Thermodynamic Properties of Cetyltrimethylammonium Bromide in Ethanol-Water Media With/without the Presence of the Divalent Salt

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Abstract: The physicochemical properties of cetyltrimethylammonium bromide (CTAB) in pure water and ethanol-water mixtures in the presence and absence of MnSO₄.6H₂O were studied by measuring the conductivity at room temperature. The concentration range of CTAB was ~1.00 × 10⁻⁵ M to ~1.00 × 10⁻³ M and the concentration of MnSO₄.6H₂O was 0.001 M, 0.005 M, 0.01 M. With increasing ethanol content in the solvent composition, the critical micelle concentration (CMC) and the degree of micellar dissociation (α) of CTAB increased. With the help of CMC and α, the standard free energy of micellization (Δ𝐺ₘ⁰) was evaluated. With an increase in ethanol content, the negative values of Δ𝐺ₘ⁰ decreased. CTAB micellization was tested in the context of specific solvent parameters. The solvent conductivity ratio at CMC to limiting conductivity was employed as a solvophobic influence. The addition of salt (MnSO₄.6H₂O) decreases the CMC of CTAB due to the screening of the electrostatic repulsion of the head groups. Here, we report that micellization is strongly influenced by salt concentration.

Key words: CMC, CTAB, divalent salt, ethanol-water, thermodynamic parameter

1 Introduction

The major concerns of science and technology are still about energy and the environment. Surfactants are versatile chemicals in synthesized compounds due to their self-association into organized molecular structures such as micelles¹, vesicles², microemulsions, ellipsoid, bilayers membranes, DNA³, chromonics⁴, microemulsions⁵ and liquid crystals⁶. They possess unique properties concerning affinity towards the medium of solution⁷. The structure of a surfactant molecule containing both hydrophilic and hydrophobic parts plays a crucial role in the determination of micellization parameters like aggregation number, critical micelle concentration, etc. and physicochemical properties like additives, temperature as well and solvent composition⁸–¹⁰.

The study of micelle formation is a very important problem in contemporary research in chemistry, industry and material science. Ethanol is an organic solvent mostly used in research and industry¹¹. Different materials have different solubilities towards water and alcohol (hydrophilic and hydrophobic). The hydrophilic part is soluble in water, which changes the properties of the solvent and affects the micellization process. On the other hand, the hydrophobic part takes part in the micellization process and becomes a unique component of the micelle aggregates. A cosolvent is a mixture of water and alcohol, whose various physical properties lie between those of water and alcohol; therefore, this solvent has significant importance in many applications.

The effect of salts on surfactants is still a hot issue in many areas. Recently, Ullah et al. studied the effect of salts on potassium N-cocoyl glycinate (KCGl) to see the interfacial behaviors using the oscillating drop shape analysis method. The experimental data of KCGl with salts may provide a hypothetical basis for its useful application in detergents, pharmaceuticals, cosmetics, petroleum and daily chemical industries¹². Forland et al. studied the behavior of the micellar shape and size of sodium dodecyl sulfate in sodium chloride solutions using alcohol as the solvent media using small-angle neutron scattering (SANS), dynamic light scattering (DLS), and viscosity measurements. They found that sodium chloride and alcohols strongly influence the process of micellization¹³. Niraula et al. evaluated the CMC of SDS in water and methanol-water mixtures in the presence of studied salts is found in the order NaCl>NaBr>KCl>KBr by conductivity methods at different temperatures. They also calculated the standard...
free energy of micellization, standard enthalpy of micellization, the standard entropy of micellization, the standard free energy of transfer and heat capacity of micellization.\textsuperscript{20, 21} Shah \textit{et al.} investigated the effect of methanol and potassium chloride on the conductivity of an aqueous solution of CTAB at various temperatures. They reported that conductivity increases with increasing concentration of potassium chloride, whereas conductivity decreases with an increase in the volume fraction of methanol. The CMC values of CTAB in the presence and absence of potassium chloride increase with temperature.\textsuperscript{20}

There have been many studies on CTAB in the presence of monovalent salts.\textsuperscript{13–17} However, studies of CTAB in the presence of divalent salts are limited.\textsuperscript{17–19} The CMC and various physical parameters of CTAB in the presence and absence of MnSO\textsubscript{4}.6H\textsubscript{2}O by varying the concentration of the cosolvent at room temperature have not been studied yet.

