



Interaction of a cationic gemini surfactant with conventional surfactants in the mixed micelle and monolayer formation in aqueous medium

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ABSTRACT

Mixed micellization and surface properties of binary mixtures of cationic gemini surfactant butanediyl- α,ω -bis(dimethylcetylammmonium bromide) (G4, 16-4-16) with conventional surfactants cetylpyridinium chloride (CPC), sodium bis(2-ethylhexyl)sulfosuccinate (AOT), and polyoxyethylene 10 cetyl ether (Brij56) have been studied using conductometric and tensiometric methods. To explain and compare the results theoretical models of Rubingh, Rosen, Clint, and Maeda have been used to obtain the interaction parameter, minimum area per molecule, surface excess, mixed micelle composition, free energies of micellization and adsorption, and activity coefficients. The activity coefficients and experimental critical micelle concentration (cmc) values are less than unity indicating synergism in micelles as well as at interface. Also, expansion of the minimum area per molecule was observed in the binary systems supported by low values of packing parameter.

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1. Introduction

Gemini surfactants are an interesting class of surfactants that have emerged in recent years—they have two hydrophilic heads connected to two hydrophobic tails separated by covalently bonded rigid/flexible spacer [1]. Their structure, together with their low critical micellar concentration (cmc) values, make them very efficient in reducing surface tension [2,3], leading to potential applications such as detergents, fabric softeners, stronger biological activity, better solubilizing ability, wetting, foaming and lime-soap dispersing properties compared to conventional one tail, one head surfactants [4–8].

With the progress in industrial technology, demands for high performance surface active compounds are increasing. To meet these challenges, mixed micellar systems including geminis and conventional surfactants are receiving much attention. Most of the studies, however, are made from the point of view of synergism or blending effects in surfactant mixtures [9,10] as mixing of different species of surfactants has a possibility to result in more useful performance caused by synergism [11,12].

The thermodynamic treatment of mixed micelles of surfactants [13] and a treatment of excess thermodynamic quantities [14] of adsorption are of importance. Various theoretical models are available to interpret the formulation of mixed micelles. The first model

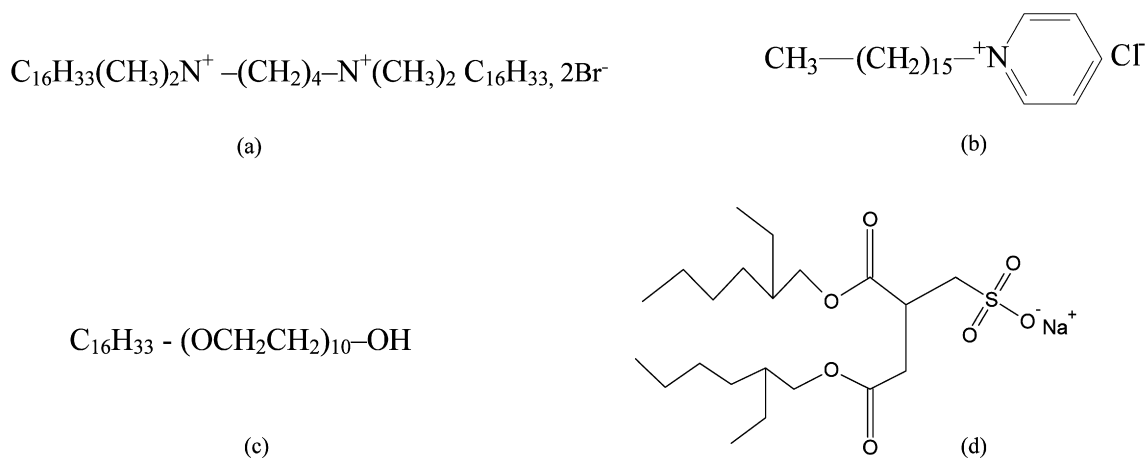
given by Lange [15], and used by Clint [16], is based on phase separation model and assumes ideal mixing of the surfactants in the micellar phase. Rubingh [17] proposed a treatment based on regular solution theory (RST) for nonideal mixed systems which have been extensively used. Maeda [18] introduced a term G_{Maeda} as a measure of stability for mixed ionic–nonionic systems. Apart from this, Rosen et al. [19–21] have extended the nonideal solution treatment of Rubingh [17] for mixed micelle formation by binary surfactant systems to estimate, from surface tension data, the surfactant molecular interaction and also the composition in the adsorbed monolayer at the air/water interface. The molecular thermodynamic approach [22–24], on the other hand, suggests that electrostatic interactions among the ionic and polar head groups cause nonideality of the surfactant mixing.

The types of molecular interactions in surfactant systems include: (1) electrostatic interaction between ionic hydrophilic groups, (2) ion–dipole interaction between ionic and nonionic hydrophilic groups, (3) steric interactions between bulky groups, (4) van der Waals interactions between hydrophobic groups, and (5) hydrogen bonding among constituent surfactant molecules.

