

Effect of Electrolyte (NaCl) and Temperature on the Mechanism of Cetyl Trimethylammonium Bromide Micelles

(Kesan Elektrolit (NaCl) dan Suhu terhadap Mekanisme Setil Trimetilammonium Bromida Misel)

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ABSTRACT

In the last few decades, surfactants and electrolyte interaction has gained considerable attention of researchers due to their industrial and domestic applications. In this work, the effects of electrolyte (NaCl) on the critical micelle concentration (CMC) of the cationic surfactant cetyltrimethyl ammonium bromide (CTAB) at different temperatures were investigated through different techniques such as conductometry, surface tensiometer and viscosimeter. The results showed that the values of CMC of CTAB decreased with the increase in temperature as well as with the addition of NaCl. The value of CMC for pure CTAB was calculated 0.98M at 303K, which was observed to decrease as temperature increased and got value of 0.95M at 318K. Moreover the addition of electrolyte NaCl into the surfactant lead to lowering of the CMC and obtained value of 0.90M at 3M of NaCl, indicating significant electrostatic interactions between surfactant and electrolyte. Moreover the degree of ionization(α) calculated for pure cationic surfactant CTAB was 0.219, which tends to increase with the addition of electrolyte, while that of counter ion binding values (β) was observed to decrease from 0.780 to 0.201. Furthermore, the conductivity of charged micelle of surfactant and free ions of electrolyte contributed to electric conductivity of aqueous micellar solution of surfactant. The results can be helpful to develop better understanding about interaction between electrolyte and surfactant.

Keywords: Electrical conductance; electrolyte NaCl; surface tension; surfactant CTAB; viscosity

ABSTRAK

Beberapa dekad kebelakangan ini, surfaktans dan interaksi elektrolit telah mendapat perhatian para penyelidik kerana kegunaannya dalam perindustrian dan domestik. Dalam kertas ini, kesan elektrolit (NaCl) ke atas kepekatan kritikal misel (CMC) of kationik surfaktans setiltrimetil ammonium bromida (CTAB) pada suhu yang berbeza telah dikaji melalui teknik yang berbeza seperti konduktometri, permukaan tensiometer dan meter kelikatan. Hasil kajian menunjukkan bahawa nilai CMC untuk CTAB berkurang dengan peningkatan suhu serta penambahan NaCl. Nilai CMC untuk CTAB tulen ialah 0.98M pada 303K dan diperhatikan menurun apabila suhu meningkat dan memperoleh nilai 0.95M pada 318K. Selain itu, penambahan elektrolit NaCl ke dalam surfaktans membawa kepada penurunan CMC ini dan memperoleh nilai 0.90M pada 3M NaCl yang menunjukkan interaksi elektrostatik yang penting antara surfaktans dan elektrolit. Tambahan pula, darjah pengionan(α) yang dikira untuk surfaktans kationik tulen CTAB ialah 0.219, yang cenderung untuk meningkat dengan penambahan elektrolit, manakala perbandingan nilai ikatan ion (β) diperhatikan menurun daripada 0.780 untuk 0.201. Seterusnya, konduktiviti misel bercaj surfaktans dan elektrolit ion bebas menyumbang kepada kekonduksian elektrik larutan akueus misel surfaktans. Keputusan kajian diharap dapat membantu meningkatkan pemahaman interaksi antara elektrolit dan surfaktans.

Kata kunci: Elektrolit NaCl; CTAB surfaktans; kekonduksian elektrik; kelikatan; ketegangan permukaan

INTRODUCTION

Surfactants are chemical substances which decrease the surface tension of water through low concentrations. They have plenty of industrial and domestic applications including dispersing, emulsifying, wetting, cleaning, washing, foaming and preparation of medicines. Because of their characteristic surface activity and wider applications in industries, research work on surfactants and their physicochemical properties is gaining momentum and causing environmental concern at the same time (Knaebel & Oda 2000; Urata & Takaishi 2001). 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 (Ramanathan et al. 2013). 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 (Caron et al. 1995; Rio et al. 1995; Rosen et al. 1982; Shinoda et al. 1987). One of the main characteristics of surfactants is their tendency, in dilute aqueous solutions, to self-assemble and form aggregates by exposing polar headgroups to water and segregating hydrophobic tails from water (Antonello et al. 2016). Through this method, at certain concentration, the surface active ions in a solution associate to form

larger units, which are called micelles. The concentration at which this phenomenon occurs is called critical micelle concentration (CMC). The CMC is the concentration of surfactants above which micelles form and all additional surfactants added to the system go to micelles.

