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RESEARCH ARTICLE

An Investigation of the Effect of Ionic Strength on Micellization Behaviors of a Cationic Surfactant

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Highlights

- $NaNO_3$ and Na_2SO_4 increase ionic strength and reduce the CMC of TTAB in water
- Divalent counter-anions more effectively reduce the CMC of TTAB aqueous media
- TTAB CMC increases from 298.15 to 318.15 K in $NaNO_3$ and Na_2SO_4 solutions

Abstract

The conductivity measurement of tetradecyltrimethylammonium bromide (TTAB) provides information about its micellization behaviors in the presence of salts $NaNO_3$ and Na_2SO_4 in aqueous solutions. The presence of $NaNO_3$ and Na_2SO_4 in aqueous solutions of TTAB greatly influences the critical micellization concentration (CMC) of TTAB at 298.15, 308.15, and 318.15 K temperatures. Precisely measured conductivity data were used to determine CMC, degree of counter-ion dissociation(α), free energy of micellization (ΔG_m^0), enthalpy of micellization (ΔH_m^0), and entropy of micellization (ΔS_m^0) of the TTAB in aqueous solutions in the presence of inorganic salts. The ionic strength in solution due to the presence of $NaNO_3$ and Na_2SO_4 affects the micellization thermodynamics of the TTAB in salt-water solvent systems. The study provides valuable insights regarding the effect of ionic strength, hydrophobic interaction, enthalpy change, and entropy change on micellization behaviors of TTAB. The ΔG_m^0 and ΔH_m^0 of TTAB becomes more negative in the presence of both $NaNO_3$ and Na_2SO_4 in aqueous solution, whereas ΔS_m^0 found to be maximum in the presence of Na_2SO_4. An increase in temperature in the investigated range increases the CMC of the TTAB in salt-water solvent systems.

Key words: *CMC, counter-ions, ionic strength, micelles, TTAB*

Introduction

Surface-active agents, which are also called surfactants, have both hydrophilic and hydrophobic domains in a molecule. These compounds are also sometimes known as amphiphiles because of the presence of the two domains in the same molecule. The amphiphilic nature of surfactants helps to lower interfacial tension between liquid-solid or liquid-liquid or liquid-air interfaces (Banat et al., 2000; Onuche et al., 2016; Fardami et al., 2022). Surfactants tend to keep their hydrophobic part or domain away from polar solvents like water and tend to keep the hydrophilic part in the bulk of polar solvents (Senturk Parreidt et al., 2018).

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Among various surfactants, Tetradecyltrimethylammonium bromide (TTAB) is a cationic surfactant with a positively charged polar head along with non-polar tail in Tetradecyltrimethylammonium ion (TTA^+) and a bromide (Br^-) counter ion, i.e. ($TTA^+ + Br^- = TTAB$) (Yang & Pal, 2020). The molecular formula of TTAB is $C_{17}H_{38}N.Br$, with a positively charged head group neutralized by bromide counterion (Br^-) as just mentioned above. The average length of a single TTAB molecule is approximately 21.5 Å, with a cross-sectional area of 50–54 Å², and a hydrophilic head diameter in the range of 4-6 Å. The TTAB can be used in various fields like agriculture, pharmaceuticals, cosmetics, corrosion inhibition, and other industrial areas. (Schramm et al., 2003; Chowdhury et al., 2019). CMC value is an important property of ionic surfactants (Khamis et al., 2020) that determines the optimum concentration for their effective use in various applications (Khalfallah, 2024). The CMC of surfactants, including TTAB, is related to various parameters such as pH, temperature, solvent nature, dielectric constant of solvent, ionic strength of solutions, etc. (Sharma, 2016). CMC of either type of surfactant can be determined using various methods, observing some deviation in physical properties after CMC (Perinelli et al., 2020). We can easily measure the conductivity of ionic surfactants in aqueous solutions to determine their CMC. The Conductivity method is based on the fact that the electrical conductivity of ionic surfactants in aqueous solutions linearly increases with the increase in surfactant concentration. The slope of the curve in the conductivity versus concentration plot changes after CMC because of the start of micelle formation.

The presence of inorganic salts on surfactant solutions increases the ionic strength of the solution, and that can significantly alter their physicochemical properties, including CMC, Krafft temperature, and surface tension (Islam et al., 2015). Few studies have shown that an increase in ionic strength tends to a decrease in CMC for nonionic and ionic surfactants (Palladino & Ragone, 2011). The reduction in CMC of surfactants on increasing ionic strength by adding inorganic salt can be explained as a decrease in an electrostatic repulsion between the charged head groups of molecules of ionic surfactants (Sharker et al., 2017). Generally, inorganic salts are used to increase the ionic strength in surfactant solutions. Inorganic salts such as NaX help to decrease the CMC of some cationic surfactants (Hou et al., 2018). The ability of different inorganic salts to lower the CMC is mainly affected by the specific nature of the counter-ions and follows the same trend of the Hofmeister series. Increasing ionic strength in the surfactant solution helps to reduce the extent of the electrical double layer, which causes a decrease in the electrostatic repulsion acting between the charged head groups of the molecules of the ionic surfactant (Schott & Han, 1976). Furthermore, temperature affects the CMC of ionic surfactants differently compared to non-ionic surfactants (Kumar et al., 2012). For ionic surfactants, CMC generally follows a V-shaped trend with increasing temperature, i.e., showing a minimum value at a certain temperature, usually at room temperature (Alam et al., 2019).

