



## Physico-chemical properties of cationic surfactant cetyltrimethylammonium bromide in the presence of electrolyte

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### Abstract

This work reports the effects of electrolyte lithium chloride (LiCl) on the physico-chemical properties of the cationic surfactant cetyltrimethylammonium bromide (CTAB) at different temperatures. The conductometry, surface tensiometry and viscometry techniques were employed to evaluate these physico-chemical and thermodynamic properties. The thermodynamic parameters like free energy of micellization ( $\Delta G_m$ ), free energy of absorption ( $\Delta G_{ads}$ ), surface excess concentration ( $\Gamma$ ) and minimum area per molecule ( $A$ ) were calculated through surface tension measurements. Critical Micelle Concentration (CMC), degree of ionization ( $\alpha$ ) and degree of counter ion binding ( $\beta$ ) were measured by conductometry technique. The results showed that the values of CMC of CTAB decreased with the increase in temperature. The value of CMC calculated through conductometry for pure CTAB was 0.98 M at 303 K, which was observed to decrease as temperature increased and got value of 0.95 M at 318 K. Moreover the addition of electrolyte LiCl into the surfactant lead to lowering of the CMC and got value of 0.90 M at 3 M of LiCl. The addition of electrolyte was also observed to decrease the values of CMC of CTAB, indicating significant electrostatic interactions between surfactant and electrolyte. Moreover the value of  $\alpha$  calculated for pure cationic surfactant CTAB was 0.219, which tends to increase with the addition of electrolyte, while that of  $\beta$  value was observed to decrease from 0.780 to 0.206. This is due to the fact that greater charge density at micellar surface and diminishing in the aggregation number of micelle as well as an increase in the micellar ionization due to the incorporation of electrolyte LiCl.

## 1. Introduction

The self assembly properties of surfactant in selective solvents have been the subject of great interest in the last few decades. Particular emphases have been given on the interaction between ionic surfactant and electrolyte. In the last few decades, interaction between surfactants and electrolytes have attracted greater attention due to its worldwide applications in different fields, for example, pharmaceutical, drug delivery, coatings, petroleum and detergent formulations [1-3]. The diversity of such uses has been a powerful driving force behind the design and preparation of new families of surface-active agents over the last several decades [4,5].

Surfactants are the surface active agents which decrease the surface tension of liquids through lowering the interfacial tension between two liquids. These are the versatile chemical compounds which are amphiphilic in nature consisting of hydrophilic head which may be anionic, cationic, non ionic and zwitterionic as well as hydrophobic tail that may be hydrogenated, fluorinated linear or branched [6]. Even in small amount, these surfactants can alter the surface or interfacial free energies to a marked degree due to their property of adsorbing onto the surfaces or interfaces of the system. Many industrial and domestic applications including dispersing, emulsifying, wetting, cleaning, washing, foaming and preparation of medicines have been reported for surfactants. Because of their characteristic surface activity and wider applications in industries, research on surfactants and their physic-chemical properties have gained momentum which alternatively, causing severe environmental concerns [7,8]. Surfactants have two main features, i.e., surface activity and the ability to form

micelles in solutions which in turn, affects the functionality of surfactants [9-13]. One of the main characteristics of surfactants is their tendency, in dilute aqueous solutions, to self-assemble and form aggregates by exposing polar head groups to water and segregating hydrophobic tails from water [14]. When a surfactant is dissolved in solution, the hydrophobic groups associate together and the polar head groups orient them towards the aqueous medium. Through this method, At certain concentration, the surface active ions in a solution associate to form larger units, which are called micelles. Previously, reports regarding the development of new methods to study the behavior of surfactants in many chemical reactions and the effects of various factors on their properties have been carried out. It has been observed that interaction between the surfactants and small molecules was helpful to analyze the mechanism of surfactants [15].