Previously, many studies concerning the development of new methods so as to study the behavior of surfactants in many chemical reactions and the effects of various factors on their properties have been carried out. It was observed that interaction between the surfactants and small molecules was helpful to analyze the mechanism of surfactants (Chiranjeevi et al. 2009).

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). Physicochemical properties such as CMC, degree of ionization and thermodynamics of micellization depend on the nature of the hydrophobic tail, the hydrophilic headgroup and the counter ion species (Sujit et al. 2016). 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 (Ghos 2001; Ghos & Moulik 1998). Cautious experimental measurement used in a highly purified system shows a continuous and gradual change in physiochemical characters of surfactants when it reached to the CMC (Kameyama et al. 1997). When the surfactant reached to such a concentration then their properties are changed very quickly. The properties of surfactant which are now changed 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 electrolyte which are added (Lindman & Wennerstrom 1980). Abuin and Scaiano (1984) reported the determination of CMC at various temperatures and addition of electrolyte 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 electrolyte 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 headgroup which facilitate the aggregation behavior (Neumann' & Tiera 1997).

The present study demonstrates the effects of electrolyte NaCl concentration at different temperatures so as to show the mechanism of micelle - electrolyte interaction, i.e. CMC of cetyl trimethyl ammonium bromide (CTAB) as affected by different factors which is important surfactant for most of the industries and other chemical process.

MATERIALS AND METHODS

The surfactant, cetyl trimethyl ammonium bromide (CTAB) of analytical grade was used without further purification. Distilled water was used as a solvent. Sodium Chloride (NaCl) was used as electrolyte in this research work which was obtained from Merck Germany and was used without further purification.

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 (NaCl) 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 electrolyte. Procedure preference to CMC determination electrolyte with different concentration used to get information about surfactant using various techniques like conductance, surface tension and viscosity measurement.

CONDUCTANCE MEASUREMENT

In temperature range of 30°C to 50°C, the conductance of electrolyte added to the surfactant was measured using conductometer. The external temperature of conductometer was controlled with the help of a temperature regulated water bath.

SURFACE TENSION MEASUREMENT

In temperature range of 30°C to 40°C, the surface tension of the solution was measured through stelogmometer and Tensiometer (TE 3 LAUDA) using adjusting water bath.

VISCOSITY MEASUREMENT

The viscosity of electrolyte 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.

RESULTS AND DISCUSSION

CRITICAL MICELLE CONCENTRATION (CMC)

Mukherjee and Mysels 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.

