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# Study of Micellar Behavior of Crown Ether and Tetraethylammonium Bromide in Aqueous Media

R.D.SINGH* and RAJNI GARG

*Department of Chemistry,
Gurukula Kangri University, Haridwar -249404, India.
Department of Chemistry and Centre of Advanced Studies,
Panjab University, Chandigarh-160014 India.
*chemnews@ymail.com*

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**Abstract:** Conductivity measurements have been carried out to study the micellar behavior of tetraethylammonium bromide in presence of 15-crown-5 in aqueous media. The measurements were carried out at 298.15 K as a function of surfactant concentration with varying concentrations of crown ether. The influence of this association on the micellar parameters, such as the cmc (critical micellization concentration) and β (degree of counterion dissociation) have been analyzed. Thermodynamics of the systems were discussed in terms of the change in free energy of micellisation, $\Delta G^0_m$ by applying the charged pseudo-phase separation model. The trend shows that the micellization becomes less spontaneous in presence of crown ether. The influence of the presence of the inclusion complex on the micellization process of the surfactant has been studied.

**Keywords:** Crown ether, Tetraethylammonium bromide, Critical micellization concentration, Degree of counterion dissociation.

## Introduction

Surfactant organized assemblies have great potential applications in day to day life. Surfactants have micellar properties, which are effected by addition of small amount of electrolytes, non-polar and polar organic compounds[1]. During the last decades, the study of the behavior of ionic surfactants has received much attention. Surfactant solutions at times are characterized by micelle formation at a particular concentration known as cmc. The effect of different kinds of additives, on the micellization has also been widely studied[2-9]. Such system, in general can be analyzed for various quantities that characterize micellization in a solution. The thermodynamic properties are of peculiar importance as they permit quantitative study of various phenomenons[10-14].

Crown ethers are macrocyclic polyethers. The property of complex formation along with the selectivity shown by crown ethers towards cations distinguishes them from most non-cyclic ligands. The formation of complexes between the crown ether cavity and the counterions is expected to lead to significant alterations of the micellar properties[15-20]. How this micellisation is affected by the addition of crown ethers can be an interesting area to investigate.

In the present work, efforts have been made to study the effect of addition of crown ether, 15-crown-5 (CE) on the cmc of aqueous solutions of anionic tetraethylammonium bromide (TEAB) using conductivity technique. In addition, the thermodynamic parameter, $\Delta G^0_m$, has also been estimated and analyzed in aqueous media.

## Experimental

Tetraethylammonium bromide (TEAB) (Purity>99%, water content <1%) obtained from Merck was recrystallized with chloroform-ether mixture and carefully dried in a hot air oven to constant weight. The crown ether, 15-crown-5 (CE) from Fluka (Purity>99%) was used as received. The water used to prepare the aqueous solutions was triply distilled with the conductance <3.0 μS. The conductivity of ternary mixtures was measured in a thermostatic glass cell with two platinum electrodes and Pico conductivity Meter from Lab India. The conductivity meter was calibrated by measuring the conductivity of the solutions of potassium chloride (Merck, purity > 99%) of different concentrations (0.001 M, 0.01 M and 0.1 M). Electrodes were inserted in a double walled glass cell containing the solution. The glass cell was connected to the thermostat controlled to better than ±0.01K temperature variation, read on Beckman thermometer set at the working temperature. The cell constant of the cell used was 1 $cm^{-1}$. The measurement of conductivity was carried out with an absolute accuracy up to ±3%. The solutions were prepared by weight using an analytical balance with an accuracy of $\pm 1.10^{-4}$ g. The conductivity measurements were made at 298.15K for ternary TEAB/CE/W systems, as a function of surfactant concentration with varying concentration of crown ether (0 mM- 3 mM).

## Results and Discussion

Conductivity technique has been widely used to obtain the cmc of pure or mixed ionic surfactants in water[2-14] and thus is important tool to study the thermodynamics of the systems. The cmc of a pure surfactant is determined by the appearance of a discontinuity in the slope of plots of conductivity as a function of surfactant concentration. Figure 1 depicts the behavior of conductivity, $k$, as a function of surfactant concentration for the aqueous solutions of surfactant in the presence of varying concentration of crown ether at 298.15K. Complex formation is also detected clearly in the plots of the molar conductance, $\Lambda$, *vs.* surfactant concentration as shown in Figure 2. As can be seen in the Figure 2, $\Lambda$ decreases more sharply in the presence than in the absence of crown ether because the surfactant mobility is decreased upon complexation.

