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Mixed micellization of tetradecyltrimethylammonium bromide and Triton X-100 in water–ethanol mixtures, using potentiometric and surface tension techniques

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Abstract

The mixed micelles of tetradecyltrimethylammonium bromide (TTAB) and Triton X-100 (TX-100) in mixed solvent have been investigated using potentiometric and surface tension techniques. In order to estimate the interaction between the surfactants and ethanol, the cmc data were treated by using the conventional regular solution theory for mixed micelles. It was found that the interaction parameter values (β) varied with variation of solvent composition. In all cases the results showed deviation from ideal behavior. The stability of the mixed micelles was also discussed based on Maeda's approach. The obtained data show that mixed micellization became unfavorable with increasing alcohol concentration. Also, the maximum synergism in ethanol/water mixtures has been determined according to Rosen's new approach. The observed maximum synergisms were obtained from $x_1 = 0.25$ to $x_1 = 0.35$ at different concentrations of ethanol.

Keywords: Surfactant; Mixed micelle; Synergism; Surface tension; Potentiometry; Regular solution theory (RST)

1. Introduction

Surfactant solutions are used widely in numerous technical applications such as in detergents, cosmetics, pharmaceuticals, enhanced oil recovery or surfactant-based separation processes (flotation). Surfactants are often mixed in water or hydroorganic media. This is so because (i) technical-grade surfactants are mixtures themselves, hence their purification process may be difficult or excessively expensive and (ii) the mixed system often behaves better than a single surfactant [1–4]. Surfactant mixtures often exhibit features deviating significantly from individual surfactants (i.e., they exhibit substantial synergism) [5,6]. To maximize beneficial effects of mixtures over individual surfactants, it is helpful to understand the interactions among surfactants in the mixtures.

The micelle formation in an aqueous solution is known to be affected by organic additives, and there have been many investigations concerning the effect of organic additives on the cmc of individual surfactants [7–11]. Recently, increasing attention has been devoted to the study of the incorporation or solubilization of neutral molecules into micelle in aqueous solution. Some of the most studied solubilizates are alcohols, because of the important role they have in the preparation of microemulsions [12–18]. It is generally accepted that the alcohol binds to the micelle in the surface region, leading to three principal effects: (a) intercalation of alcohol molecules between the surfactant ionic head groups [19–23]; (b) decrease in dielectric constant at the micellar interface [24]; and (c) change in the molecular order of the interface region of the micelle [12]. For the literature cited here, the physicochemical studies on alcohols in aqueous mixture of surfactants are of chief interest, and it seems that the effect of alcohol addition in micellar solution of various mixed surfactant solutions has not been studied. In continuation of our work on micelle formation in non-aqueous solvents [25–29], a systematic attempt has been made to study the effect of alcohols on the micelle of various surfactants in mixed states.

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The analysis of micellar systems made of mixed surfactants requires experimental techniques that provide unambiguous determination of the distribution of different species in solution and their partition between solution and aggregates. For electrically charged amphiphiles, potentiometric methods can be considered, using selective electrodes. Recent extensive development of these electrodes permits their use in the study of different equilibrium reactions involving ionic surfactants [30–33].

For the simplest case of a binary surfactant system without any significant net interaction between surfactant types, the mixture cmc ($\mathrm{cmc_{Mix}}$) obeys the ideal solution theory [34]. When two surfactants forming a mixed micelle have different head groups, the cmc is not predicted by the ideal mixing theory. An extension of the Lang–Shinoda approach [35–37] has been developed to include mixtures of nonionic and ionic surfactants. A simpler approach has been given by Rubingh [38] and it applies the regular solution theory (RST) to the mixed micelle, thus allowing for the interaction between the surfactant molecules within the mixed micelle.

In analyzing the mixtures of surfactants, RST is the most widely used model. In the present work, the various aspects of micellization of TTAB and TX-100 mixture in the presence of ethanol have been investigated, using potentiometric and surface tension techniques. We use an ion-selective electrode sensitive to cationic surfactant (i.e. TTAB) and other surfactant (i.e. TX-100) is neutral with a low cmc. Moreover, though the experimental results are very precise, the interpretation of the electromotive force (emf) curves lacks precision and thus surface tension is required to analyze the data.