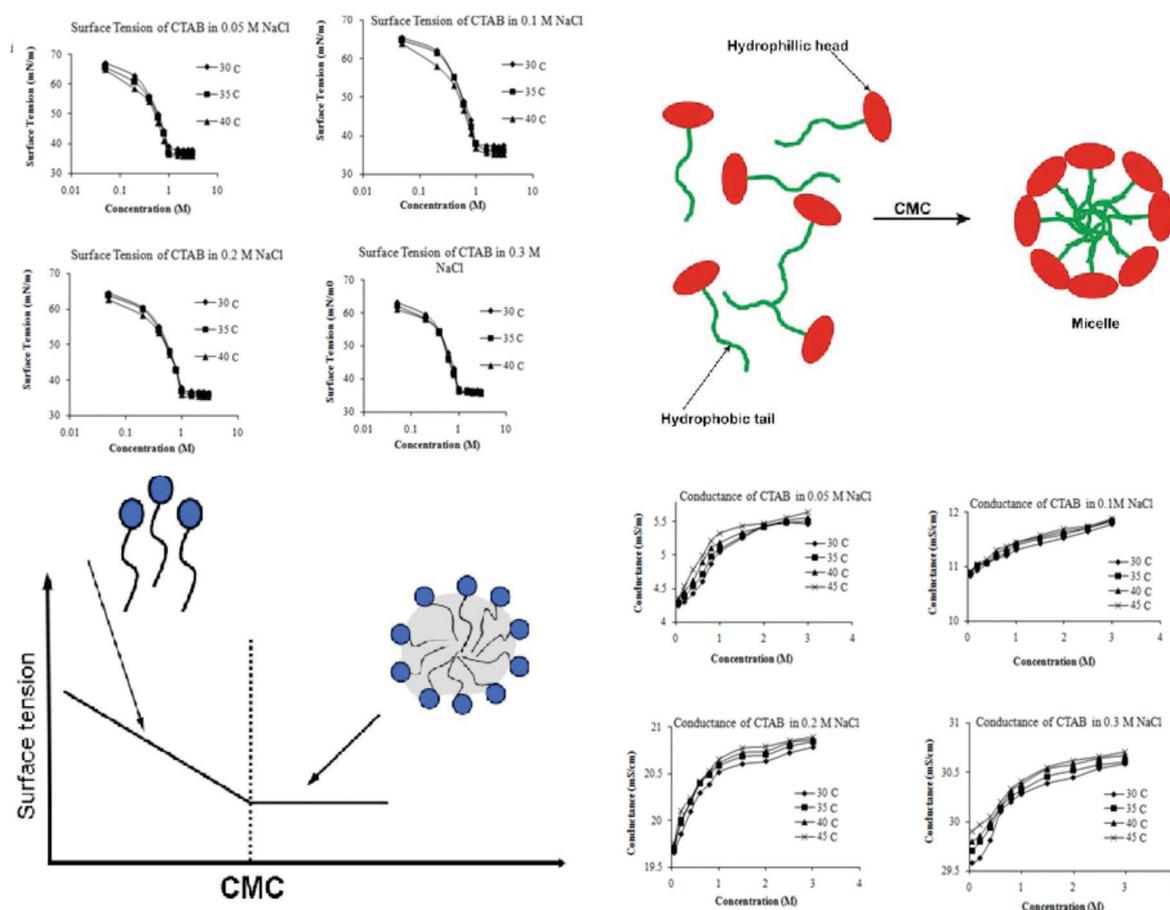
It is known fact that most of physical properties like surface tension, conductivity, viscosity and density change abruptly their trend when the concentration of surfactants approaches to CMC. It is observed from the conductance measurement that the values of CMC of the surfactant decreases as the concentration of electrolyte and temperature increases as given in the Table 1. 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. Through conductance method it was possible to get accurate results at any ionic strength and temperature.

CONDUCTANCE MEASUREMENT

Conductometry is one of the important tools for the characterization of electrolyte-surfactant concentration. The specific conductivities change with the total surfactant concentration in a linear fashion. The conductivity measurements were performed for cationic surfactant (CTAB) solutions as well as electrolyte-surfactant at different temperatures as shown in Figure 1. The increase in CTAB ions concentration should result in a conductivity increase. The specific conductivity increases linearly in both pre-micellar and postmicellar regions with surfactant concentration being the slope in the premicellar region is greater than that in the post micellar region. The increase in the conductance in premicellar region is due to availability

TABLE 1. CMC of CTAB with NaCl electrolyte at various temperatures through conductance measurement

Concentration of electrolyte	Temperature (°C)			
	30°C	35°C	40°C	45°C
0M	0.98M	0.97M	0.96M	0.95M
0.05M NaCl	0.99M	0.98M	0.96M	0.95M
0.1M NaCl	0.97M	0.96M	0.96M	0.95M
0.2M NaCl	0.95M	0.93M	0.92M	0.93M
0.3M NaCl	0.90M	0.88M	0.87M	0.90M



