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Experimental and theoretical approach to mixed surfactant system of cationic gemini surfactant with nonionic surfactant in aqueous medium

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ABSTRACT

The surface and mixed micellization properties of the aqueous binary mixed system of alkanediyl-α, ω-type cationic gemini surfactant, 14–4–14 and conventional nonionic surfactant, Brij-58 in an aqueous medium have been investigated over the entire mole fractions at 298.15 K. The critical micelle concentration (*cmc*) for each mixture have been measured by tensiometric and fluorescence measurements. The solution and adsorption characteristics like composition, activity coefficients and mutual interaction parameters have been computed using different proposed theoretical models like Clint, Rosen, Rubingh, Motomura and Maeda. The strength of interaction of the surfactant is attributed to the sterical and electrical factors on mixed monolayer and micelle formation and of surfactant–surfactant interactions. The micellar aggregation number (N_{agg}) has also been measured using steady state fluorescence quenching method at a total concentration of ~1 mM of pure components as well as their mixtures of different ratios. The micropolarity and binding constant were determined from the ratio of intensity (I_1/I_3) of peaks of pyrene fluorescence emission spectrum.

1. Introduction

Mixing of two or more surfactants in an aqueous solution leads to the formation of mixed micelles. In solution, mixtures containing amphiphiles or surfactants aggregate substantially at lower concentration compared with the solution containing a single amphiphile or surfactant. The effect of surfactant mixtures on various physicochemical properties such as micellization, adsorption, solubilization, stabilization action, wetting etc. is extensively studied previously [1]. The use of surfactant mixture, rather than single surfactants, makes it possible to more efficiently regulate the properties of disperse systems and the relevant property. In some of the cases, two surfactants interact in such a fashion that the critical micelle concentration (*cmc*) of the mixture is intermediate in value between those of two pure components. In other cases, they interact in such a way that the *cmc* of the mixture at some ratio of the two surfactants is less than either of *cmc* value. When this situation arises, the system is said to exhibit synergism, the condition in which the properties of the mixture are better than those attainable with the individual components by themselves. In still other cases, when the *cmc* of the mixture is larger than *cmc* of individual surfactant, the system is said to exhibit antagonism in mixed micelle formation.

Ionic–nonionic surfactant mixtures are important from the fundamental as well as technological point of view. These systems exhibit strong synergism on mixing because of the complementary behavior in the mixed micelle causing a decrease in *cmc* values [2]. The cationic surfactants being antifungal, antibacterial and antiseptic have attracted attention with respect to their interaction with DNA and lipids [3]. On the other hand, nonionic surfactants are useful as detergents, solubilizers, and emulsifiers [4]. Recently interest has grown in outlandish surfactant molecules such as gemini surfactants [5] due to the unusual morphologies and physical properties of their aggregates in solution. The gemini surfactants show remarkably lower *cmc*, greater efficiency in reducing surface tensions of water, and better wetting, solubilizing and foaming properties so far than monomeric surfactants [5–7].

With the growing demands of industrial technology, a search for high performance surface-active compounds is increasing. One such attempt is the gemini–conventional surfactant mixtures that would be superior on the application front compared to the pure systems. Fatma et al. [8] has worked on cationic ester bonded gemini surfactants with cationic, anionic and non-ionic surfactants in an aqueous medium. Surface and solution properties of gemini (16–6–16) with cationic, anionic and nonionic surfactants were studied by Panda and Kabir-ud-Din [9]. Mixed micellization of Brij-58 with Brij-56 was investigated by Bhadane and Patil [10]. Solubilization and conductivity studies between anionic/nonionic surfactants were carried out by Chaterjee et al. [11]. However, no attempt has been made regarding mixed micellization of 14–4–14 gemini with Brij 58 surfactant mixture. Keeping in

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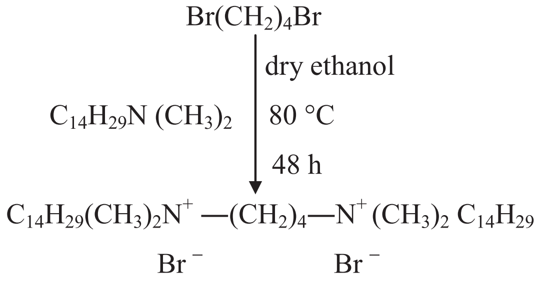
mind, cationic and nonionic surfactant mixtures have been investigated in detail in the present study with respect to their mixed micelle formation and adsorption characteristics. The established theories of Clint [12], Rosen [13], Rubingh [14], Motomura et al. [15], and Maeda [16] have been used to quantify the interaction parameters, composition, packing parameter, and theoretical *cmc*. Regular solution theory (RST) and pseudophase model of micellization have been applied to determine various thermodynamic functions.

2. Experimental

The gemini surfactant was synthesized by reaction by a dibromoalkane with tetradecyl dimethylamine. The detail for its synthesis and purification has been reported elsewhere [17].



The nonionic surfactant, Brij-58 was the product of Sigma. Pyrene, used as a micellar probe in the fluorescence measurements, was a Sigma product with purity >98%. A stock solution of pyrene was prepared in absolute methanol. All solutions were prepared in double–triple-distilled water (specific conductivity 2–3 μS cm^{-1}) and experiments were done under thermostatic conditions at 298.15 K with an accuracy of ±0.5 K.

