

## Studies of mixing behavior of cationic surfactants



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### ABSTRACT

The behavior and properties of mixed surfactant systems are discussed in the context of experimental techniques. The aggregation behavior of tetradecyltrimethylammonium bromide (TTAB), hexadecyltrimethylammonium bromide (CTAB), and hexadecyltriphenylphosphonium bromide (HTPB) and their mixtures in aqueous medium was investigated using conductance, fluorescence and NMR techniques. The critical micelle concentration (cmc), counterion binding, thermodynamic parameters of micellization, aggregation number ( $N_{agg}$ ) etc. have been quantitatively estimated. Results were analyzed using regular solution theory (RST) to obtain the composition of the mixed micelles and the interaction parameter,  $\beta^m$ , to evaluate the type and strength of interactions of surfactants in the mixed micelle. Activity coefficients and excess free energy of mixing were also determined. <sup>1</sup>H NMR studies suggested that when mixed with CTAB or TTAB, the bulky head group of HTPB induce steric hindrance. <sup>1</sup>H NMR results suggest that CTAB + HTPB produced compact mixed micelles.

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### 1. Introduction

Surfactant mixtures are frequently used in many applications as they show synergism and provide desirable properties to the formulated products. These synergistic interactions in mixed surfactant systems often result in enhanced interfacial activity, detergency, and emulsifying/solubilizing characteristics. Micellar properties of cationic surfactants in bulk aqueous systems have been extensively studied [1–5]. A literature survey shows that innumerable publications have been devoted since long to the world of surfactants in order to understand the physicochemical aspects of surfactant systems in its single as well as mixed states [3–10]. The critical micelle concentration and aggregation number are two parameters on which the practical applications of amphiphile substances largely depend. Both these parameters depend upon the molecular characteristics of surfactants, presence of electrolytes and non electrolytes and on temperatures, pressure and pH. Treatments based on regular solution theory use interaction parameters to measure the interactions between surfactants in mixed micelles.

In my previous communications [11–14], I have reported the effect of alcohols (medium to long chain) on the micellization behavior of some of the ionic surfactants. Although, the behavior depends on the nature of the surfactant, a reduction of critical

micelle concentration (cmc) and elevation of aggregation number ( $N_{agg}$ ) upon the addition of alcohols is generally observed.

The aim of the present investigation is to explore the thermophysical properties of mixed cationic surfactants. In this work, conductance and fluorescence techniques are utilized along with NMR approach to investigate the process and mechanism of the mixed surfactant micelle formation. The surfactants chosen are cationic quaternary conventional surfactants, tetradecyltrimethylammonium bromide (TTAB) and hexadecyltrimethylammonium bromide (CTAB) and hexadecyltriphenylphosphonium bromide (HTPB), which has three phenyl rings in the head group region. The intension behind the selection of these cationic surfactants is to study the influence of head group compatibility on the mixed micelles formation. While CTAB and TTAB are well explored surfactants, limited literature is available on solution properties of HTPB [3,15–18]. Theories proposed by Clint [19] and Rubingh [20], have been used to analyze and compare experimental results to reveal the synergistic and antagonistic behavior of the surfactant mixtures. Conductance method has been used to obtain cmc and degree of counterion dissociation at the studied temperature range. Fluorescence spectroscopic technique has been applied to further analyze the aggregation behavior of mixed surfactants. Nuclear magnetic resonance, NMR, spectroscopy has unique advantages of not only providing microscopic information at molecular levels but also offering the advantages of being able to observe independently the behavior of the surfactants in the mixture.

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## 2. Experimental

### 2.1. Materials

TTAB and CTAB of purity >97% was purchased from Merck and were dried under vacuum and stored over  $P_2O_5$  in vacuum desiccators. HTPB with purity 98+% was obtained from Lancaster, Alfa Aesar Research Chemicals business unit of Johnson Matthey. For NMR spectral studies, deuterium oxide ( $D_2O$ ), supplied by Aldrich of 99.9% isotopic purity was used. In fluorescence studies, the chemicals were used without any purification. Pyrene was received from Aldrich, cetylpyridinium chloride (CPC) from Loba Chemie, Mumbai, India and methanol (99.9% purity) was obtained from Ranbaxy Chemicals. For the experimental measurements, deionized, double distilled water of conductance  $1 \times 10^{-6} \text{ S cm}^{-1}$  at 298.15 K was used. For weighing, an electronic balance (Afcoset-R120A) with a precision of 0.0001 g was used.

### 2.2. Apparatus

#### 2.2.1. Conductivity measurements

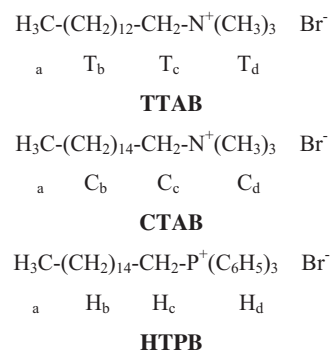
The conductivity measurements of pure surfactants in water were performed in a thermostatic glass cell coupled to digital conductivity meter of Systronics (306). Instrument was calibrated with KCl solution. The temperature of the cell was kept constant to within  $\pm 0.01 \text{ K}$  by circulating thermostated water. The cmc of surfactant in an aqueous solution was taken as the surfactant concentration at the break point in the plot of specific conductance versus surfactant concentration in  $\text{mol dm}^{-3}$ . The accuracy in conductance measurements is  $\pm 1\%$ .