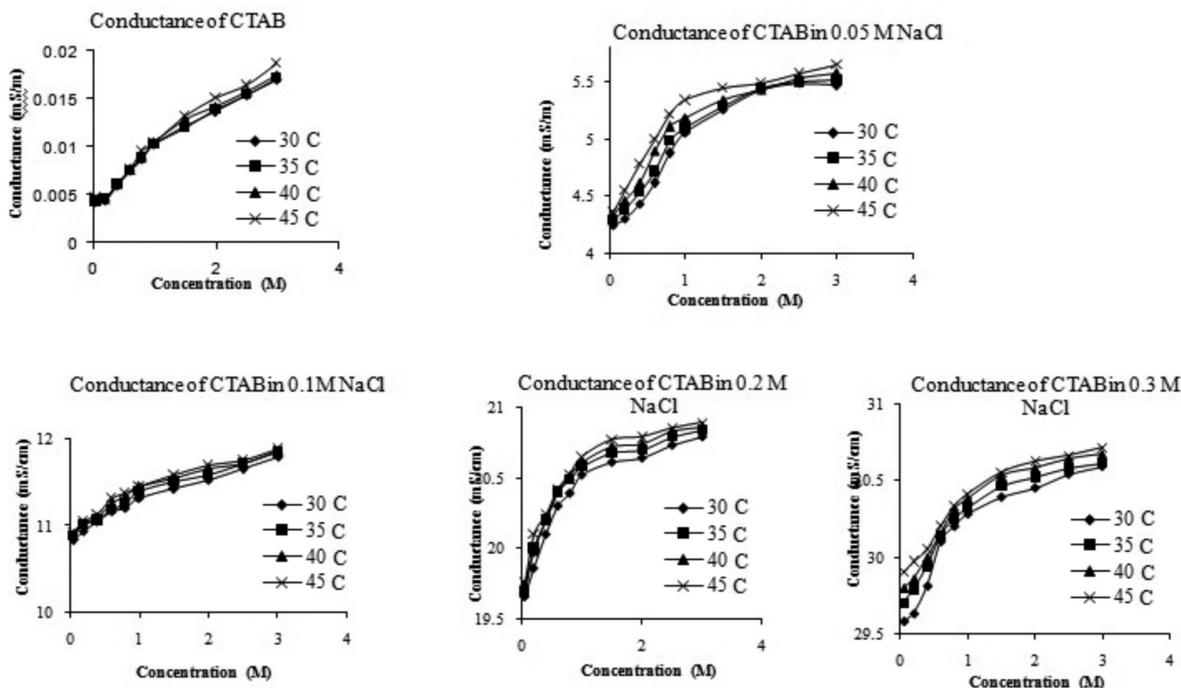


FIGURE 1. Plot of electrical conductivity as a function of concentration of CTAB in the presence of (a) 0 M NaCl (b) 0.05 M NaCl (c) 0.1 M NaCl (d) 0.2 M NaCl (e) 0.3 M NaCl at various temperatures ($^{\circ}\text{C}$)

of free surfactant ions but at higher surfactant concentration (in postmicellar region), the movement of surfactant free ions reduces due to the formation of CMC. The intersection point between the two straight lines gives the CMC of CTAB solutions.

These results showed that conductance of the surfactant increased as the concentration and temperature increased while CMC of the surfactant decreased with increase in concentration and temperature. From Table 1, it can be seen that the value of CMC calculated through conductance measurement for pure CTAB was 0.98 at 303K, which was observed to decrease as temperature increased and got value of 0.95 at 318K. Moreover the addition of electrolyte NaCl into the surfactant leads to lowering of the CMC and got value of 0.90 at 3M of NaCl. The values of CMC calculated through surface tension and viscosity measurement are given in Tables 3 and 4, respectively, which have close agreement to that calculated through conductance technique.

Degree of ionization (α) To calculate the degree of ionization, the following equation is used

$$\alpha = \frac{S_2}{S_1}$$

S_1 = Slope for pre micellar concentration

S_2 = Slope for post micellar concentration.

The values of degree of ionization (α) were determined for pure CTAB and with electrolytic solutions as given in the Table 2.

TABLE 2. Parameters calculated from conductivity method i.e. degree of ionization (α) and degree of counter ion binding (β) 303K

S. No	Sample	α	β
1	Pure CTAB	0.219	0.780
2	CTAB+ 0.05 M NaCl	0.368	0.601
3	CTAB+0.1 M NaCl	0.568	0.417
4	CTAB+0.2 M NaCl	0.637	0.343
5	CTAB+0.3 M NaCl	0.773	0.201

The value of α calculated for pure cationic surfactant CTAB is 0.219, these values of α tends to increase with the addition of electrolyte. In the table, it was observed that the higher the electrolyte concentration, the higher is the α values, this is due to the fact that 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.