The variation of cmc with change in concentration of crown ether for the ternary TEAB /CE/W systems is shown in Figure 3 and the values are listed in Table 1. There is a gradual decrease in cmc in the concentration range investigated. This observed decrease may be due to two reasons. Firstly, the decrease in the degree of hydration of the hydrophilic group with increase in the concentration of crown ether which favors the micellization and secondly the interaction of crown ether cavity with the molecular entities leading to complexation.

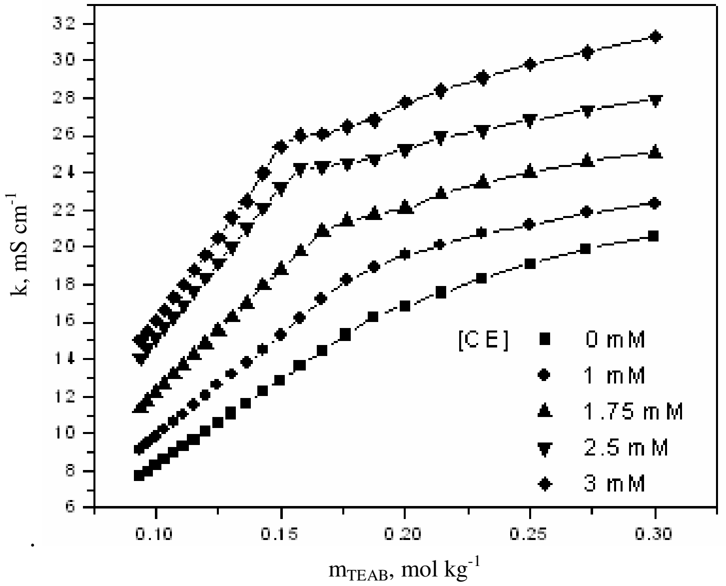


**Figure 1.** Conductive plots for TEAB/CE/W ternary systems at 298.15K for different concentrations of crown ether.

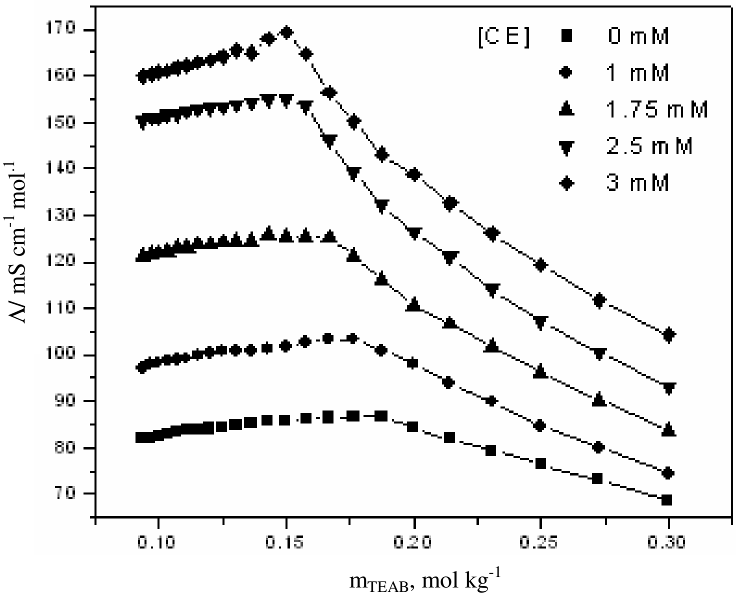


**Figure 2.** Molar conductivity plots for TEAB/CE/W ternary systems at 298.15K for different concentrations of crown ether.

The ratio between the slopes of the post-micellar region to that in the pre-micellar region gives the degree of counterion dissociation, β Figure 3 shows the variation of β for the ternary TEAB /CE/W systems as a function of concentration of crown ether. The values of degree of counterion dissociation β are tabulated in Table 1.