In aqueous media, surfactant with and without addition of foreign material form micelles and this concentration of the surfactant is called the critical micelles concentration (CMC). Physico-chemical properties such as CMC, degree of ionization and thermodynamics of micellization depend on the nature of the hydrophobic tail, the hydrophilic head group and the counter ion species [16]. The resolution of CMC has concrete value in getting the behavior of surfactants in various processes. Many studies have previously reported the structure of micelle under various situations [17,18]. Cautious experimental measurement used in a highly purified system shows a continuous and gradual change in physico-chemical characters of surfactants when it reach to the CMC [19]. The rapid changes in their properties are due to the formation of colloidal aggregates in a narrow concentration range. The monomers combined in aqueous solution to form big molecules depend on the molecular structures of the surfactant, concentration, temperature and different electrolytes which are added [20]. Abuin and Scaiano [21] reported the determination of CMC at various temperatures and addition of electrolytes to surfactant in detail. They also observed that these systems also formed hydrophobic domains, although clusters were formed because aggregations were completely different from the micelles formed in aqueous homogeneous mixture. This can be explained in the sense that they (cluster) were formed at concentrations lower than the CMC of the surfactants concentration and the aggregation numbers found were also smaller. The opposite charged groups of the electrolytes and the surfactant are attracted electrostatically. So, electrolyte works as a pattern for the aggregation of the surfactants, which finally results in the reduction of the repulsive interaction among surfactant heads group, which facilitate the aggregation behavior [22].

The present study shows the effect of electrolyte LiCl on the surfactant CTAB at different temperatures to observe and measure the electrolyte interaction which affects the mechanism of micelle, i.e.; CMC of cetyl trimethylammonium bromide (CTAB) an important phenomenon in most of the industrial and chemical process.

## 2. Experimental

Cetyltrimethylammonium bromide (CTAB, analytical grade) was used as surfactant in distilled water while lithium chloride (LiCl) was used as electrolyte, purchased from Merck (Germany). All the chemicals were used without further purification.

### 2.1. Preparation of Solutions

A stock solution of CTAB was prepared by dissolving known amount of the surfactant in distilled water. The known concentration of electrolyte (LiCl) was also prepared in the distilled water. Depending upon the technique used such as surface tension measurement, conductance measurement and viscosity, solutions were prepared by dilution method to determine the CMC value i.e. the interactions of electrolyte with surfactant. Various techniques such as conductance, surface tension and viscosity measurement were employed to get information about surfactant's characteristics, for instance, CMC determination with different concentrations of electrolytes. Procedure preference to CMC determination, the electrolyte with different concentrations was used to determine the surface properties using various techniques like conductance, surface tension and viscosity measurements.

### 2.2. Characterization

#### 2.2.1. Conductance measurement

Conductance measurements were obtained using *Jenway 4310* digital conductometer with the temperature range of 30 °C to 50 °C, attached with a temperature regulator *IRMICO I-2400*. The CMC were obtained in specific conductivity against surfactant concentration.

### 2.2.2. Surface tension measurement

Surface tension of dilute aqueous solutions as well as surfactant-electrolyte mixed system was measured in temperature range of 30 °C to 40 °C. The surface tension measurement was performed through platinum ring bearing Tensiometer (White Electric Instrument Co. Ltd.). All the measurements were repeated calibration with pure water.

### 2.2.3. Viscosity measurement

The viscosity of electrolyte which was added to the surfactant was determined using Ostwald viscometer in temperature range of 40 °C to 60 °C. The temperature was controlled by thermostat. For flow time measurement, fixed volume of solution was taken.

