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Effect of short chain length alcohols on micellization behavior of cationic gemini and monomeric surfactants

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ABSTRACT

Micellization of a cationic gemini, decanediyl-1,10-bis (dimethylhexadecylammonium bromide) and monomeric surfactants viz. cetyltriphenylphosphonium bromide (CTPB), tetradecyltripheylphosphonium bromide (TTPB) and cetylpyridinium bromide (CPB) in the presence of short chain length alcohols has been investigated at 300 K. The effect of short chain length of alcohols (methanol, ethanol and 1-propanol) on critical micelle concentration (cmc), and degree of micellar ionization (α) were investigated by using conductivity measurements. The experimental data show that the cmc values of cationic surfactants increase with addition of methanol to ethanol and decreases with 1-propanol. The thermodynamics parameters i.e. standard Gibb's free energy (ΔG°_{m}), enthalpy (ΔH°_{m}) and entropy (ΔS°_{m}) of micellization of cetylpyridinium bromide (CPB) are also calculated.

1. Introduction

Micellar solubilization is technologically important phenomenon and has attracted significant attention in the area of surface science and solution chemistry [1–4]. Some of the most studied solubilizers are alcohols, because of their important role in the preparation of microemulsions [5–8]. In addition to the importance of the theoretical study, researches on the effects of alcohol on the cmc and thermodynamic parameters of various surfactants in non-aqueous solutions have some industrial applications [9,10]. The effect of alcohols on the self-association processes of ionic surfactants and hence on the properties of the micelles formed has been investigated for several systems using a variety of techniques. The addition of alcohol can strongly influence the behavior of the micelles and increase or decrease the micellar size depending on the hydrophilic/hydrophobic character of the alcohol. The hydrophobic alcohol molecules take part in the micellization process and become unique components of the micelle aggregates [11].

Cationic gemini surfactants contain two head and two tail groups linked by spacer. Gemini surfactants are relatively new class of surfactants that are often described as being as two monomeric surfactants connected at or near the polar head group by different spacers [12,13]. They are of wide current interest because of their enhanced properties, such as low critical micelle concentration (cmc), high viscoelasticity and a higher propensity to lower the oil–water interfacial tension than for single chain analogues [14–16]. When compared to their single chain, single headed counterparts (i.e. conventional surfactants), gemini surfactants are more efficient in lowering surface or interfacial tension and also have better wetting/solubilization properties, superior foaming abilities and better cold water solubility. Therefore, the use of gemini surfactants has been well studied in academic and industrial laboratories [17–19]. Moya et al. [20] have studied the micellization and micellar growth of alkanediyl-α,ω-bis(dimethyldodecylammonium bromide) surfactants in the presence of medium-chain length alcohols. They observed that the presence of alcohol in the micellar solution provokes a decrease in the average micellar aggregation number. Similarly Bahadur et al. [21] have focused on qualitative and quantitative effects of partitioning of butanol into cationic surfactants of different types and bulk solution. They found that alcohols affect the micellization and micellar properties of the cationic gemini and conventional surfactants. The effect of 1-alcohols (C_2, C_4, C_6) on the properties of micellar solution of different cationic surfactants has been examined by Kuperkar and his co-workers [22]. They have shown that the incorporation of alcohol into the micelles produces noticeable changes in different micellar size nonpolar tail, polar head group size, counterion and in its micellar properties. Menger et al. [23] have developed a new model, which provides a qualitative explanation for the balancing force to the solvophobic effect and morphological transitions. Limited work has been done on micellization of ionic surfactants in dilute aqueous solutions of alcohol chain lengths, $n = 1-3$ due to solubility [24,25]. The manuscript provides a novel contribution to the micellar solutions investigations. It gives valuable information for a better understanding of the effects of short chain-length alcohols on

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the self-assembly of amphiphilic compounds, by examining the effect of different headgroup, chain length and dimerization (gemini structure).

In our previous paper, we have investigated the effect of solvents on physiochemical properties of cationic gemini and monomeric surfactants [26–29]. Herein, we extend in this work the study of the micellar properties of cationic gemini (C_{16}-10-C_{16}, $2Br^-$) and monomeric surfactants i.e. cetyltriphenylphosphonium bromide (CTPB), tetradecyltriphenylphosphonium bromide (TTPB), cetylpyridinium bromide (CPB) in water and water–alcohol systems at varying mole fraction (0–0.19) of alcohols (Fig. 1). The alcohols were chosen i.e. methanol (MeOH), ethanol (EtOH) and (1-PrOH) 1-propanol. The thermodynamic parameters, viz. standard Gibb's free energy (ΔG°_m), enthalpy (ΔH°_m) and entropy (ΔS°_m) of micellization of cetylpyridinium bromide (CPB) in short chain length alcohols have also been investigated.