Thermodynamic studies of ionic surfactants using inorganic salts in aqueous solutions are very important for understanding the energetics of micellization and the forces that control micelle stability and self-assembly of micelles (Hu et al., 2020). These studies involve the determination of thermodynamic properties such as entropy, Gibbs free energy, and enthalpy of micellization. This study provides more insights into the spontaneity process and driving forces behind the process of micellization in salt-water solvent systems.

Both salts $NaNO_3$ and Na_2SO_4 are kosmotropic in water; they have an influential effect to modify solvent structure and can interact differently with the positive polar head of the TTAB. The salts $NaNO_3$ and Na_2SO_4 have various important properties such as being easily available, low-cost, non-toxic, and environmentally friendly etc. Because of these features, the salts are broadly used in many surfactant-related products, and their broad applications make them model compounds for investigating the micellization behaviors of cationic surfactants such as TTAB in salt-water solvent systems. The present study provides an insight into ion-ion interactions, ion-solvent interactions, and micellization thermodynamics of cationic surfactant in the presence of strong electrolytes in aqueous solutions. The study helps to guide the optimal use of surfactant in the modern surfactant-demanding age.

So, we have investigated the effect of $NaNO_3$ and Na_2SO_4 on the micellization behaviors of TTAB at 298.15, 308.15, and 318.15 temperatures by using the conductivity method in aqueous solutions. The method is a simple as well as reliable technique to determine the CMC of ionic surfactants. The work aims to study the comparative electrostatic effect of monovalent and polyvalent (divalent) anions on the polar head of surfactant and the effect of their kosmotropic nature on the micelle formation process of cationic surfactant in salt-water solvent systems. Thermodynamic properties such as Gibbs free energy (ΔG_m^0), entropy(ΔS_m^0), and enthalpy (ΔH_m^0) of micellization were calculated using temperature-dependent CMC values. Furthermore, the results of the work can be applied to the formulation of pharmaceutical, cleansing, cosmetic, and corrosion preventive products.

Experimental

The experimental technique is the most crucial part of research to meet the objectives. So, the experimental section of the work is explained in the following subheadings.

Chemicals:

All required chemicals and materials were purchased from different suppliers for the study. Chemicals were used without applying a further purification process; however, the suitable ones were stored in a desiccator. A summary of the chemicals employed in the present work was mentioned in Table 1.

Table 1. Information on chemicals used in the study.

S.N.	Materials	Suppliers	Purity	Further Purified
1.	TTAB	Sisco Research Laboratories, India	99 %	NA
2.	$NaNO_3$	Loba Chemicals, India	99%	NA
3.	Na_2SO_4	Merk Scientific Pvt.Ltd., India	98%	NA

Preparation of solutions and conductivity measurements

Solvents containing $NaNO_3$ and Na_2SO_4 were separately prepared using distilled water. Electrical conductivity of the distilled water used for solvent preparation in the work was about ~ $5x10^{-6}$ Scm^{-1}. The prepared solvents were applied to prepare stock solutions of TTAB separately at 298.15 K, 308.15 K, and 318.15 K temperatures. The conductivity cell was calibrated using the method described by Lind et.al (Lind et al., 1959). The conductivity of the stock solutions of TTAB having concentration 0.0075 mol L^{-1} in the absence and presence of $NaNO_3$ (0.0025 M & 0.005 M) and Na_2SO_4 (0.0025 M) was measured. The conductivity of the stock solution was measured by applying the internal dilution method using a dip-type conductivity cell. The conductivity measurements were carried out maintaining constant temperatures of 298.15 K, 308.15 K, and 318.15 K using a thermostat. EI (Electronics India) conductivity meter, having model number 601 and cell constant 1.0 cm^{-1} was used to measure the conductivity data. The produced primary data were replicated three times to verify the reliability of the research.CMC determination:

The measured electrical conductivity data and [TTAB] (concentration of TTAB solution) were plotted to obtain the CMC of the TTAB as shown in Figure 1. The two straight lines intersect each other, and the intersection point on the x-axis (or concentration axis) gives the CMC of the TTAB (see figure 1).

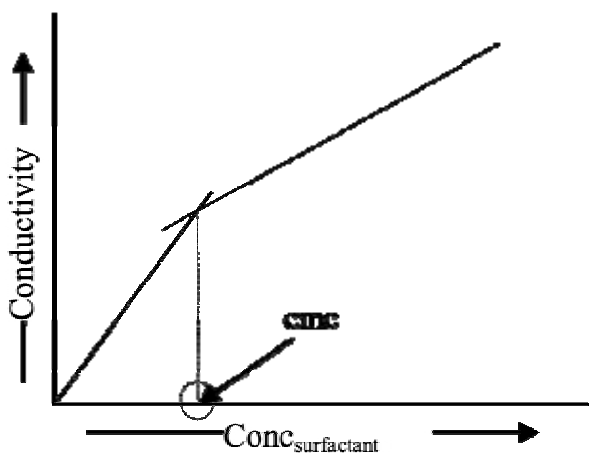

Fig. 1. Schematic representation for the plot of the variation of conductivity against the [conc.] of a TTAB solution.