The *cmc* was determined by the surface tension (γ) measurement. Sigma 700 (Attention) performed the tensiometric experiments using a platinum ring, the ring detachment method in a calibrated tension at a constant temperature of 298.15 K. A detailed description of the procedure has been reported earlier [18]. Each experiment was repeated at least three times.

The *cmc* and micellar aggregation number (N_{agg}) of single and mixed surfactant solutions were determined by steady-state fluorescence quenching measurements. Pyrene was used as a probe and cetylpyridinium chloride (CPC) was used as a quencher throughout the study. The steady-state fluorescence experiments were performed with a Hitachi F-7000 spectrofluorometer, connected to a PC. A 3 cm^3 silica cell was used for the spectral measurements at a constant temperature. By selecting 335 nm as the excitation wavelength of the fluorescence probe (pyrene), the emission spectra of solution components prepared in pyrene were recorded from 350 to 450 nm. The first and third vibronic peaks of pyrene appear at 373 and 384 nm respectively (Fig. 1). At a constant probe concentration of 1×10^{-6} M, the quencher concentration was varied from 0 to 1×10^{-5} M to ensure a Poisson distribution for equilibration of solubilizates between micelles.

3. Results and discussion

The reported surface tension and fluorescence methods are extremely useful. It is an important tool for the quantitative determination of surface and micellar composition of a range of surfactant mixtures. By analyzing meticulously the surface tension and fluorescence data, collective information of surface composition and phenomena underlying adsorption of surfactants at the air/water interface, micellar aggregation number (N_{agg}), and micropolarity for binary surfactant mixtures can be obtained. In order to provide a detailed discussion, this section has been divided into following subheadings.

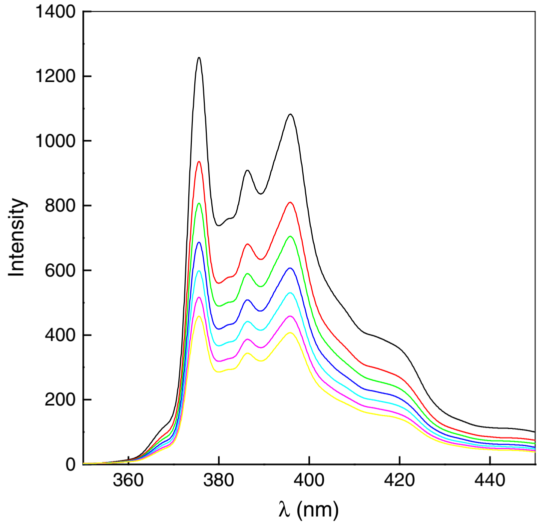


Fig. 1. Representative illustration of variation of I_1/I_3 as a function of concentration of quencher (CPC) for Brij-58 + 14–4–14 mixture ($\alpha_1 = 0.1$).

3.1. Properties of surfactant mixtures at air/water interface

The amphiphilic systems possess an intrinsic property to get oriented towards the air/water interface and hence change the surface properties of water. Understanding the physical properties of the interface can be very important in all types of natural phenomena and industrial processing operations. The amount of surfactant adsorbed per unit area of the air/aqueous solution interface the Gibbs surface excess (Γ_{max}) was calculated from the slope γ vs. log *C* profile (Fig. 2) near the *cmc* point using the relation [19,20]

$$\Gamma_{max} = -\frac{1}{2.303nRT}\left[\frac{\partial\gamma}{\partial\log C}\right]_T \tag{1}$$

where $\left[\frac{\partial\gamma}{\partial\log C}\right]_T$ is the maximal slope of γ vs. log *C* plot, *n* is the number of species in solution (for nonionic surfactant $n = 1$ and for gemini surfactant $n = 2$), *R* is the universal gas constant and *T* is temperature in absolute scale. The $\left[\frac{\partial\gamma}{\partial\log C}\right]_T$ value is called the adsorption effectiveness and describes the adsorption tendency of surfactant molecules at the interface. The adsorption effectiveness is an important factor determining vital properties [21–24], such as foaming, wetting, emulsification, solubilization, drug delivery and biological activities. The higher the Γ_{max}, the steeper is the approach to *cmc* and the higher is the surface activity. Gemini has a higher Γ_{max} than that of Brij-58 (Table 1) so the gemini surfactant is more surface active. The average area of exclusion at saturated air/solution interface per surfactant molecule was calculated using

$$A_{min} = \frac{10^{20}}{N_A\Gamma_{max}} \tag{2}$$

where N_A is the Avogadro number. Analyzing the data in Table 1 reveals no specific trends in the variation of the Γ_{max} and A_{min} values for all the studied systems. Table 1 shows that the value of A_{min} is much less for 14–4–14, implying the greater number density of 14–4–14 monomer at the interface. The Π_{cmc} is the surface pressure at the *cmc* and is equal to $\gamma_0 - \gamma_{cmc}$, where γ_0 is the surface tension of pure solvent and γ_{cmc} is that of the solution at the *cmc*. The lower Π_{cmc} value for 14–4–14 than Brij-58 indicates its enhanced surface activity.