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Conductometric studies on micellization of cetyltrimethylammonium bromide in various alcohols

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ABSTRACT

The effect various aqueous solutions of methanol, ethanol, and propanol on Critical Micelle Concentrations (CMC) of cetyltrimethylammonium bromide (CTAB) has been studied at 30 and 35°c using Conductometry technique. The values of CMC at various conditions were determined. The trend of variation of CMC Values with temperature and alcohol percentage has been interpreted on the basis of molecular viewpoint and influencing factors on the structure stability of micelle. The results represent a little change in CMC with respect to these factors. The values of CMC at various temperatures do not show significant change indicating the entropy driven of micellization process. This mater can be related to the predominant role of hydrophobic forces in the micelle formation process with respect to electrostatic interaction.

Keywords: Conductometric; CTAB; Alcohols; Critical Micelle Concentrations (CMC)

INTRODUCTION

Surfactant molecules are monomer in dilute solutions, of course may be there were dimer and trimmer but when concentration of surfactant molecules reaches to a proper amount, spontaneous aggregation of surfactant molecules arises and micelle is formed. In this micelle, hydrophobic part is in the center of micelle and polar groups interact with water and are hydrated by some molecules of water. On the basis of chemical structure of these molecules, micelles can be cationic, anionic, Zwitter ion or nonionic [1], the number of monomers which form a micelle is known as aggregation number (N).
This number determines the size and geometric structure of micelle [2]. One of the surfactants properties is their micelle aggregation number. This parameter shows the average number of surfactant molecules in the micelle, which depends on hydrocarbon chain length, charge and ionic strength. Negarajan and Ruckenstien have discussed about surfactants aggregation using thermodynamic viewpoint [3,4]. Aggregation number depends on the number of carbon atoms in the hydrocarbon chain [5,6]. Increasing the concentration of surfactant molecules, increases the number of micelles, but the number of free monomers are constant and are nearly equal to their amount at CMC point. CMC is influenced by different parameters like chemical structure of surfactant, temperature, pressure, pH and ionic strength. One of the properties of micelles is solution of organic molecules [7-10]. Other property is optimizing the reaction rate changes and changing the nature of products [11]. Adding a little amount of different additives like electrolytes [12], nonpolar and polar organic liquids [12-14], change the properties of surfactant solutions especially ionic surfactants excessively.

CMC can be determined using empirical methods. In this regard we can use the plot of physical or chemical properties changes of surfactants such as electrical conduction, surface tension, solubility, refractive index, density, spectroscopic properties and UV-VIS spectroscopy versus concentration of surfactant [15,16]. Our purpose in this report is investigation of the concentration effect of various alcohols on the micellization of (CTAB) at 30 and 35°C.

MATERIALS AND METHODS

Materials

Cetyltrimethylammonium bromide (CTAB), Methanol, Ethanol, Propanol and chloridric acid were obtained from Merck and Sigma.

We used double distilled water for preparing all solutions. Experiments were done at 30 and 35°C. We used conductometer apparatus on the model of Horiba-F_{12} and accurate balance with accuracy of 0.01.

Method

In this research, we used conductometry technique to study the micellization process of cetyltrimethylammonium bromide (CTAB) in methanol, ethanol and propanol with concentrations of 5%, 10%, 15%, 20%, 30% and 40% and determined critical micelle concentration (CMC) at different conditions and related plots were constructed using Excel software.

Conductometry method

This method is used just for measuring the (CMC) of ionic surfactants. Changing of the electrical conductivity of aqueous solution of ionic surfactants at (CMC) point is in proportion to different degrees of surfactant ionization before and after the (CMC) point.

Before (CMC), surfactant monomers behave like a strong electrolyte, and after (CMC), ionization of micelles is partial.

If aqueous solutions of surfactant follow the Kohlroush's law [16], conductivity of surfactant solution (K), is calculated based on ionic molar conduction (λ_i) of ions.

$$\lambda_i = Z_i \mu_i F$$

Where Z_i, μ_i are charge and movement of ion respectively, and F is faraday constant. With eliminating the ionic charges, we consider two stages for description of the conduction changing process with respect to surfactant concentration, (CTAB has been considered as an example).

The first stage is before (CMC), in which micelle doesn't form and conductivity of (CTAB) in aqueous solution is based on miliziemens per centimeter that contains anions of (Br^-) and cations of (CTA^+), and follows equations stated as below:

$$K = m_1[CTAB]$$

Where m_1 is the slope of the plot of conduction versus concentration of [CTAB], before (CMC). After (CMC) at second stage we have:

$$K = K_0 + m_2[CTAB]$$

Where m_2 is the slope of conduction plot versus [CTAB], after (CMC) and $K_\circ$ is intercept of the second stage. We can determine the values of (CMC) using refraction point of plots (see Figs.1 to 4).