Degree of counter ion binding (β) The degree of ionization is related to the degree of counter- ion binding (β) by the equation.

$$\beta = 1 - \alpha.$$

The values of degree of counter ion binding (β) were obtained both for pure CTAB and with its NaCl solution

(Table 2). The results showed that the value of counter ion binding (β) calculated from above equation for pure cationic surfactant CTAB was 0.780. These values get reduced with the addition of electrolyte to the pure cationic surfactant. These decrease in β values for the surfactant-electrolytic solution as compare to that of pure CTAB indicating an increase in the micellar ionization due to the incorporation of electrolyte NaCl.

SURFACE TENSION MEASUREMENT

Surface tension measurement provides an effective way to trace the micellization and aggregation behavior in surfactant solutions. Surface tension is one of the important tools to investigate surface properties of the single component (pure surfactant or pure electrolyte) as well as mixture of two or more components.

Surfactants show surface tension curve as a function of surfactant concentration. The CMC values for CTAB were obtained from plot of surface tension vs. concentration, in water at different temperature as shown in Figure 2. Initially at low surfactant concentration, the surfactant molecules was adsorbed at the surface and surface tension decreases linearly with the logarithm of surfactant concentration. When the surface is saturated with surfactant molecules a further addition of surfactant has no effect on the surface tension. It is well known that there is distinct break of the physical properties with respect to concentration which is associated with the formation of supramolecular aggregates (this concentration is called the critical micelle concentration (CMC) in the case of surfactant.

Surface tensions of surfactant N-Cetyl N, N, N trimethyl Ammonium bromide (CTAB) with and without the addition of electrolyte at different temperature are plotted in Figure 2.

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. As is known that the temperature at which the surface tension becomes constant is CMC. Electrolyte decrease the surface activity of surfactants (Pethica 1954) and thus the CMC and surface tension of aqueous solution often decrease in presence of electrolyte. The values of CMC for pure surfactant and in the presence of electrolyte at various temperatures calculated from surface tension measurement are shown in Table 3.

The data shows that the addition of electrolyte decreases the values of CMC. Actually the addition of electrolyte results in a decrease of thickness of solvation layer around ionic head of surfactant and electrostatic repulsive interaction between positive ions of surfactant so that hydrophilic property of surfactant is decreased i.e. its surface activity is enhanced and its molecules aggregated easily on the surface and in the solution yielding/producing a decrease in both CMC and surface tension. On the other hand, water matrix is broken in the presence of additive like glycerin since it has good hydrophobicity that forms more micelle easily and decreases the CMC (Sharma & Rakshit 1989; Sharma et al. 1989; Sudha et al. 2012).