## 3. Results and discussion

### 3.1. Conductance measurement

#### 3.1.1. Critical micelle concentration (CMC)

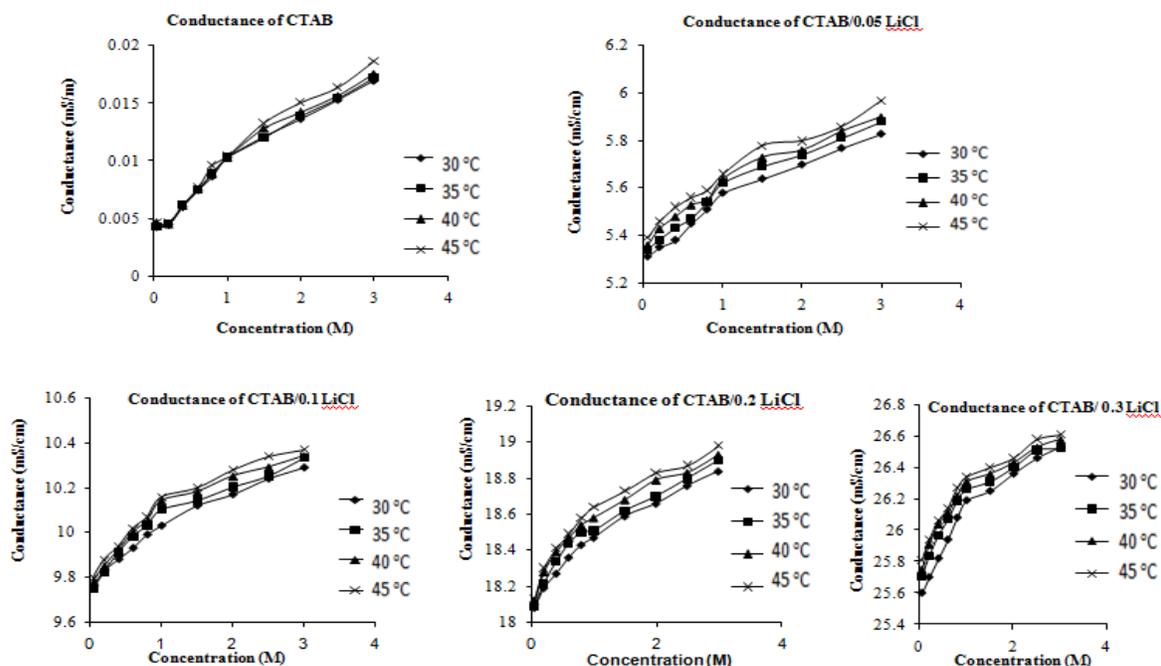
Micelles are the larger molecules formed in the solutions when the active surface ions combines at certain concentration and this phenomenon is termed as critical micelle concentration (CMC). Mukherjee and Mysels [23] explained that the CMC and number of molecules in a micelle are most important parameters characterizing the surfactants, their ability and proper use. As a result a great deal of effort has been directed towards such work. It is known fact that most of physical properties like surface tension, conductivity, viscosity, density etc. change abruptly their trend when the concentration of surfactants approaches to CMC. It is observed that CMC of the surfactant decreases as the concentration of electrolytes and temperature increases. The results are shown in Table 1. It may be due to the fact that conductivity of charged micelle of surfactants and free ions of electrolytes contribute to resulting electric conductivity of aqueous micelle solution of surfactant. In electrical conductivity measurement the intersection of the two lines of concentration, conductivity plot gives the CMC value of the surfactants and mixed systems. The first straight line corresponds to pre micellar region while the second one is assigned to the post-micellar region [24]. The various values of CMC calculated from conductance measurements are give in Table 1 below.

**Table 1:** CMC of CTAB with LiCl electrolyte at various temperatures through conductance measurement

| Concentration of electrolyte | CMC of CTAB with LiCl electrolyte at various temperature through conductance measurement |        |        |        |
|------------------------------|--|--------|--------|--------|
|                              | 30 °C  | 35 °C  | 40 °C  | 45 °C  |
| 0 M LiCl                     | 0.98 M   | 0.97 M | 0.96 M | 0.95 M |
| 0.05 M LiCl                  | 0.99 M   | 0.98 M | 0.95 M | 0.94 M |
| 0.1 M LiCl                   | 0.96 M   | 0.95 M | 0.95 M | 0.94 M |
| 0.2 M LiCl                   | 0.90 M   | 0.87 M | 0.85 M | 0.84 M |
| 0.3 M LiCl                   | 0.88 M   | 0.86 M | 0.84 M | 0.81 M |

Conductivity of surfactant cetyltrimethylammonium bromide (CTAB) with and without the addition of electrolyte at different temperature was plotted in Figure 1. The results show that conductance of the surfactant increased as the concentration and temperature increased while CMC of the surfactant decreased with increase in concentration and temperature. Table 1 show that the value of CMC for pure CTAB was calculated 0.98 M at 303 K, which was observed to decrease as temperature increased and got value of 0.95 M at 318 K. Moreover the addition of electrolyte LiCl into the surfactant leads to lowering of the CMC and got value of 0.88 M at 3 M of LiCl.