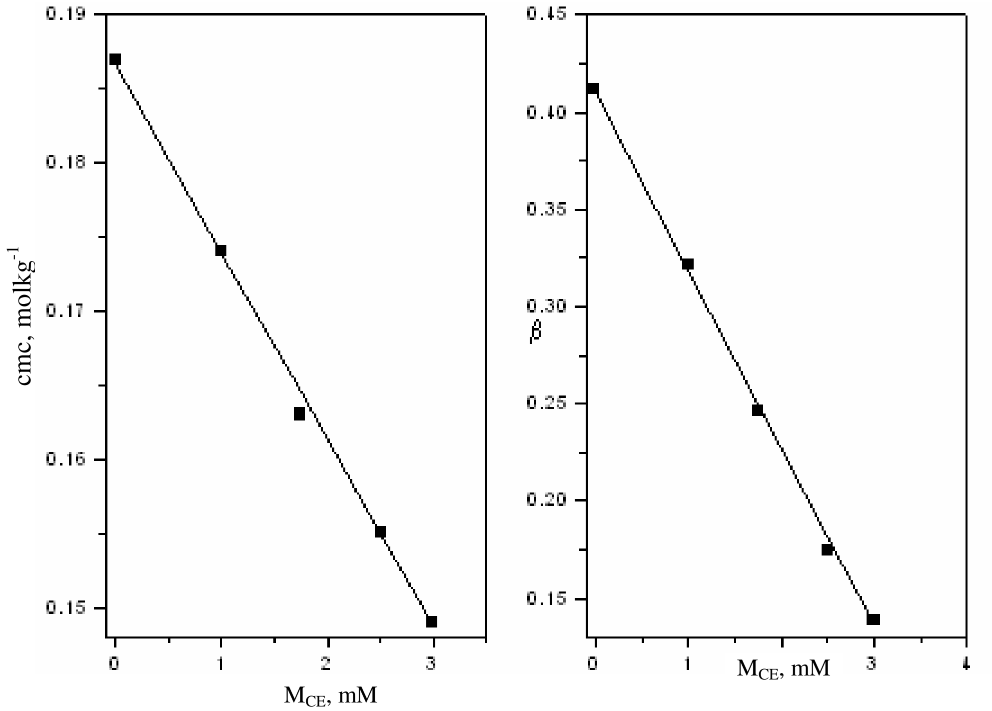


**Figure 3.** Concentration department of cmc and β.

**Table 1.** Values of cmc, degree of counterion dissociation (β) and change in free energy of micellization, $\Delta G^0_m$, for TEAB/ CE/ W at various concentration of crown ether.

| $M_{CE}$, mM | cmc, mol $kg^{-1}$ | β | $\Delta G^0_m$, kJ $mol^{-1}$ |
|---|---|---|---|
| 0 | 0.187 | 0.412 | -16.18 |
| 1 | 0.174 | 0.321 | -17.13 |
| 1.75 | 0.163 | 0.236 | -18.03 |
| 2.5 | 0.155 | 0.174 | -18.68 |
| 3 | 0.149 | 0.138 | -19.07 |

The regular decrease in β with increase in concentration of crown ether may be attributed to the increase in the charge density at the micellar surface caused by the increase in the aggregation number of the micelle. Such behavior indicates that micelles of smaller aggregation number and/or higher degree of ionization, β, are formed at lower concentration of crown ether. In accordance with the charged pseudo-phase separation model, the standard free energy of micellization per mole of surfactant, $\Delta G^0_m$, was calculated from the relation,

$$\Delta G^0_m = (2-\beta)\ RT\ \ln X_{cmc} \qquad (1)$$

Where R is the gas constant, T is the temperature, and $X_{cmc}$ is the cmc value expressed in terms of mole fraction[2].

The values of $\Delta G^0_m$ at various temperatures are listed in Table 1. $\Delta G^0_m$ values decrease with increase in concentration of crown ether indicating the decrease in the spontaneity of micellization and increase in hydrophobic interaction.

## Conclusions

Effect of addition of crown ether on the micellar behavior of anionic tetraethylammonium bromide in aqueous media has been investigated with the help of conductivity measurements at 298.15K. A linear fall in cmc was observed in the ternary systems probably due to an increase in the hydrophobic character of molecule along with the interaction with crown ether. Thermodynamics of the system reveals that the micellization is less spontaneous in presence of crown ether. No Doubt more investigation to explore such novel systems is highly desirable.

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