2. Experimental section

2.1. Materials

The gemini surfactant was synthesized by refluxing the corresponding 1,10-dibromodecane and the N,N-dimethylhexadecylamine in dry ethanol for 48 h and the crude product was recrystallized from hexane/ethyl acetate mixtures [30]. The cationic surfactants CTPB and TTPB were obtained from Prof. R. M. Palepu, St. Francis Xavier University, Antigonish, Canada. CPB was obtained from Sigma. Methanol and 1-propanol were obtained from Qualigen (India; 99%) and ethanol (absolute alcohol) was obtained from Changsu Yangyuan Chemical, China. All surfactants were of highly pure (>99.0%) and were used without further purification. All solutions were prepared in triply distilled water.

2.2. Method

The critical micelle concentration of monomeric and gemini surfactants were evaluated by conductivity measurements (Type 306) at 300 K. KCl (0.1 M and 0.01 M) solution was used for calibration of conductivity cell. Accuracy of measured conductance was within ±0.5%. The pure surfactant solutions were prepared by diluting the concentrated stock solution. The temperature of the thermostat was maintained constant within ±0.01 K. The conductance was measured after thorough mixing and temperature equilibrium at each dilution. The measurement was started with a dilute solution and the subsequent concentrated solutions were prepared by adding a previously prepared stock solution. Establishment of equilibrium was checked by taking a series of readings after 15 min intervals until no significant change occurred.

3. Results and discussion

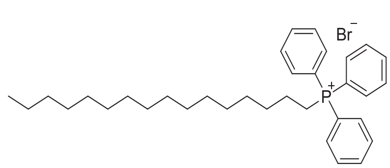
3.1. Effect of short chain length alcohols on critical micelle concentration

The critical micelle concentrations (cmc) of cationic gemini and monomeric surfactants in methanol, ethanol and 1-propanol solution have been studied by conductometric measurements at 300 K. One of the most efficient methods which are being used recently [31] is that proposed by Carpena et al. [32]. It is based on the fitting of the conductivity data (κ) as a function of surfactant concentration to the integral of Boltzmann-type sigmoidal equation

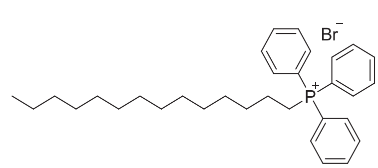
$$F(x) = F(0) + A_1 x + \Delta x (A_2 - A_1) \ln\left(\frac{1 + e^{(x - x_0)/\Delta x}}{1 + e^{-x_0/\Delta x}}\right) \quad (1)$$

where $F(0)$ is the initial conductivity of water, A_1 and A_2 are the limiting slopes for low and high concentration respectively, x_0 is the central point of the transition, i.e. the cmc and Δx is the width of the transition. The α value, representing the degree of micellar ionization can be deduced from the ratio A_2/A_1.

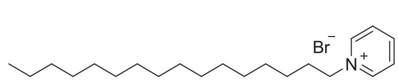
The data were fitted to this non linear equation and the resulting cmc and degree of micellar ionization of cationic surfactants in alcohol solution (methanol, ethanol, 1-propanol) systems are given in Table 1. As expected, all the cationic surfactants exhibited changes in their micellar properties in the presence of alcohols shown in Figs. 2, 3 and S1. The conductivity is linearly correlated to the surfactant concentration in both the pre-micellar and post micellar regions, having a slope in the pre-micellar region greater than that in the post-micellar region. The ratio of the slopes of the post-micellar region to that in the pre-micellar region is usually taken as the degree of micellar ionization (α) [33]. The short chain alcohols are solubilized mainly in the aqueous phase and affect the micellization process by modifying the solvent properties. Table 1 shows that the cmc values in methanol and ethanol are increased and decreased in 1-propanol. The influence of methanol, ethanol and 1-propanol on the micellar behavior of surfactants can be explained on the basis of several different roles of alcohols in the case of surfactants. On the other hand, alcohol molecules are bound to surfactant molecules in the aqueous phase and stabilize the surfactant



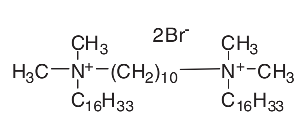
Cetyltriphenylphosphonium bromide (CTPB)



Tetradecyltriphenylphosphonium bromide (TTPB)



Cetylpyridinium bromide (CPB)



Decanediyl-1, 10 -bis(cetyldimethylammonium bromide) (C_{16}-10-C_{16}, $2Br^-$)

Fig. 1. Structure of surfactants.