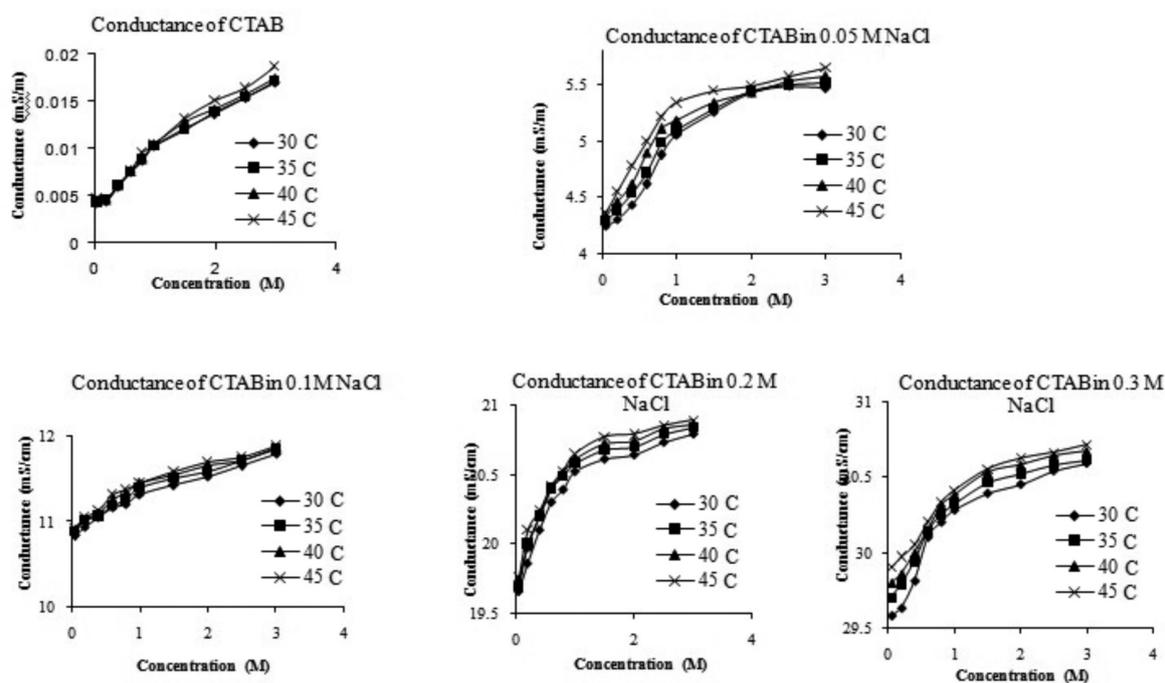


FIGURE 2. Plot of surface tension as a function of concentration of CTAB in the presence of (a) 0 M NaCl (b) 0.05 M NaCl (c) 0.1 M NaCl (d) 0.2 M NaCl (e) 0.3 M NaCl at various temperatures ($^{\circ}$ C)

TABLE 3. CMC of CTAB with NaCl electrolyte at various temperatures through surface tension measurement

Concentration of electrolyte	Temperature (°C)		
	30°C	35°C	40°C
0M	0.98M	0.97M	0.96M
0.05M NaCl	0.99M	0.97M	0.96M
0.1M NaCl	0.97M	0.96M	0.96M
0.2M NaCl	0.96M	0.93M	0.92M
0.3M NaCl	0.91M	0.89M	0.88M

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. 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. 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 electrolyte increased and decreased with the increase in temperature. Viscosity remained constant at low concentration of electrolyte, however, it was observed distinctly that it increased at higher concentration of added electrolyte. 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 headgroup. 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 electrolyte. Further increase in viscosity with increase in concentration of surfactant might be due to cross linking of several aggregation of micelle form by free surfactant monomers and electrolyte (Hoff et al. 2001; Schweitzer et al. 2006). Viscosity increases with the increase of concentration of electrolyte (Bakshi & Kaur 2003). It has been well established that micelle of surfactants in aqueous media or solution may grow to form large cylindrical aggregates either at high surfactant concentration or in the presence of additives (Anaker & Ghose 1968, 1963; Gamboa & Rios 1989). Increase in viscosity is usually identified with shape transition from small to large rod like micelle (Gamboa & Rios 1989). Viscosity decrease with increase in temperature leads to micelle to break and smaller micelle are formed.