Here, we determine several parameters like pre-micellar, post-micellar slopes, critical micelle concentration (CMC), degree of micellar dissociation ($\alpha$), standard free energy of micellization ($\Delta G^\circ_m$), the free energy of surfactant tail transfer ($\Delta G^\circ_{\text{bulk}}$) of CTAB in the presence and absence of MnSO\textsubscript{4}.6H\textsubscript{2}O in the ethanol-water system at room temperature using conductivity methods and their correlation with the percentage of ethanol (\%). We also correlate the values of the ratio of initial conductance to conductance at CMC ($K_0/K_{\text{CMC}}$) with the percentage of ethanol (\%). We included the Harkins–Corrin plot of CMC versus CMC+MnSO\textsubscript{4}.6H\textsubscript{2}O. We not only correlate $\Delta G^\circ_m$ with the Gordon parameter but also with other solvent parameters like the dielectric constant, viscosity and Reichardt’s parameter. Finally, we correlate $\Delta G^\circ_m$ with the solvophobic parameter ($S_p$).

### 2 Experimental Method

Cetyltrimethylammonium bromide (>99.0\%) was purchased from Merck Specialities Pvt. Ltd., Mumbai, India. Cetyltrimethylammonium bromide was used after drying for 1 h. The CMC of CTAB was measured 1.50 mM at 298.15 K, which is matched to the literature\textsuperscript{22} where the CMC of CTAB is 1.12 mM at 298.15 K by conductivity. There was also the literature value of the CMC of CTAB in pure water is 0.93 mM.\textsuperscript{23} The reason for the higher CMC in our case is due to the presence of impurities that slow down the dielectric constant of water.\textsuperscript{22, 23} Ethanol (E, Merck, India, 99\% pure) and salt (MnSO\textsubscript{4}.6H\textsubscript{2}O) from Merck Specialities Pvt. Ltd., Mumbai, India were used. Double-distilled water containing a fair conductivity under 10\textsuperscript{-15} S cm\textsuperscript{-1} was utilized during the formulation of the mixed solvents at room temperature. Double-distilled water and 10\%, 20\% and 30\% percentage of ethanol were used to make cetyltrimethylammonium bromide solution in the presence and absence of (MnSO\textsubscript{4}.6H\textsubscript{2}O).

The specific conductance of cetyltrimethylammonium bromide solution in the presence and absence of MnSO\textsubscript{4}.6H\textsubscript{2}O was measured on a Pye-Unicam PW 9509 conductance meter data frequency of 2000 Hz utilizing a dip-type cell with a cell constant of 1.15 cm\textsuperscript{-1} with an uncertainty of 0.01\%. The cell was calibrated with the help of aqueous potassium chloride solution (0.1 Demal and 0.01 Demal).\textsuperscript{24} This type of calibration with the help of aqueous potassium chloride was also found in the literature.\textsuperscript{25}

### 3 Results and Discussion

#### 3.1 Study of conductance

The specific conductance of an electrolyte solution is a measure of its ability to conduct. The conductometric method is the most widely used because it is simple and accurate. The specific conductance of CTAB increased with an increase in the concentration of salt which is due to the increase in the number of ions per unit volume of the solution. The specific conductance of CTAB in distilled water was found to be the highest in comparison with the different volume fractions of ethanol. The reason for the decrease in specific conductance of CTAB with the addition of ethanol in the absence and presence of the salt is due to the decrease in the dielectric constant of the solution.\textsuperscript{25}

Such a decrease in the specific conductance of CTAB with the addition of ethanol was also found in the literature.\textsuperscript{26} The specific conductance of CTAB in distilled water in the presence of 0.005 M salt was found to be higher than that of the different percentage of ethanol (\%) in the presence of 0.005 M salt (Fig. 1). Figure 1 is an illustration of the comparative study of specific conductance of CTAB in distilled water and different percentage of ethanol (\%) with a concentration in the presence of 0.005 M salt.