RESULTS AND DISCUSSION

Figs.1 to 4, represent conduction changes of solutions versus [CTAB] in methanol, Ethanol and propanol with different percentages at 30 and 35°C. All plots contain two linear parts before and after the refraction point, with slopes of m_1 and m_2. Slopes of plots represent amount of ionic dissociation of surfactants and amount of formed micelle. In all plots except for methanol (5%) slope is positive before CMC and negative after the CMC, and amount of slope before CMC is less than that after the CMC, and it is more obvious with increasing the percentage of alcohol and hydrocarbon groups that can be due to wide aggregation of ions with opposite signs around the micelle. Increasing the percentage of alcohol causes to reduce the polarity and dielectric coefficient of solution, that causes to increase the binding forces between ions with opposite signs, and causes to create ionic aggregation around the micelle, otherwise ionic charge of micelle will be neutralized widely.

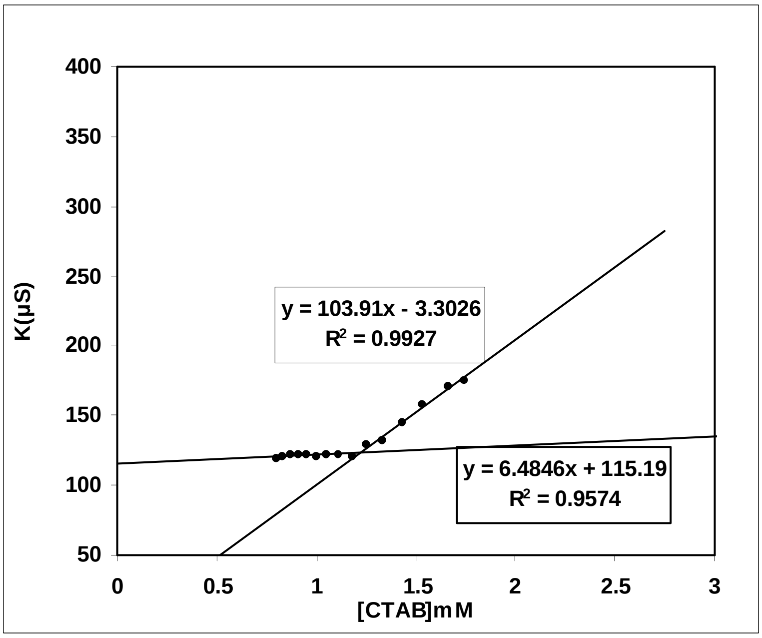

Fig.1. Variations of conduction versus [CTAB] in methanol (5%) and at 35°C

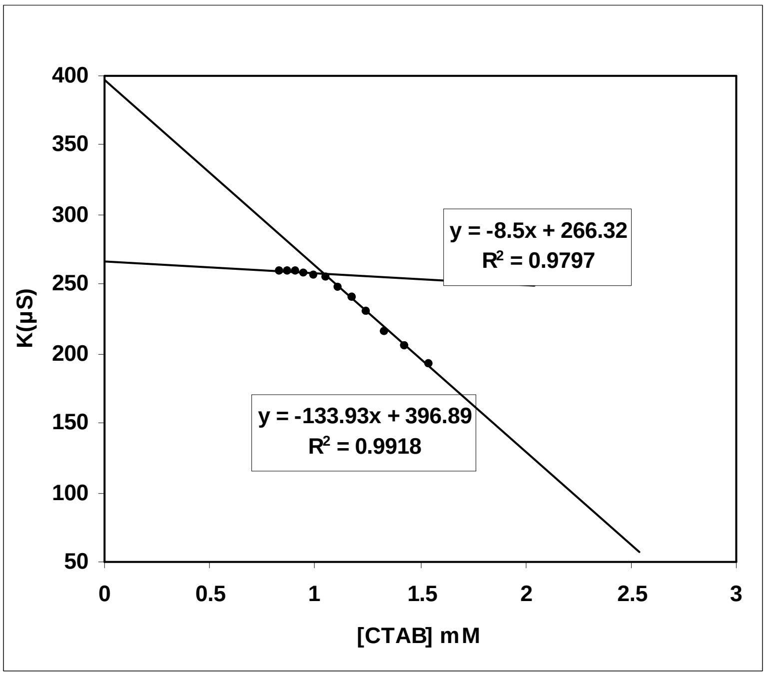

Fig.2. Variations of conduction versus [CTAB] in ethanol (15%) and at 35°C

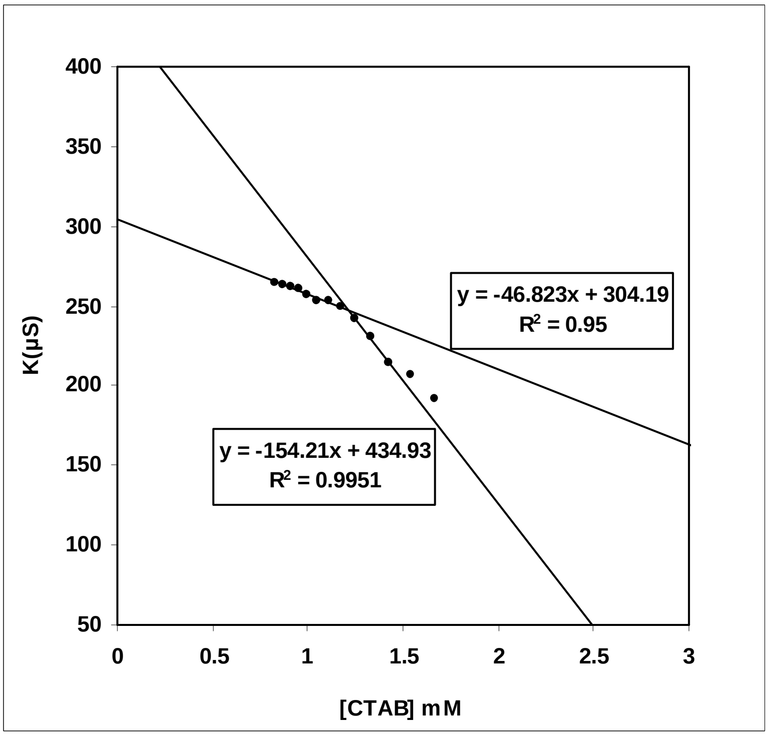

Fig.3. Variations of conduction versus [CTAB] in propanol (30%) and at 30°C

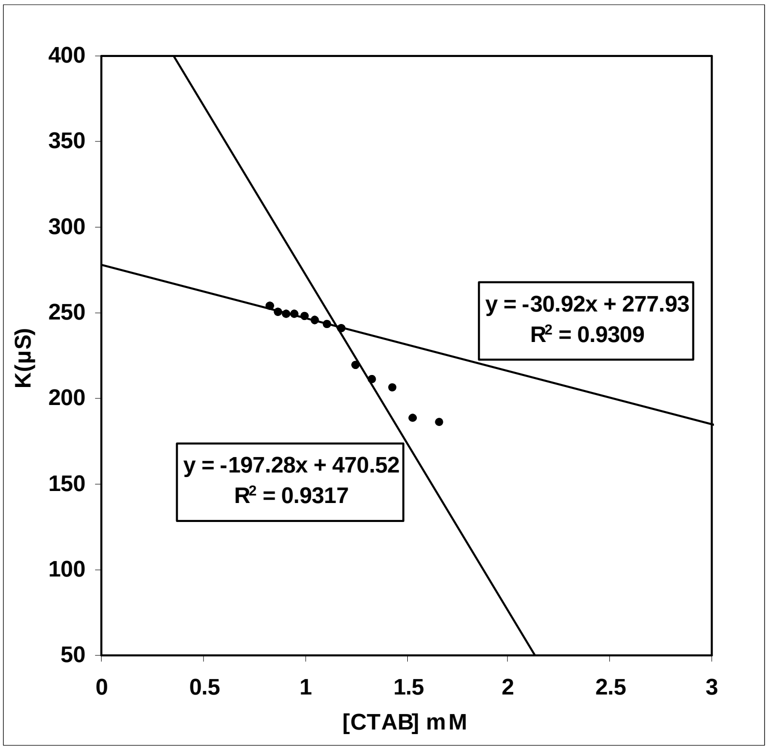

Fig.4. Variations of conduction versus [CTAB] in propanol (30%) and at 35°C

Fig. 5 and Fig. 6 show amounts of CMC changes versus various percentages of different alcohols at 30 and 35°C, based on these plots, CMC at first stage shows an intense decrease with increasing the methanol percentage, and then shows a light decrease. Also ethanol shows the same behavior, but for propanol CMC is nearly constant. According to Fig.5 changes of CMC at various percentages of alcohol don't follow a specified process and its changes aren't very intense.

