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THERMODYNAMICS STUDIES ASSOCIATED WITH MICELLIZATION OF CETYLTRIMETHYLAMMONIUM BROMIDE IN THE PRESENCE AND ABSENCE OF KCl AND NaCl IN AQUEOUS MEDIA

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Abstract- ***Precise measurements on conductivity of cetyltrimethylammonium bromide in the presence and absence of KCl and NaCl in aqueous media. The results showed a sharp increase in conductivity with increase in concentration of cetyltrimethylammonium bromide. Also, the conductivity increases with addition of salts. The conductance of cetyltrimethylammonium bromide is found more in the presence of KCl than NaCl in aqueous media. In the presence of monovalent salts the critical micelle concentration (CMC) value decreases which is explained on the basis of nature and ion size of the added ion. With the help of critical micelle concentration (CMC) and degree of dissociation (α) of CTAB in the presence of KCl and NaCl, the standard free energy of micellization are calculated.***

Keywords - Cetyltrimethylammonium bromide; Conductivity; Critical micelle concentration; Aqueous media

I. INTRODUCTION

The aggregation behaviour of surfactant molecules under different experimental conditions is of great scientific and practical interest, primarily due to their common use in practice [1-5]. The solution properties of surfactant are all reflected from surfactant ions comprising various combinations of hydrophobic tail with hydrophilic head and from counter ion species. Cationic surfactants offer some additional advantages over other class of surfactants [6–9]. These substances besides their surface activity do show antibacterial properties and are used as cationic softeners, lubricants, retarding agents and antistatic agents and in some cases consumer use etc.

Almgren *et al.*[10] suggested that the hydrogen bonding ability is prerequisite for micellization to happen. The effect of inorganic salt is explained in terms of the shielding of the electrostatic repulsion by the counterions [11, 12]. Chung *et al.*[13] studied the effect of KCl and alcohol on the CMC of Cetylpyridinium Chloride (CPC). They observed the decrease in CMC with the addition of electrolyte and vice versa. In this paper, we report a study of the aggregation process of CTAB at room temperature in the absence and presence of KCl and NaCl by the conductivity method in aqueous media.

II. EXPERIMENTAL

Conductance measurements were carried out on a Pye-Unicam PW 9509 conductivity meter at a frequency of 2000 Hz using a dip-type cell with a cell constant of 1.15 cm^{-1} and having an uncertainty of 0.01 %. The cell was calibrated by the method of Lind and co-workers [14] using the aqueous potassium chloride solution. Several independent solutions were prepared and runs were performed to ensure the reproducibility of the results.Cetyltrimethylammonium bromide (CTAB), KCl and NaCl were used as purchased from Loba Chemical, India. The water used in the experiments was doubly distilled. The solutions prepared at room temperature (301.15 K).

III. RESULTS AND DICUSSION

The specific conductivities increase with increase of concentration of CTAB and there is a pronounced break and then further increase with concentration. The breaking point is known as Critical Micelle Concentration, CMC (Fig. 1).
Results show that potassium chloride (KCl) has the higher conducting capability than sodium chloride (NaCl) in CTAB; this is due to the degree of solvation which is higher in sodium chloride (NaCl) than potassium chloride (KCl)[15]. Moreover, the Na^+ ions are much smaller than K^+ ions. The conductivities of CTAB in the presence of KCl is more than in the presence of NaCl because the smaller ions are strongly hydrated, so they need to pull more water molecules with them which makes them less mobile. Hence the conductivity values of CTAB in the presence of KCl are high in comparison with NaCl as shown in Fig. 1.

The degree of dissociation, α, which is the ratio of slopes above and below the CMC in the dependence conductance versus surfactant concentration and is given by the relation:

$$\alpha = S_2/S_1 \qquad (1)$$

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where S_1 is the pre-CMC slope and S_2 is the post-CMC slope[16]. The surfactant has shown the largest pre-CMC slopes and smallest post-CMC slopes leading to the smallest degrees of dissociation (Table1 and 2).

It is observed that pre-CMC slopes and the post-CMC slopes of CTAB decrease more in KCl than NaCl (Table1). In water the *CMC*s of CTAB were reported [17] to be 1.007 mM from conductometry, and 1.102 mM from tensiometry respectively at 308.15 K. As we know that the CMC of surfactant increases with temperature. Hence our experimental data for CMC of CTAB at 301.15 K is lower than 1.007mM (Fig. 1). Also, fig.1 shows the CMC decreases with the presence of NaCl and KCl. As the salt is added, the electrostatic repulsive force between ionic head groups of the surfactant molecules is reduced by shielding of micelle charge, so that spherical micelles are more closely packed by the surfactant ions[18-20], hence a decrease in the CMC values after adding monovalent salts like NaCl and KCl. Also, salts decrease the CMC of ionic surfactants [21] due to screening of the electrostatic repulsion among the polar head groups and movement of the hydrophobic alkyl chain away from aqueous environment, so that less electrical work is required to form micelles.