![Fig. 1](image-url) Comparative study of specific conductance of CTAB in distilled water and different percentage of ethanol (\%) with a concentration in the presence of 0.005 M salt.
interesting plot of conductance with concentration and gives linear fitting curves below and above the breakpoint. The description of the breakpoint of two straight-line fitting curves will be discussed later.

3.2 Study of critical micelle concentration (CMC)

The plots of specific conductance versus the concentration of cetyltrimethylammonium bromide in pure water and 10%, 20% and 30% of ethanol in the absence and the presence of 0.001 M and 0.01 M salt are depicted in Figs. 2a-c, respectively. The point of intersection of the two straight lines of the plot is the CMC. The CMC of CTAB increases with an increase in the volume fraction of ethanol. An increase in the volume fraction of ethanol results in increases in CMC at a fixed temperature. Such types of agreement were also found in the literature.\(^\text{27}\) It is observed that the conductance of surfactant solutions decreases with an increase in the percentage of ethanol (%) in both the premicellar and post-micellar regions.

In the conductance versus concentration graph, the slope of the line below the CMC is called the premicellar slope ($S_1$) and the slope of the line above the CMC is called the Post-micellar slope ($S_2$). The values of the Pre-micellar slope ($S_1$) and Post-micellar slope ($S_2$) of CTAB in water and the presence of salts for the percentage of ethanol (%) at room temperature are given in the form of log $S_1$ and log $S_2$ in Table 1.

The degree of dissociation ($\alpha$) is the ratio of the post-micellar slope to the premicellar slope. Here, we use an approximation that both the straight lines do not change gradually about CMC. Straight lines are drawn through the upper and the lower part of the plot; the point of intersection showed the concentration at which micelles are formed. Such plots are shown in Fig. 1 as well as in Figs. 2a-c for the CTAB with and without salt in water and water-ethanol mixtures where there is more pronounced curvature near the point of intersection.\(^\text{29}\) The intersection point between two slopes indicates the CMC and was determined by fitting the data points above and below the break to two equations of the form $y = mx + c$ where $m$ is the slope and $c$ is the intercept and solving simultaneously for the point of intersection. These results of CMC and $\alpha$ ($S_2/S_1$) are summarized in Table 2. Besides, the CMC value changes largely with temperature and the surfactant may decompose at high temperature so to avoid this effect on CMC we fixed all the measurements at room temperature. If the room temperature becomes less than 298.15 K, the solution is heated to the desired temperature (298.15 K) just before the conductance measurement. This minimizes
the possibility of surfactant decomposition. An analysis of Benzinger’s compensation hypothesis shows that the same conclusions also applied to micellization in aqueous solution at 298.15 K.

The Harkins–Corrin plot is a common plot of log CMC versus log \( \log \text{CMC} \), as shown in Fig. 3. The log CMC values were found to decrease with the increase in salt concentration. The reason maybe because of the structural transitions in micelles as the increase of concentration of salt.

3.3 Correlation of log \( S_1 \) and log \( S_2 \) with the percentage of ethanol (%)

The plot of log \( S_1 \) with the percentage of ethanol in the presence and absence of salt is depicted in Fig. 4a. The value of log \( S_1 \) decreases with increasing the percentage of ethanol. The value of log \( S_1 \) is very high in the presence of salt.
Similarly, the value of log S₂ decreases with increasing the percentage of ethanol both in the presence and absence of salt. The plot of log S₂ with the percentage of ethanol (%) in the presence and absence of salt is depicted in Fig. 4b. Similarly, the value of log S₂ decreases with increasing the percentage of ethanol (%). Like log S₁, the value of log S₂ is very high in the presence of salt in comparison to the absence of salt.