2. Experimental

2.1. Chemicals

Tetradecyltrimethylammonium bromide (TTAB) was obtained from Sigma (approx. 99%) and used without further purification. TX-100 (>99%) and ethanol (>99%) were obtained from Merck and used as received. All solutions were prepared with doubly distilled water.

2.2. Methods

All experiments were carried out at a temperature of 30 °C and this was maintained with ±0.1 °C by circulating thermostated water (Pharmacia Biotech).

The surface tension of surfactant solutions was determined using an automatic tensiometer, KSV Instruments, model Sigma 70 (Helsinki, Finland) employing the ring method.

The ion-selective electrode sensitive to $\mathrm{TTA^+}$ was used for the measurement of the free concentration of surfactant ion, $[S]_f$, in equilibrium with micelles at different conditions. The membrane ion-selective electrode (MISE) used in the present work was originally constructed to investigate the behavior of mixed surfactants in water/ethanol media. The procedures used to construct this MISE are well documented [26–29].

The emf measurements of the surfactant selective electrode were measured relative to a commercial sodium ion electrode (Methrohm 60501-100), as reference electrode. The cell configuration used for the potential measurements was

Surfactant Electrode (MISE) | test solution | reference electrode

The following equations can be written for different electrode potentials, according to Nernst's equation

$$E_{\mathrm{sur}^+} = E^\circ_{\mathrm{sur}^+} + \frac{RT}{F}\ln a_{\mathrm{sur}^+} \tag{1}$$

$$E_{\mathrm{Na}^+} = E^\circ_{\mathrm{Na}^+} + \frac{RT}{F}\ln a_{\mathrm{Na}^+} \tag{2}$$

where T, R, F, a_{sur^+}, and a_{Na^+} represent the absolute temperature, gas constant, Faraday's constant, activity of surfactant ion, and activity of sodium ion, respectively. E_{sur^+}, E_{Na^+}, $E^\circ_{\mathrm{sur}^+}$ and $E^\circ_{\mathrm{Na}^+}$ indicate the sodium, surfactant and corresponding standard electrode potentials, respectively. We have assumed that at low ionic strength the mean activity coefficient of different ions irrespective of charge and shape leads to unity.

At constant sodium ion concentration, which applies to this experiment, we can use the following equation for the determination of free surfactant concentration

$$\mathrm{emf} = E^\circ_{\mathrm{sur}^+/Na^+} + 2.303\frac{RT}{F}\log[S]_{\mathrm{f}} \tag{3}$$

where

$$E^\circ_{\mathrm{sur}^+/\mathrm{Na}^+} = E^\circ_{\mathrm{Na}^+} - E^\circ_{\mathrm{Na}^+} - 2.303\frac{RT}{F}\log[C]_{\mathrm{s}} \tag{4}$$

where $[S]_f$ and $[C]_s$ are concentration of free surfactant and co-ion (here, sodium ion from backing electrolyte), respectively.

Since the surfactant is dissociated completely into ions below the cmc, the plot of emf against $\log[S]_t$ ($[S]_t$ is total concentration of surfactant) obeys Nernstian behavior. Hence, the slope of the line is referred to $2.303\frac{RT}{F}$ and the intercept, $E^\circ_{\mathrm{sur^+/Na^+}}$. This calibration line can be used for the determination of monomer surfactant ion concentration above the cmc by adjusting data on the calibration line. A least mean squares method was used for determination of the slope, $2.303\frac{RT}{F}$, and intercept, $E^\circ_{\mathrm{sur^+/Na^+}}$, for each set of data [26,28,30,39,40].

3. Results and discussion

In the absence of any significant net interaction between surfactant types, the ideal solution theory predicts the cmc of mixture as follows

$$\frac{1}{\mathrm{cmc_{Mix}}} = \frac{y_1}{\mathrm{cmc_1}} + \frac{1-y_1}{\mathrm{cmc_2}} \tag{5}$$

where y_1 is the solution mole fraction of the surfactant 1 (solution composition) with critical micelle concentration $\mathrm{cmc_1}$, and $\mathrm{cmc_2}$ denotes the cmc for the second surfactant alone. The ideal mixing theory has been successful in explaining the properties of mixtures composed of surfactants with similar chemical structures; however, it fails for mixtures containing chemically