Salts decrease the CMC in the order: NaCl<KCl [22]. Here Na^+ is least effective in decreasing the CMC due to small size and large hydrated radius and would act as a water-structure promoter decreasing the availability of water to the micelles. Therefore, upon addition of NaCl and KCl; KCl is more effective in reducing the CMC. Hence in our case KCl decrease the CMC more than NaCl(Table 2).

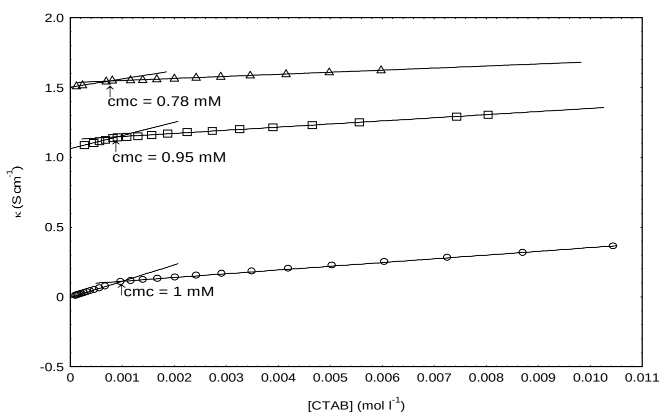

Fig.1 Variation of the specific conductivity (κ) with the concentration for CTAB solution in aqueous meida at 301.15 K in the presence of 0.10 mol.L^{-1} NaCl (squares), 0.10 mol.L^{-1} KCl (triangles).

Table 1

The pre-CMC slope (S_1) and post-CMC slope (S_2) for CTAB System from conductance measurement in Pure water and in the presence of NaCl and KCl at room temperature

Pure Water S_1, S_2	NaCl S_1, S_2	KCl S_1, S_2
117, 26.7	95, 22.4	59.5, 14.87

Table 2

Critical Micelle Concentratiom (CMC) and degree of dissociation, α, obtained from conductivity methods of cetyltrimethylammonium bromide in pure water and presence of NaCl and KCl at room temperature.

T (K)	Water *CMC*(mM), α	0.01 mol.L^{-1} NaCl *CMC*(mM), α	0.01 mol.L^{-1} KCl *CMC*(mM), α
301.15	1.00, 0.228	0.95, 0.236	0.78, 0.250

As we know that the higher degree of dissociation results in an increase of the specific conductivity [23]. In the presence of KCl, the degree of dissociation of CTAB is high because KCl has a higher specific conductivity than NaCl.

The standard free energies of micelle formation of cetyltrimethylammonium bromide in pure water and in the presence of NaCl and KCl are -21.99 KJ/mol, -22.02 KJ/mol and -22.40 KJ/mol respectively which are calculated by using the equation [24]:

$$\Delta G_m^o = RT(1.5-\alpha)\ln cmc \qquad (2)$$

Here high standard free energies of micelle formation of CTAB are found in pure water in comparison with salts because when salts are present, the dissociated salt ions approach the charged surfactant and screen it, allowing them to come together more easily. Moreover, when we add electrolyte to surfactant, we increase the ionic strength so the diffuse electric layer electro-neutralizes our micelle much more efficiently. In pure water, the charged surfactants in our micelle repulse each other strongly, and the added salt decreases this repulsion through Debye-Huckel screening, thus decreasing the energy for micelle formation. There is also a well-known ion specific effect due to the specific ion-micelle interactions such as van der Waals, hydration and other forces.

In the presence of KCl, the standard free energies of micelle formation of CTAB are found to be less than in comparison with the presence of NaCl because it might be related to Fajans rules[25]: which say that KCl should have a more ionic character in comparison with NaCl.

IV. CONCLUSION

The results showed that the specific conductance of cetyltrimethylammonium bromide increases with increase of concentrations. The specific conductance of cetyltrimethylammonium bromide in the presence of KCl found higher than in the presence and absence of NaCl. In the presence of KCl, the degree of dissociation of CTAB is high in comparison with the presence and absence of NaCl.
It is found that the CMC of cetyltrimethylammonium bromide deceases with the addition of salts. The CMC of cetyltrimethylammonium bromide decreases more in the presence of KCl in comparison with the presence and absence of NaCl.

In the presence of KCl, the standard free energies of micelle formation of CTAB are found to be less than in comparison with the presence and absence of NaCl.

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