Hence the values of log S₁ and log S₂ decrease with increasing the percentage of ethanol both in the presence and absence of salt.

### 3.4 Calculation of Gibbs free energy of micellization

The thermodynamic property, Standard Gibb’s free energy of micellization ($\Delta G^\circ_m$), was calculated from the following relation$^{30, 31}$.

$$\Delta G^\circ_m = (2 - \alpha)RT \ln X_{cmc}$$ (1)

Here, $R$ is the universal gas constant, $T$ is the absolute temperature and $X_{cmc}$ is the mole fraction of surfactant at CMC. The critical micelle concentration (CMC), degree of micelle ionization ($\alpha$) and standard free energy of micellization ($\Delta G^\circ_m$) of CTAB in the absence and presence of salt in water and 10%, 20% and 30% of ethanol are given in Table 2.

Table 2 displays the value of CMC (critical micelle concentration), $\alpha$ (degree of ionization), $\Delta G^\circ_m$ (standard free energy of micellization) in water and presence of salt in water, 10%, 20% and 30% of ethanol measured at different concentrations. The data shows that the CMC, as well as degree of ionization ($\alpha$), increases with an increase in the percentage of ethanol, firstly due to the alcohol molecule intercalated between surfactant ions which increase the average distance between ionic head groups for steric reasons and the dielectric constant of the palisade layer is the second effect. Such types of results have been reported for the surfactants in alcohol and alcohol-like polar solvent and water mixture$^{35, 36}$. It is observed that the values of $\alpha$ of CTAB are higher in the presence of ethanol than in the absence of it. With an increase in the concentration of ethanol $\alpha$ value keeps on increasing due to an increase in the surface area of the ionic head group.

The values of CMC of CTAB increase with the increase in ethanol content which can be explained based on hydrophobic interaction between tails and electrostatic repulsion between ionic heads. These are two important factors for micellization. Hydrophobic interaction depends on the dielectric constant of the medium$^{39}$. The value of the dielectric constant of alcohol is lower in comparison to water. When alcohol is added to water, the dielectric constant of the medium decreases due to which hydrophobic interaction becomes less, which increases the CMC. Due to the lower dielectric constant of the medium, the electrostatic repulsion between the head group increases and the formation of CMC is less favorable, hence CMC increases$^{27}$.

CMC decreases in the presence of salt. With the increase in concentrations of salt, $\alpha$ as well as CMC also further decreases. Such types of results were reported in the previous literature$^{33}$. By adding salt, the Debye length is decreased$^{34}$, the repulsive force between two ions decreases because of the screening effect. The screening affects the head groups of CTAB. The screening induces closing to CTAB each other and forming micelle at a lower concentration. But the decrease in the dielectric constant cause increases Debye-length, which eventually decreases the CMC.

In other words, as the salt is added, the electrostatic repulsive force between ionic head groups of the CTAB molecules is reduced by shielding of micelle charge, so that spherical micelles are more closely packed by the surfactant ions$^{35, 36}$, hence a decrease in the CMC values after adding salt. It is noticed that salt decreases the CMC of ionic surfactant (CTAB)$^{37}$ due to the screening of the electrostatic repulsion among the polar head groups and movement of the hydrophobic alkyl chain away from the palisade layer.
aqueous environment, so that less electrical work is required to form micelles.

At the point when metal ions are included in a surfactant arrangement, hydration happens pretty much for various metal ions. Since hydration cycles may likewise be a purpose behind separating the “icebergs structure” of liquid water around the monomer, the degree of hydration ought to be a direct deciding element for the degree of separation of “icebergs”, thus, the degree of entropy increment. On this premise, it may be presumed that the entropy driving impact is stronger for trivalent metal ions than for divalent metal ions because the hydration impacts of the trivalent metal ions are much stronger than those of the divalent metal ions, subsequently causing a stronger impact of bringing down the CMC of CTAB. Additionally, this idea can be applied for monovalent metal ions\(^{39}\). Hence the CMC of CTAB in the presence of 0.01 M of \(\text{MnSO}_4 \cdot 6\text{H}_2\text{O}\) seems 0.15 mM in Table 2 whereas the CMC of CTAB in the absence and presence of 0.01 M NaCl was found 0.924 mM and 0.56 mM respectively from the literature\(^{39}\).