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

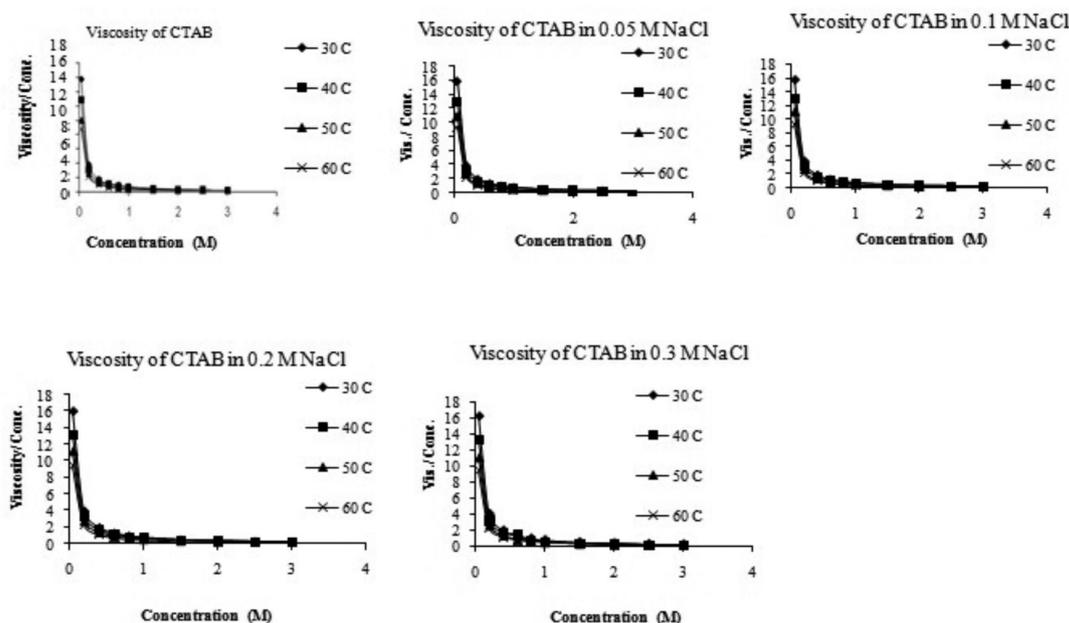


FIGURE 3. Plot of viscosity as a function of concentration of CTAB in the presence of (a) 0 M NaCl (b) 0.05 M NaCl (c) 0.1 M NaCl (d) 0.2 M NaCl (e) 0.3 M NaCl at various temperatures (°C)

TABLE 4. CMC of CTAB with NaCl electrolyte at various temperatures through viscosity method

Concentration of electrolyte	Temperature (°C)			
	30°C	40°C	50°C	60°C
0M	0.98M	0.97M	0.96M	0.96M
0.05M NaCl	0.98M	0.96M	0.95M	0.95M
0.1M NaCl	0.97M	0.95M	0.95M	0.94M
0.2M NaCl	0.96M	0.95M	0.94M	0.94M
0.3M NaCl	0.91M	0.89M	0.88M	0.87M

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 electrolyte at different temperature are given in Table 3, which show that addition of electrolyte with different concentration decreases the CMC value of surfactant. Electrolyte decreases CMC; because the ions of the salts neutralized the charge on the micelle surface thus decreasing the thickness of ionic compound around the surfactant and electrostatic repulsion between them helping in this way to micellization process (Paredes et al. 1984). Electrolyte like NaCl lowered the CMC of surfactants that can be explained by the fact that Na⁺ and Cl⁻ ions in solution can affectively screen the attractive electrostatic attraction between charged headgroups with surfactant 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. (Zana et al. 1981) showed that CMC of CTAB in water and in 0.05M NaBr decrease the CMC value as Br⁻ concentration is increased. The CMC of surfactant decrease if electrolyte 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 (Rakshit & Sharma et al. 2003). This factor contributes to the micelle and decreasing the CMC. Another factor which was studied was the effect of the temperature on CMC of surfactant. It was noted from results that temperature has less effect than that of electrolyte. The CMC of surfactant decreases with the increase in the temperature and it can be describing by three ways; Thermal motion of surfactants molecule in the interior of the solution increased with the increase in the temperature. Thus affinity between surfactant and water increased but electrostatic force between surfactant and electrolyte weakened the tendency to absorb surfactant molecule of surface layer decreases. At high temperature,

the dehydration ratio is higher which strengthens the surface activity producing micellization.

Increase in the temperature also causes disruption of water structure surrounding the hydrophobic group and this is unfavorable for micellization (Gracian et al. 2005, Zhu et al. 1996). The rate of change in conductivity with varying electrolyte 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 electrolyte and surfactant (Li et al. 2003) was named as 'negative deviation from ideality' (Balakrishnan et al. 2005). 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 (Balakrishnan et al. 2005).

CONCLUSION

From all this discussion we came across the conclusion that the values of CMC of CTAB decrease with the increase of temperature and concentration of surfactant. The value of CMC for pure CTAB was calculated 0.98M at 303K, which was observed to decrease as temperature increased and got value of 0.95M at 318K. Moreover the addition of electrolyte NaCl into the surfactant leads to lowering of the CMC and got value of 0.90M at 3M of NaCl. Surface properties suggest that surfactant act as surface active agents and alter the surface properties by competing with the electrolyte for interfacial adsorption. The degree of ionization(α) for pure cationic surfactant CTAB was 0.219, which tends to increase with the addition of electrolyte, while that of counter ion binding values (β) was observed to decrease from 0.780 to 0.201. 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 NaCl. The results can be helpful to develop better understanding about interaction between electrolyte and surfactant.

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