

Conductometric and fluorometric investigations on the mixed micellar systems of cationic surfactants in aqueous media

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Abstract

Micellar properties of binary mixtures of hexadecyldiethylethanolammonium bromide surfactant with tetradecyldimethylammonium, trimethylammonium, triphenylphosphonium, diethylethanolammonium, and pyridinium bromide surfactants have been characterized employing conductometric and fluorescence techniques. The critical micelle concentration (cmc^*) and the degree of counter-ion binding values (δ) of the binary systems were determined from the conductivity measurements. The results were analyzed in light of various existing theories to calculate micellar composition, activity coefficients, and the interaction parameter (β). Partial contribution of each surfactant, cmc_1^* , cmc_2^* , to the overall cmc^* value was also evaluated. Aggregation numbers and micropolarity of the mixed micelles were determined from fluorescence measurements. The results were discussed in terms of synergetic interactions in these systems on the basis of the head group/head group and tail/tail interactions and the counter-ion binding.

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1. Introduction

Mixed surfactant systems are preferably used instead of single surfactant systems for industrial applications such as detergents, cosmetics and pharmaceuticals. It is well known that when compared to single surfactant systems, mixed surfactant systems have the ability to provide better performance [1–4]. Because of the presence of more than one species, it is not necessary that the surfactants in use are of high purity, and as a result, the mixed system is far less expensive. For this reason, mixed surfactant systems are widely used in industry [5,6].

Many investigations have been carried out in the literature on binary surfactant systems [7–17]. The focus has been on the overall effect of the surfactant combination and the determination of the critical micelle concentration (cmc^*), the degree of counter-ion binding, and to analyze the results in terms of well known theories to determine the composition and the nature of interactions of individual monomers of the two surfactants in

the mixed micelle [1,4]. In comparison, there is relatively little information presented in literature about the contribution of each surfactant in the monomeric and micellar phases of the mixed system. Recently Junquera and Aicart [18–20] investigated the partial contribution of cmc_1^* and cmc_2^* of the surfactants in mixed systems to the monomeric phase cmc^* and micellar phase through aggregation number N_i^* . The authors focused on synergistic interactions of near ideal systems using surfactants with equally sized chain lengths and very similarly structured head groups.

In the present study, a total of six systems were investigated using tetradecyl and hexadecyl species as the binary components, employing both conductometric and fluorometric techniques. In five of the six systems, the hexadecyldiethylethanolammonium bromide (C_{16}DEEA), was investigated in combination with five tetradecyl species with different head groups namely: diethylethanolammonium bromide (C_{14}DEEA), pyridinium bromide (C_{14}PyBr), triphenylphosphonium bromide ($\text{C}_{14}\text{PPh}_3\text{Br}$), dimethylammonium bromide (C_{14}DABr) and trimethylammonium bromide (TTAB). The sixth system studied employed tetradecyltriphenylphosphonium bromide ($\text{C}_{14}\text{PPh}_3\text{Br}$) and tetradecylpyridinium bromide

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(C₁₄PyBr). These systems were chosen to study the effects of head group/head group as well as tail/tail interactions.

Micellar properties were investigated as a function of concentration and composition using conductometric techniques. The contribution of each surfactant to the mixed micelles in terms of cmc_1^* and cmc_2^* to the cmc^* of the mixture, and N_1^* and N_2^* to N^* where the subscripts 1 and 2 denote the C₁₄ and C₁₆ components in the mixed system, respectively, were evaluated employing the procedure outlined by Janquera and Aicart [18].

2. Materials and methods

2.1. Materials

The tetradecyltriphenylphosphonium bromide surfactant (C₁₄PPh₃Br) was obtained by Lancaster chemicals (England) and used as received. Tetradecyltrimethylammonium bromide (TTAB) (99% pure) and the fluorescence probe pyrene (99% optical grade) were obtained from Sigma–Aldrich. The pyrene was purified by repeated crystallization, followed by sublimation. The diethylethanolamine surfactants (C₁₆DEEA, C₁₄DEEA), tetradecyldimethylammonium bromide (C₁₄DAB) and tetradecylpyridinium bromide (C₁₄PyBr) were the same samples that were used in our previous investigations [21–23].

2.2. Conductivity measurements

Conductivity measurements were carried out on a CDM 83 conductivity bridge. The cell constant was 1.01 cm⁻¹ and the operating frequency of the conductivity bridge was 1000 Hz. The conductivity experiments were taken at a constant temperature maintained within ± 0.1 °C. Temperature control was maintained by placing the solution to be studied in a jacketed beaker and allowing water to circulate through the beaker. All solution preparation was done using triply de-ionized water. Each conductivity measurement was estimated to have an error of ± 0.5 $\mu\text{S cm}^{-1}$.