To the best of our knowledge, only sporadic attempts have so far been made to explain the mixed micellization of gemini bisquaternary ammonium bromides with nonionic and ionic conventional surfactants. The main objective of the work is, therefore, to investigate mixed micellization and adsorption properties of gemini butanediyl- α,ω -bis(dimethylcetylammmonium bromide) with conventional cationic cetylpyridinium chloride (CPC), anionic sodium

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Scheme 1. Structure of surfactant molecules used in this study: (a) dimeric gemini (G4), (b) cetylpyridinium chloride (CPC), (c) Brij56, and (d) sodium bis(2-ethylhexyl)-sulfosuccinate (AOT).

bis(2-ethylhexyl)sulfosuccinate (AOT) and nonionic polyoxyethylene 10 cetyl ether (Brij56) surfactants (Scheme 1).

The purpose of selection of these surfactants is two fold: (a) their similar hydrophobic chain lengths, a factor expected to lead ideal mixing, and (b) a large difference in their cmc values. Such an investigation is expected to lead to insight in the applicability of thermodynamic molecular model to binary systems.

The analysis of data has been made in the light of various theoretical models, including those of Rubingh, Rosen, Clint, and Maeda to reveal the comparative performance of these models. This paper thus presents a systematic study of surface and micellar properties of the above mentioned surfactants using conductometry and tensiometry.

2. Materials and methods

2.1. Materials

The surfactants (nonionic Brij56, cationic CPC, and anionic AOT) were all Aldrich products and used as received. The dimeric gemini butanediyl- α,ω -bis(dimethylcetylammmonium bromide), $\text{C}_{16}\text{H}_{33}-(\text{CH}_3)_2\text{N}^+-(\text{CH}_2)_4-\text{N}^+(\text{CH}_3)_2\text{C}_{16}\text{H}_{33}\cdot 2\text{Br}^-$ (16-4-16), was synthesized by refluxing α,ω -dibromobutane with *N,N*-dimethylhexadecylamine in dry ethanol for 48 h. The solvent was removed under vacuum and the solid thus obtained was recrystallized thrice from hexane/ethyl acetate mixtures to obtain the pure surfactant (ascertained on the basis of elemental and ^1H NMR data [25]).

2.2. Surface tension measurements

The surface tension (γ) measurements were made with a Krüss 9 tensiometer by the platinum ring detachment method. Surfactant concentration was varied by adding concentrated surfactant solution in small installments, and the readings were noted after thorough mixing and temperature equilibration. The measured γ values were corrected according to the procedure of Harkins and Jordan (in-built in the instrument software). The accuracy of γ measurements was within $\pm 0.1 \text{ mN m}^{-1}$. The cmc values were determined by noting inflexions in the γ vs logarithm of surfactant concentration plots.

2.3. Conductivity measurements

The conductivity of solutions was recorded at 25°C by a digital microprocessor based conductivity meter (Cyber Scan CON500)

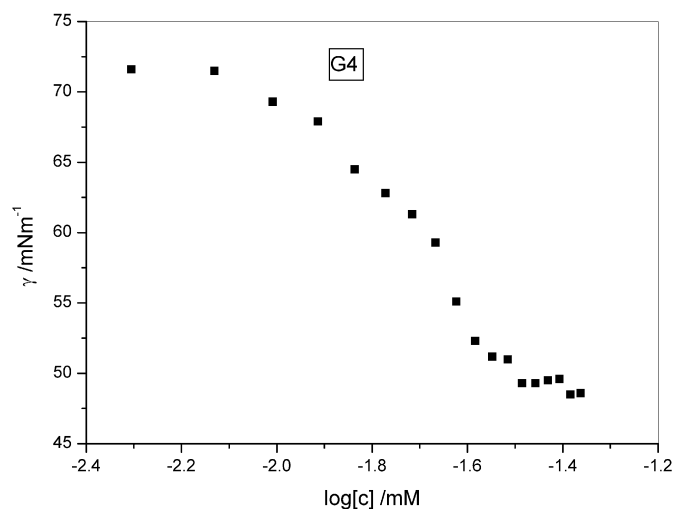


Fig. 1. Surface tension plot of pure G4 at 25°C .

from Eutech Instruments, having a sensitivity of $0.1 \mu\text{S cm}^{-1}$ and an accuracy of 0.5%.

All the solutions were prepared in de-ionised double distilled water having conductivity in the range of $2\text{--}3 \mu\text{S cm}^{-1}$. The experiments were performed at $25 \pm 0.3^\circ\text{C}$ by circulating water from a HAAKE GH thermostat.

3. Results and discussion

3.1. Properties of the micellar phase

As the technique of surface tension measurements is more accurate (owing to be able to detect small micellar aggregates), only the γ plots are given here (Figs. 1 and 2) whereas conductivity plots are given in supporting information. Distinct breaks in the measurement of physical properties with respect to concentration are recognized as cmc of the surfactants. Table 1 records the experimental as well as ideal cmc values along with other related parameters. The cmc's of pure surfactants agree well with the literature [26–29] values.

Since the cmc values obtained by different methods vary, the cmc and cmc-derived parameters are found to depend upon the methodology adopted for cmc determination. For general correlation [30], we have, therefore, used average cmc values determined by the two methods (tensiometry and conductometry). The surfac-

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