It may be because of the fact that the conductivity of charged micelle of surfactants and free ions of electrolyte contribute to the electric conductivity of aqueous micelle solution of the surfactant. Furthermore, the free ion concentration decreased due to the association of counter ion with micelle as well as with the encapsulation of a part of free ions. Additives in surfactants lead to lowering of the CMC. Through conductance method it was possible to get accurate results at any ionic strength and temperature. It was observed that with the increase in electrolytic concentration some errors in results were also noted, which may be attributed to the impurities present in the salts or with increase in electrolyte concentration.



**Figure 1:** Plot of electrical conductivity as a function of concentration of CTAB in the presence of (A) 0 M LiCl (B) 0.05 M LiCl (C) 0.1 M LiCl (D) 0.2 M LiCl (E) 0.3 M LiCl at various temperatures (°C)

### 3.1.2. Degree of ionization ( $\alpha$ )

To calculate the degree of ionization, the following equation is used

$$\alpha = \frac{S_2}{S_1} \quad (1)$$

$S_1$  = Slope for pre micellar concentration

$S_2$  = Slope for post micellar concentration

The values of  $\alpha$  were determined both for pure CTAB and with electrolytic solutions are given in Table 2. For pure CTAB, the value of degree of ionization ( $\alpha$ ) calculated was 0.219 which was observed to increase due to the addition of electrolyte LiCl and got value of 0.793. This is because of greater charge density at micellar surface and diminishing in the aggregation number of micelle. The stability of micellar charge increases probably due to the decrease in electrostatic repulsions. Especially at higher micellar charge, the formation of smaller salt-bound micelles, since electrostatic repulsion is diminishes and the increase in hydrocarbon-water contact area is stabilized by the salt.

**Table 2:** Parameters calculated from conductivity method i.e. degree of ionization ( $\alpha$ ) and degree of counter ion binding ( $\beta$ ) 303 K

| S. No | Sample             | $\alpha$ | $\beta$ |
|-------|--------------------|----------|---------|
| 1     | Pure CTAB          | 0.219    | 0.780   |
| 2     | CTAB + 0.05 M LiCl | 0.378    | 0.621   |
| 3     | CTAB + 0.1 M LiCl  | 0.570    | 0.429   |
| 4     | CTAB + 0.2 M LiCl  | 0.647    | 0.353   |
| 5     | CTAB + 0.3 M LiCl  | 0.793    | 0.206   |

### 3.1.3. Degree of counter ion binding ( $\beta$ )

The degree of ionization is related to the degree of counter- ion binding ( $\beta$ ) by the equation.

$$\beta = 1 - \alpha \quad (2)$$

The values of degree of counter ion binding ( $\beta$ ) for pure CTAB and in the presence of LiCl solution are given in Table 2. The results showed a decrease in  $\beta$  values for the surfactant-electrolytic solution 0.206 as compare to that of pure CTAB having a value of 0.780 indicating an increase in the micellar ionization due to the incorporation of LiCl.

