of using micelle-solubilized acid–base indicators [35,36] with *p*-nitrophenol as a probe [37], as described previously [38]. The UV–vis spectroscopy method of critical micelle concentration (*cmc*) determination was performed in accordance with the dye Orange OT solubilization procedure [39]. The measurements of pH were carried out in a thermostatically controlled cell at 25 ± 0.1 °C with Hanna type 211 and Metrohm 744 pH-meters within the accuracy 0.05 pH units.

2.2.2. Conductivity measurements

Conductivity measurements were performed using inoLab 7110 and LF 315 instruments (both WTW). The conductivity (κ) versus total surfactant concentration (C_{tot}) was plotted, and the *cmc* was obtained from the concentration, which corresponds to the intersection of κ extrapolated from the experimental values below and beyond the *cmc*. Since the change of slope was not always very clear, the first derivative [16] was also analyzed.

2.2.3. Surface tension measurements

The surface tension (γ) measurements were performed with a K6 tensiometer (Krüss) using du Noüy ring detachment method at