Accordingly, the addition of inorganic electrolytes brings down the CMC of surfactants\(^{40}\) and upgrades the surface activity, which certainly favors their practical use since numerous industrial uses of surfactants lie in their ability to form micelles\(^{41}\). As indicated by\(^{42}\), divalent counterions are required to be more viable than monovalent ions in screening electrostatic interactions and decreasing surfactant headgroup territory because (a) a more prominent charge screens all the more successfully, (b) each divalent ion is all the more unequivocally pulled in to a total, and (c) divalent ions can now and again cause charge inversion. Furthermore, divalent salts, affect the micelle size\(^{43}\), reactivity, yield fusion of surfactant aggregates\(^{44}\) and modify the phase diagram of the surfactant\(^{45}\). Hence the stronger affinity of divalent ions to surfactant aggregates strongly complicates the understanding of the physical phenomena related to the ion specificity\(^{46}\).

It is also observed that the value of the standard free energy of micellization is negative in water as well as in all percentage of ethanol (%) (Table 2). It indicates the process of micellization is spontaneous. The values of \(\Delta G^\alpha\) generally increase with the addition of alcohol in the water at different concentrations of salt. This indicates that when ethanol is added to the mixture, the formation of micellization is less stable in the monomer state.

### 3.5 Correlation of \(\Delta G^\alpha\) with the percentage of ethanol (%)

The micellization process is affected due to the addition of alcohol, and the effect can be studied using the free energy of surfactant tail transfer \(\Delta G^\text{trans}\)\(^\alpha\).
3.7 Correlation of CMC with the percentage of ethanol (%)

The concentration of the surfactant above which the micelle form and all additional surfactant added to the system go to the micelle. The plots of CMC with the percentage of ethanol in the presence and absence of salt are depicted in Fig. 5c. For both cases, the value of CMC increases with increasing the percentage of ethanol (%). The CMC of a solution without salt is always higher than with salt. The Debye length is directly proportional to the ratio of the square root of dielectric constant to the charge on the ions. By adding ethanol, the Debye length is decreased; the electrostatic repulsion force between the head group of surfactants increased due to which the hydrophobic interaction become weak; as a result, the CMC of the solution increased.

3.8 Correlation of \( K_0/K_{CMC} \) with the percentage of ethanol (%)

Mukhim and Ismail in the year 2011 used the ratio of initial conductance to the conductance at CMC, \( K_0/K_{CMC} \) to describe the solvophobic effect. Similarly, our research group has already used the importance of \( K_0/K_{CMC} \), the ratio of initial conductance to the conductance at CMC, to relate micellization of molecular association, the fluidity, polarity, and solvent structure. The Gibbs free energy for the solution increases with the increase in the percentage of ethanol.

| Percentage of ethanol (%) | \( 1/D \) | Gordon parameter \( G \) (J m\(^{-3}\)) | Coefficient of viscosity (mPa s) | Reichardt’s parameter \( E_T/kcal mol^{-1} \) | Solvophobic parameter \( S_p \) |
|--------------------------|-----------|---------------------------------|---------------------------------|---------------------------------|-------------------|
| 0                        | 0.01278   | 2.74                            | 0.8959                          | 63.10                           | 1                 |
| 10                       | 0.0136    | 1.72                            | 1.1441                          | 61.98                           | 0.9172            |
| 20                       | 0.01424   | 1.39                            | 1.4346                          | 60.86                           | 0.8196            |
| 30                       | 0.01515   | 1.16                            | 1.7371                          | 59.74                           | 0.7004            |
crease in viscosity of the solution. For the same viscosity, Gibb’s free energy of the solvent without salt is higher than that with salt as shown in Fig. 6a.