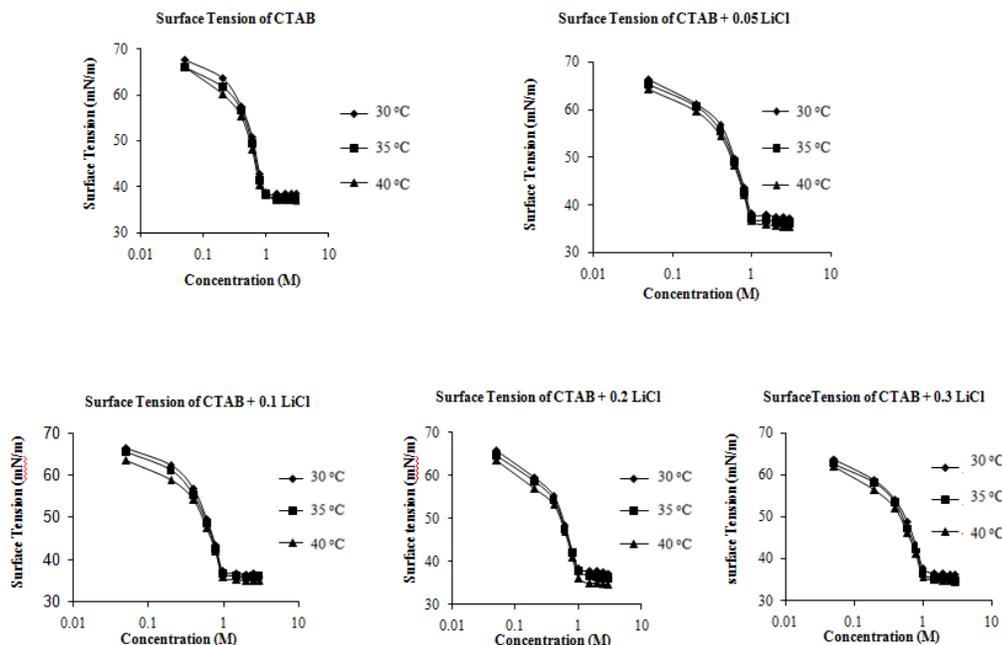
### 3.2. Surface tension measurement

Surface tensions of the surfactant cetyltrimethylammonium bromide (CTAB) with and without the addition of electrolytes at different temperature are plotted in Figure 2. The various values of CMC calculated from surface tension measurements are give in Table 3 below.

**Table 3:** CMC of CTAB with LiCl electrolyte at various temperatures through surface tension measurement

| Concentration of electrolyte | CMC of CTAB with LiCl electrolyte at various temperature through surface tension measurement |        |        |
|------------------------------|--|--------|--------|
|                              | 30 °C  | 35 °C  | 40 °C  |
| 0 M LiCl                     | 1 M  | 0.98 M | 0.96 M |
| 0.05 M LiCl                  | 0.99 M   | 0.97 M | 0.97 M |
| 0.1 M LiCl                   | 0.98 M   | 0.98 M | 0.96 M |
| 0.2 M LiCl                   | 0.97 M   | 0.96 M | 0.96 M |
| 0.3M LiCl                    | 0.96 M   | 0.96 M | 0.95 M |

The surface tension decreased as the concentration and temperature of surfactant increased in the absence of electrolyte. This decrease in surface tension continued till a point, and then it became constant, resulting in the formation of CMCs. Electrolytes decrease the surface activity of surfactants [25] which ultimately decrease the surface tension of the solution. Furthermore, due to the addition of electrolyte, the solvation layer around the surfactant ionic head decreases along with a decrease in the electrostatic repulsive interactions between the surfactant positive charges. These consequently decrease the hydrophilic characteristics of surfactants. Collectively, the surface activity enhance, molecules aggregate and a decrease is caused in CMC and surface tension. The presence of additives like glycerin, which has good hydrophobicity, the water matrix is broken, micellization occur easily and the CMC decreases [26-28].



**Figure 2:** Plot of surface tension as a function of concentration of CTAB in the presence of (A) 0M LiCl (B) 0.05 M LiCl (C) 0.1 M LiCl (D) 0.2 M LiCl (E) 0.3 M LiCl at various temperatures ( $^{\circ}\text{C}$ )

### 3.2.2. Surface parameters of adsorption and micellization

#### A. Surface excess concentration ( $\Gamma_m$ )

The study of interfacial properties of surfactant in Lithium chloride solution (LiCl) solutions provides useful information about the Gibbs surface excess concentration ( $\Gamma_m$ ) by using Gibbs adsorption isotherm equation;

$$\Gamma_m = -1/2.303RT (\partial \gamma / \partial \log C_2)_T \quad (3)$$

The values obtained for  $\Gamma_m$  for both pure and in the presence of electrolytic solutions were in close agreement with previous reports. The addition of surfactant to electrolytic solution decrease  $\Gamma_m$  due to the removal of electrolytes by surfactants via adsorption and hydrophobic binding to the electrolyte and often the interaction leads to the formation of surfactant-electrolyte complex.