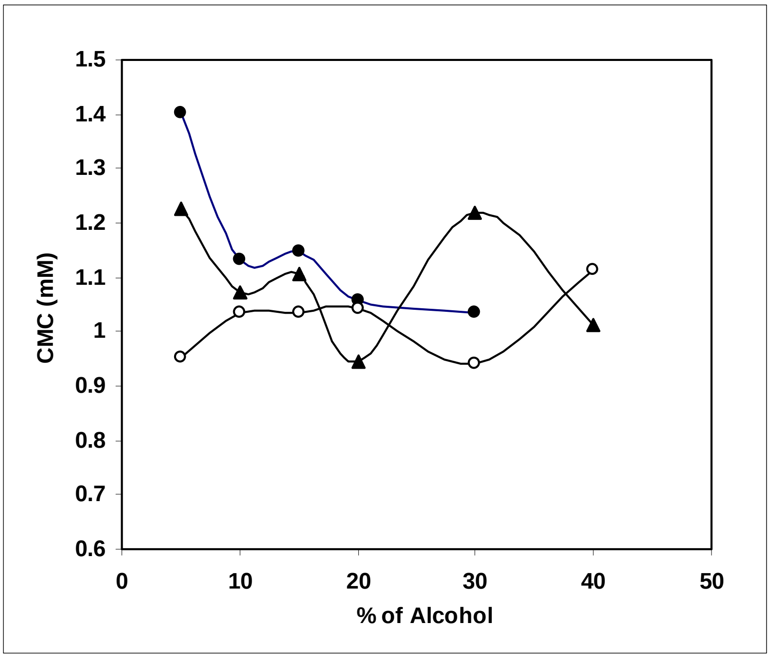

Fig.5. Variations of (CMC of (CTAB) versus) ethanol percentage at 30°C
(•) methanol, (○) ethanol, (▲) propanol

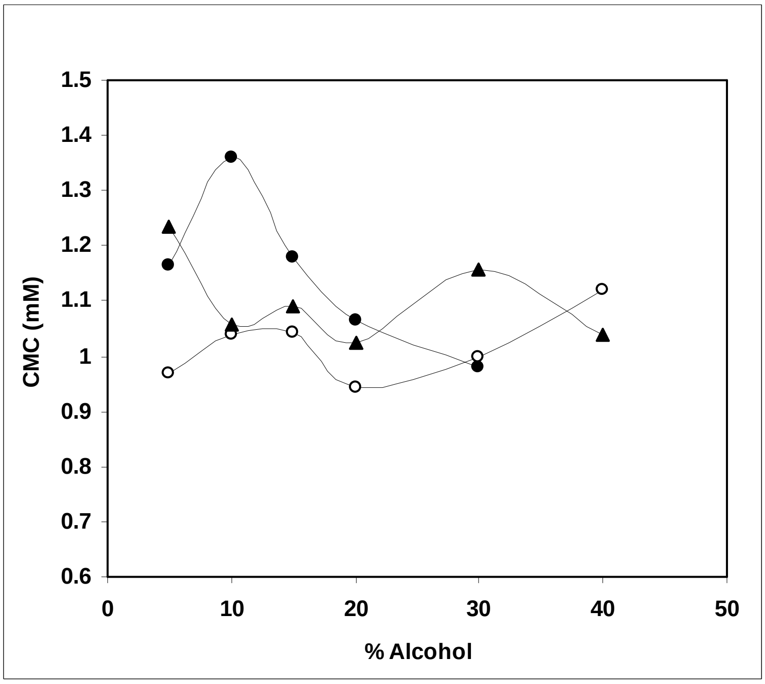

Fig.6. Variations of (CMC of (CTAB) versus) ethanol percentage at 35°C
(•) methanol, (○) ethanol, (▲) pro

CONCLUSION

There are some parameters that effect on stability of the micelle, such as size of micelle, amount of charge neutralization on the micelle surface and solution of solvent inside the micelle. In fact if the charge neutralization on the micelle surface be more, micelle becomes more stable, because electrostatic repellent forces decrease. With increasing the percentage of alcohol, amount of charge neutralization on the micelle surface increases and micelle become more stable because dielectric coefficient and concentration of solution decrease, so this factor causes to decrease CMC. Other factor is hydrophobic interactions between hydrophobic tails of surfactants that is completely a cooperative process. Increasing the percentage of alcohol destroy the structure of water and decrease the hydrophobicity of it, so hydrophobic interactions between surfactant tails for forming micelle decrease the solution of solvent specially alcohols inside the micelle and cause the micelle become more voluminous and average aggregation number increases.

Existence of these factors causes that with changing the alcohol and its percentage there do not be considerable changes in the CMC. In spit of that, bigger alcohols cause more decrease in the CMC, shows that electric charge neutralization has more roles with respect to decreasing the hydrophobicity. Comparison of the CMC values at 30 and 35°C shows that CMC changes slightly with changing the temperature, which indicates slight amount of micellization enthalpy. So we can claim that micellization is an entropic process that confirms the more roles of hydrophobic forces with respect to electrostatic interactions on the micelle formation.

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