The plots of standard Gibb’s free energy of micellization ($\Delta G_m^o$) with the reciprocal of the dielectric constant of the solution in the presence and absence of salt are depicted in Fig. 6b. The Gibb’s free energy for the solution increases with the decrease in the dielectric constant of the solution. For the same dielectric constant of the solution, Gibb’s free energy of the solvent with water is higher than that of salt. The plots of standard Gibb’s free energy of micellization ($\Delta G_m^o$) with the Reichardt’s parameter ($E_T$) of the solution in the presence and absence of salt are depicted in Fig. 6c. The Gibb’s free energy for the solution without salt shows nonlinear whereas the solution with salt shows linear relation and the value of free energy decreases with an increase in Reichardt’s parameter. The plots of standard Gibb’s free energy of micellization ($\Delta G_m^o$) with the Gordon parameter ($G$) of the solution in the presence and absence of salt are depicted in Fig. 6d. The Gibb’s free energy for the solution decreases with the increasing value of the Gordon parameter.

3.10 Correlation of $\Delta G_m^o$ with the solvophobic parameter ($S_p$)

The solvophobic parameter, $S_p$, is calculated by Gibbs energies of transfer of hydrocarbons from the gas into a given solvent. The $S_p$ values are only available for the solvent mixtures of water-methanol, water-ethanol, water-acetone, and water-ethylene glycol, although their compositions are different from those investigated in the present work. Wang et al. developed a correlation method with which the $S_p$ values of the mixed solvents can be predicted at any composition from those of the corresponding pure liquids. $S_p$ is the measure of the property of solute which avoids the solvent to make the solution.
4 Conclusions

The following conclusions have been drawn from the results and discussion. The conductivity of cetyltrimethyl ammonium bromide was measured in pure water including in 10%, 20% and 30% ethanol as well as in the presence of MnSO₄·6H₂O (0.001 M, 0.005 M and 0.01 M). The CMC of cetyltrimethyl ammonium bromide increases with the addition of ethanol, but this simultaneously decreases in 0.001 M, 0.005 M and 0.01 M respectively in the presence of MnSO₄·6H₂O. The degree of dissociation (α) was obtained for pure water including in three separate mixtures of ethanol-water as well as in the presence of MnSO₄·6H₂O. It was apparent that the standard free energy (ΔGₘₒ) of micelle formulation in most situations is negative as the ethanol concentration in the mixed solvent solution rise in the absence and presence of 0.001 M, 0.005 M and 0.01 M MnSO₄·6H₂O. Hence the various parameters as pre-micellar, post-micellar slopes, CMC, α, ΔGₘₒ, ΔGₜ𝑟,aₜ, Kₒ/Kᵤₐₚ of CTAB in the presence and absence of MnSO₄·6H₂O correlate with the percentage of ethanol (%) are useful for the researchers. The plot of CMC versus CMC vary Harkins–Corrin concept. The correlation of ΔGₘₒ with the solvent parameters as Gordon parameter, the dielectric constant, viscosity, Reichardt’s parameters give not only the stability of the solution but also relate micellization of molecular association, the fluidity, polarity, and solvent structure. The correlation of ΔGₘₒ with solvophobic parameter (Sₚ) gives the aggregation behavior of CTAB in aqueous ethanol solutions in the absence and presence of MnSO₄ 6H₂O. Thus, the relation can be modulated simply by the solvophobic parameter of hydrocarbon in the mixed solvents.

Conflicts of Interest

There are no conflicts to declare.

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Author Contributions

A.B. and T.P.N. were involved in project conceptualization and design. P.B. conducted the research and analyzed the data; prepared the manuscript and had primary responsibility for the content; and contributed to the laboratory. A.B. and T.P.N are also involved in manuscript editing. All authors read and approved the manuscript.
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