**Table 4:** Summary of thermodynamic parameters calculated from surface tension method at 303 K

| S. No | Sample             | Surface excess concentration ( $\Gamma$ ) mol/m <sup>2</sup> | Minimum area per molecule (A) nm <sup>2</sup> | Free energy of adsorption ( $\Delta G_{\text{ads}}$ ) kJ/mol | Free energy of micelization ( $\Delta G_m$ ) kJ/mol |
|-------|--------------------|--|---|--|---|
| 1     | Pure CTAB          | $4.02 \times 10^{-3}$  | $4.23 \times 10^{-4}$                         | -47.39   | -47.43  |
| 2     | CTAB + 0.05 M LiCl | $5.53 \times 10^{-4}$  | $1.79 \times 10^{-3}$                         | -43.47   | -43.44  |
| 3     | CTAB + 0.1 M LiCl  | $5.93 \times 10^{-4}$  | $2.67 \times 10^{-3}$                         | -41.22   | -41.20  |
| 4     | CTAB + 0.2 M LiCl  | $6.69 \times 10^{-4}$  | $3.37 \times 10^{-3}$                         | -39.82   | -39.81  |
| 5     | CTAB + 0.3 M LiCl  | $7.34 \times 10^{-4}$  | $4.89 \times 10^{-3}$                         | -37.04   | -37.03  |

#### B. Free energy of micellization ( $\Delta G_m$ )

The free energy of micellization for pure surfactant along with surfactant-electrolytic solution was obtained by applying the following equation.

$$\Delta G_{mic}^{\circ} = (1+\beta) RT \ln X_{cmc} \quad (4)$$

Negative values of  $\Delta G_m$  correspond to the spontaneous micellization. In case of LiCl addition to the CTAB solution, less negative  $\Delta G_m$  values were obtained which clearly indicates the interactions of electrolyte with CTAB (Table 4).

### C. Free energy of adsorption ( $\Delta G_{ads}$ )

$\Delta G_{ads}$  for pure surfactant as well as its solution in electrolytes is measured and calculated from this equation.

$$\Delta G_{ads}^{\circ} = \Delta G_{mic}^{\circ} - \frac{\pi_{CMC}}{\Gamma_m} \quad (5)$$

Table 4 illustrates the  $\Delta G_{ads}$  values for pure CTAB and its solution in LiCl. The negative values of  $\Delta G_{ads}$  were indicative of spontaneous process occurred due to the adsorption at air-water interface. The adsorption cause removal of the salt when surfactant is added leading to the formation of complexes that can disintegrate later.