#### 2.2.2. Fluorescence measurements

Fluorescence measurements were performed using a RF-5301PC Spectrofluorometer (Shimadzu) using pyrene as the polarity probe. The pyrene solution of approximate concentration  $10^{-6} \text{ mol dm}^{-3}$  was prepared in methanol. The ratio of the fluorescence intensity of the highest energy vibrational band to that of the third highest energy vibrational band, i.e. ( $I_1/I_3$ ) has been used to study the formation of the surfactant micelles. The emission spectrum of pyrene was recorded in the wavelength range 350–600 nm at a selected excitation wavelength of 334 nm with excitation and emission slit widths of 3.0 nm. To determine the aggregation number,  $N_{\text{agg}}$ , surfactant and CPC solutions were freshly prepared. Aqueous surfactant solutions of the pyrene were prepared taking appropriate aliquots of the probes in different vials and evaporating methanol. Aqueous surfactant of desired concentration was added in to the vials to achieve final probe concentration and the solution was kept for stirring for about 6 h. Fluorescence spectra of the solutions with different quencher concentrations were recorded.

#### 2.2.3. $^1\text{H}$ NMR spectroscopic studies

Bruker Avance NMR (300 MHz) spectrophotometer was used to record  $^1\text{H}$  NMR spectra. Deuterated water ( $D_2O$ ) was used for the preparation of the solutions of NMR to weaken the water signal for all solutions. The ability of the alcohols to affect the chemical shift of different proton and carbon signals of the surfactant molecules was utilized.  $^1\text{H}$  and  $^{13}\text{C}$  spectra of  $0.1 \text{ mol kg}^{-1}$  surfactant solution were recorded. The internal reference in NMR measurements is tetramethylsilane (TMS). In the present study, the chemical shift differences were only considered. The chemical shift measurements of various resonance peaks of studied surfactants have been given on the  $\delta$  scale in parts per million (ppm) of the applied frequency. Further information about the experimental techniques has been provided in literature [14]. Chemical



Scheme 1. Formulae and proton labeling of TTAB, CTAB and HTPB molecules.

structures and proton numberings of TTAB, CTAB and HTPB are shown in Scheme 1.

## 3. Results and discussion

### 3.1. Conductometric studies

Conductance was measured as a function of concentration of surfactant at the temperature 298.15, 303.15, 308.15 and 313.15 K. Plots of specific conductivity,  $\kappa$ , against aqueous CTAB at studied temperatures are reported in my previous communication [11] whereas, that of TTAB and HTPB are presented in Figs. 1 and 2 respectively. The break point in the plot of specific conductance versus surfactant concentration was taken as the cmc of surfactant in an aqueous solution. For each temperature, an increase in electrical conductivity with concentration of surfactant is seen with a gradual decrease in slope. The slope change at cmc is due to an effective loss of ionic charges because a fraction of the counterions are believed to be confined to the micellar surface. The comprehensive results are presented in Table 1 along with the available literature reports. The cmc's of the pure surfactants and their binary mixtures agree with literature values.

The plots of  $\kappa$  against various concentration of equimolar surfactant mixture of TTAB + CTAB and HTPB + TTAB have been presented in Figs. 3 and 4 whereas, cmc value have been reported in Table 2. However, cmc value obtained from conductometric method for the

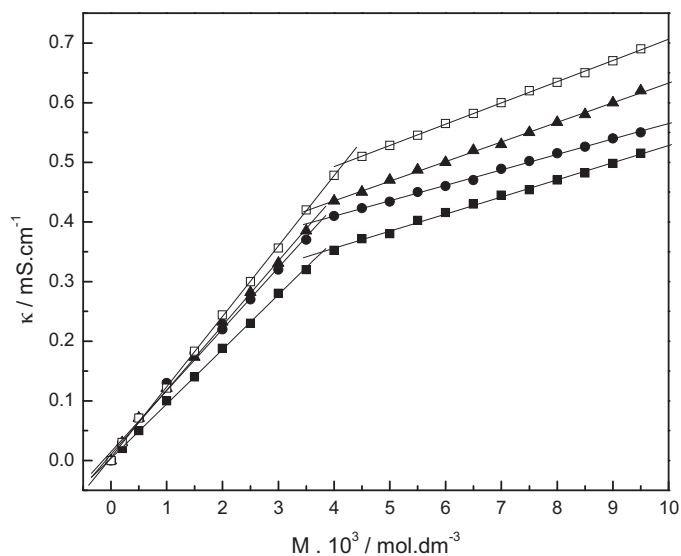


Fig. 1. Conductivity,  $\kappa$ , of aqueous TTAB: ■, 298.15 K; ●, 303.15 K; ▲, 308.15 K; and □, 313.15 K.

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