In the present study, two different conductometric methods were employed. The first method was carried out to determine the cmc^* of the mixed system, and involved measuring the conductivity as aliquots of the mixed surfactant system were added to triply de-ionized water. In Method II, a solution of the tetradecyl component in the pre-micellar range was placed in the jacketed beaker, and its concentration was taken as cmc_1^* . The tetradecyl solution was titrated with an aliquot of hexadecyl species that was dissolved in the same concentration of tetradecyl surfactant solution, and conductance was measured after each addition. The break point in the titration curve was taken as cmc_2^* .

2.3. Fluorescence measurements

Fluorescence experiments were carried out with a JY Horiba Spex Fluoromax-3 fluorometer to determine the aggregation numbers of the micelles in each system. The total concentration of surfactant was of the order of 50 mM and pyrene, used as a fluorescence probe, was maintained at a concentration of

1×10^{-6} M. The experimental details were the same as reported in earlier publications [24–27]. The I_1/I_3 ratios were also taken in the absence of quencher to determine the micropolarity of the systems.

3. Results and discussion

3.1. Conductivity

Conductance was measured for each system at a variety of bulk mole fractions (α) and cmc^* values were determined for each of these mole fractions. A depiction of a typical Method I conductivity plot is given in Fig. 1 for the C₁₄DABr and C₁₆DEEA system at various mole fractions (α) of C₁₄DABr. Similar plots were generated for each of the six systems studied, varying the composition of the C₁₄ component. From these conductivity plots, the degree of counter-ion binding (δ) was obtained from ($\delta = 1 - s_2/s_1$), where s_1 and s_2 are the pre- and post-micellar slopes [28,29]. The cmc^* and counter-ion binding values determined for each system are presented in Table 1, and the uncertainties for these values are estimated to be less than $\pm 2 \times 10^{-3}$ and $\pm 3 \times 10^{-3}$, respectively.

In all systems where C₁₆DEEA was used as one of the components, the counter-ion binding was found to decrease as the amount of C₁₄ in the mixed micelle increased, thus indicating a decrease in the head group repulsions, and thereby leading to an increase in the stabilization of the micelle. The Gibbs energy of micellization (ΔG_{mic}^0) was calculated using Eq. (1) based on the pseudophase separation model [30]

$$\Delta G_{\text{mic}} = (1 + \delta)RT \ln X_{\text{cmc}}, \quad (1)$$

where X_{cmc} is the cmc^* expressed on the mole fraction scale and the ΔG_{mic}^0 values are referred to in Table 1.

Conductivity plots employing Method II are given in Fig. 2 for the TTAB and C₁₆DEEA system. The break in each of these plots is taken to be the cmc of the hexadecyl component in the system, that is, cmc_2^* . From the value of the cmc_1^*

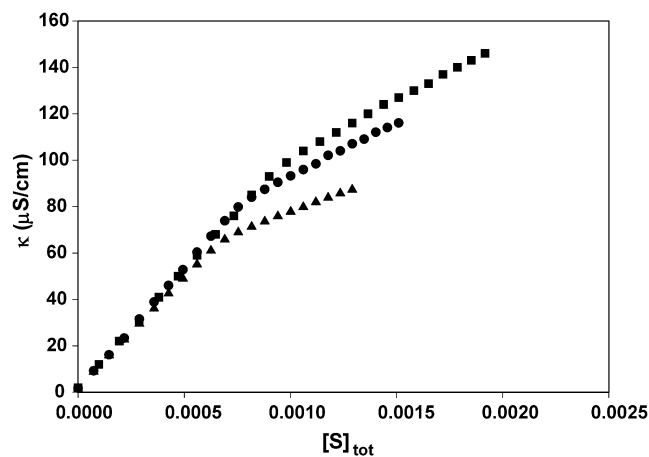


Fig. 1. Plot of specific conductance, κ , as a function of total surfactant concentration, $[S]_{\text{tot}}$ at 298.15 K, at various values of mole fraction, α_1 , for the mixed system C₁₄DABr (1) and C₁₆DEEA (2). (\blacktriangle) $\alpha_1 = 0.1$; (\bullet) $\alpha_1 = 0.3$; (\blacksquare) $\alpha_1 = 0.5$.

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