### 3.3. Viscosity measurement

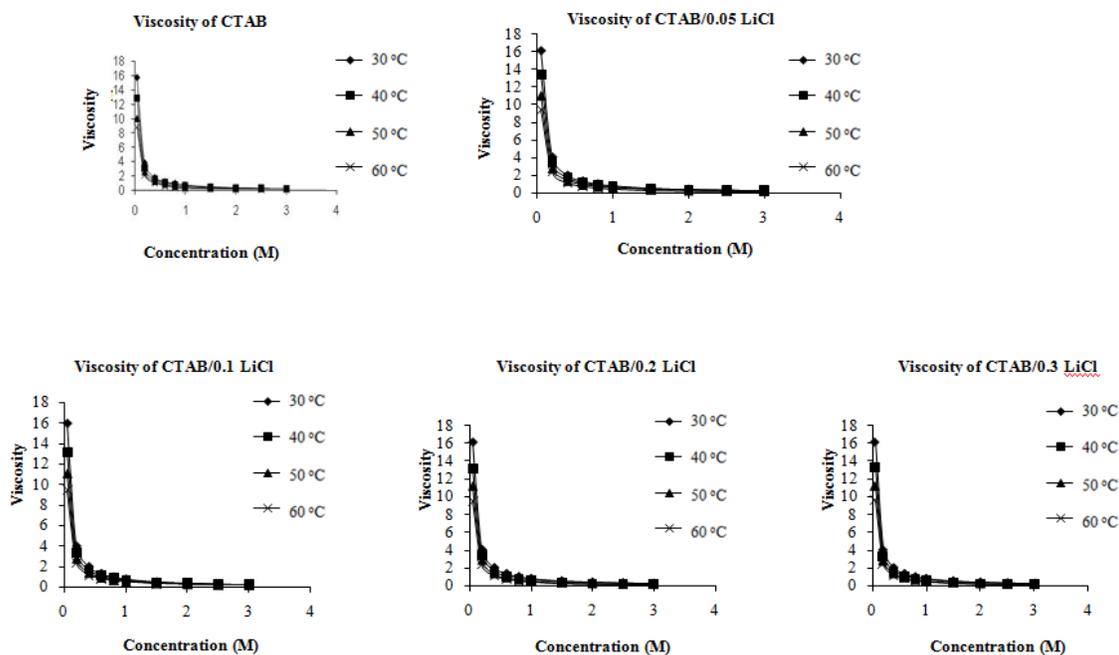
Viscosity measurement is not as much reliable technique as conductivity and surface tension but it can also be used to determine the CMC of surfactant. The studies on the viscosities of electrolyte as well as surfactant solutions are usually carried out to obtain information about the structure and properties of solutions [29]. This is due to, (i) Viscosity depends upon number and size of particles. Hence in micellization, number decrease and size increases. (ii) The micelle change to unimer and it becomes difficult to determine the CMC. The various values of CMC calculated from viscometry are given in Table 5 below.

**Table 5:** CMC of CTAB with LiCl electrolyte at various temperatures through viscosity measurement

| Concentration of electrolyte | CMC of CTAB with LiCl electrolyte at various temperature through viscosity measurement |       |       |       |
|------------------------------|--|-------|-------|-------|
|                              | 30 °C  | 40 °C | 50 °C | 60 °C |
| 0 M LiCl                     | 0.98   | 0.97  | 0.96  | 0.96  |
| 0.05 M LiCl                  | 0.98   | 0.96  | 0.95  | 0.95  |
| 0.1 M LiCl                   | 0.97   | 0.95  | 0.95  | 0.94  |
| 0.2 M LiCl                   | 0.96   | 0.95  | 0.94  | 0.94  |
| 0.3 M LiCl                   | 0.96   | 0.95  | 0.94  | 0.93  |

Viscosity versus concentration graph was plotted for surfactant by adding electrolyte at different temperatures as shown in Figure 3. It was noted that viscosity increased as concentration of electrolytes increased and decreased with the increase in temperature.

Viscosity remained constant at low concentration of electrolytes however; it was observed distinctly that it increased at higher concentration of added electrolytes. It can be explained in terms of transition of micelle from spherical to rod and subsequently enlargement of rod like micelle. For ionic micelle the addition of salt would increase the ionic strength of media, screening electrostatic repulsion between charge head group. Moreover, oppositely charged additive would be able to absorb onto the surface of micelle thus decreasing surface charge of micelle. These effects increase the packing parameters for micelles. The increase in viscosity corresponds to the binding of surfactant monomers with electrolytes. One of the major cause of viscosity increase due to the surfactant concentration increase is the cross linking of several micelles aggregation [30,31]. Viscosity increases with the increase of concentration of electrolytes [32]. Previous studies suggest that the micelles form large cylindrical aggregates in solutions due to bulk concentration. [33-35]. Increase in viscosity is usually identified with shape transition from small to large rod like micelle [35]. Viscosity decrease with increase in temperature leads to micelle to break and smaller micelle are formed.



**Figure 3:** Plot of viscosity as a function of concentration of CTAB in the presence of (A) 0 M LiCl (B) 0.05 M LiCl (C) 0.1 M LiCl (D) 0.2 M LiCl (E) 0.3 M LiCl at various temperatures ( $^{\circ}\text{C}$ )

It is observed from above results that the CMC obtained using conductivity measurement, and surface tension method are comparable to each other with some experimental error and underlying principles for different techniques. Due to theories used for purpose of different techniques. For example, conductivity is sensitive to smaller charge particles, whereas it is possible that during viscosity measurement the micelle disaggregate under high shear rate. The CMC data obtained for CTAB in the presence of electrolytes at different temperature are given in Table 5, show that addition of electrolytes with different concentration decreases the CMC value of surfactants. Electrolytes decreases CMC; because the ions of the salts neutralized the charge on the micelle surface thus cause a decrease in thickness of the electrolyte at surfactant with enhanced electrostatic repulsion which help the micellization [36]. Electrolytes like NaCl lowered the CMC of surfactants that can be explained by the fact that  $\text{Na}^+$  and  $\text{Cl}^-$  ions in solution can affectively screen the attractive electrostatic attraction between charged head groups with surfactants leading to aggregation at lower surfactant concentration which results in increase in hydrophobicity, and decrease in the CMC.

In the presence of ionic liquid, value of CMC is lowered due to increasing concentration of counter ions or due to the formation of mix micelle. Increasing salt concentration reduces electrostatic repulsion between charge groups and favors aggregation. Paredas et al [36] reported that CMC of CTAB in water and in 0.05 M NaBr decrease the CMC value as  $\text{Br}^-$  concentration is increased. The CMC of surfactants decrease if electrolytes like alcohol is present and alkyl chain of alcohol increase because alcohol molecule in micellar phase are positioned with alkyl chain towards micellar core, while their hydroxyl groups are located between ionic heads of surfactant molecule, thus increasing length between them which decrease repulsion [37]. This factor contributes to the micelle and decreasing the CMC. Another factor which was studied was the effect of the temperature on CMC of surfactants. It was noted from the results that temperature imparted less effect than that of electrolytes. The CMC of surfactants decreases with the increase in the temperature due to increase in temperature increase the thermal motion of surfactants molecule. As a result, interaction between surfactants and water increased while the electrostatic forces between surfactant and electrolyte decreased. At high temperature, the dehydration ratio is higher which strengthens the surface activity producing micellization [38].

The temperature increase cause a disruption of water molecules which around the hydrophobic group, not favoring micellization [39,40]. The rate of change in conductivity with varying electrolytes concentration was sufficiently marked at critical concentration making it a valuable method for determination of the CMC.

Decrease in CMC connected with synergistic effect of electrolytes and surfactants [41] were named as “negative deviation from ideality” [42]. When cation is inserted into the surfactant micelle the charged on anionic hydrophilic group partially counterbalance increase in micelle size and reduction of electrostatic repulsion. In other words, charged density at micelle surface decreases and absolute value of electrical potential is also reduced [42].

## Conclusions

The micellization behavior of cationic surfactant CTAB in the presence of electrolyte LiCl was investigated at different temperature through conductivity, surface tension and viscosity measurements. From all this discussion we came across the conclusion that the values of CMC of CTAB decrease with the increase of temperature. The value of CMC for pure CTAB calculated through conductance measurement was 0.98 M at 303 K, which was observed to decrease as temperature increased and got value of 0.95 M at 318 K. Moreover the addition of electrolyte LiCl into the surfactant leads to lowering of the CMC and got value of 0.90 M at 3 M of LiCl. Moreover, an increase in concentration of electrolyte results in a decrease of CMC. It is because of the fact that the conductivity of charged micelle of surfactant and free ions of electrolyte contributed to the electric conductivity of aqueous micelle solution of the surfactant. Furthermore, the free ion concentration decreased due to the association of counter ion with micelle as well as with the encapsulation of a part of free ions. The degree of ionization ( $\alpha$ ) for pure cationic surfactant CTAB was 0.219, which tends to increase up to 0.793 with the addition of electrolyte, while that of counter ion binding values ( $\beta$ ) was observed to decrease from 0.780 to 0.206. This is due to the fact that greater charge density at micellar surface and diminishing in the aggregation number of micelle as well as an increase in the micellar ionization due to the incorporation of electrolyte LiCl.

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