Results and Discussion

The findings of this work are crucial for investigating the factors influencing micellization behavior of TTAB in the presence of salts $NaNO_3$ and Na_2SO_4, which have monovalent and divalent anions, respectively.

Conductivity and TTAB concentration

The variation of conductivity of TTAB solutions in the presence of inorganic salts $NaNO_3$ and Na_2SO_4 at 298.15 K temperatures has been shown in Figures 2 & 3. The conductivity of the TTAB solutions increases with an increase in concentration of TTAB in the presence as well as in the absence of $NaNO_3$ and Na_2SO_4. The increase in electrical conductivity is due to an increase in the number of TTA^+ and Br^- ions in the solution. The increasing trend of the conductivity is steep at low concentrations of TTAB, and the slope becomes low at high concentrations of TTAB, as depicted in Figures 2 and 3. The decrease in slope of the line after a certain concentration point is because of the formation of aggregates called micelles, which have a bulky size compared to monomeric surfactant molecules. Furthermore, the presence of $NaNO_3$ and Na_2SO_4 in an aqueous solution of an ionic surfactant increases the ionic strength in the solution. Table 2 indicates the decrease in slope of the curves of plot conductivity vs. [TTAB] for both pre (S1) and post (S2) micellar curves on adding or increasing the concentration of $NaNO_3$ and Na_2SO_4 separately in the solution. The increasing ionic strength of solutions generally leads to a decrease in the conductivity of the surfactant solution (Sriprablom et al., 2018). The decreases in conductivity of TTAB on adding salts and increasing salt concentration are probably due to increasing ionic strength of TTA^+ and B^- ions in the solution, the presence of $NaNO_3$, and Na_2SO_4. Values of ionic strength are also given in Table 2, and we observed that there is a strong negative relationship between the conductivity of TTAB and the ionic strength of the solutions.

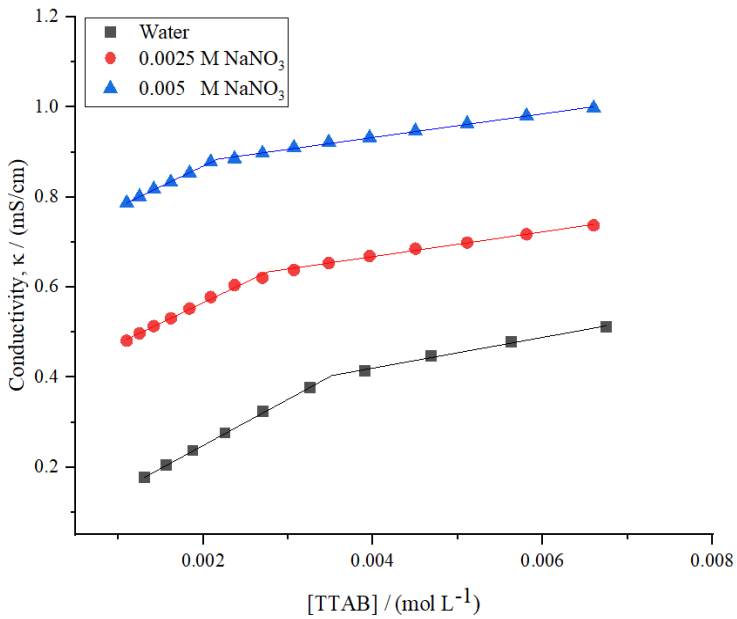

Fig. 2. Plot of conductivity against [TTAB] solution in the absence and presence of $NaNO_3$ at 298.15 K and 1 atm pressure.

CMC and presence of salts

The magnitude of CMC reduction is affected by various factors such as nature and concentration of the inorganic salts, temperature of solution, size of counter-ions, polarizability, structure of surfactant molecules, etc. (Łuczak et al., 2011; Ren, 2015).

In the present study, CMC of TTAB was found to be 0.0036 mol L^{-1} and the value is in agreement with the value reported in literature (Islam et al., 2015). It is of great significance for inorganic salts to be present in water with surfactants because they have an influential role on the micellization of cationic surfactants (Palladino & Ragone, 2011). The CMC of TTAB in the presence of $NaNO_3$ and Na_2SO_4 separately at three different temperatures is presented in Table 2. The addition of $NaNO_3$ and Na_2SO_4 separately in all aqueous solvents investigated helps to reduce the CMC of the TTAB. In the study, the maximum value of CMC for TTAB was observed as 0.0033 mol L^{-1} in the presence of 0.0025 M $NaNO_3$ at 318.15 K, and the minimum CMC was observed in the presence of 0.0025 M Na_2SO_4 at 298.15 K. It was observed that the presence of the salts in the solution helps to decrease CMC of TTAB in the given range of temperature.

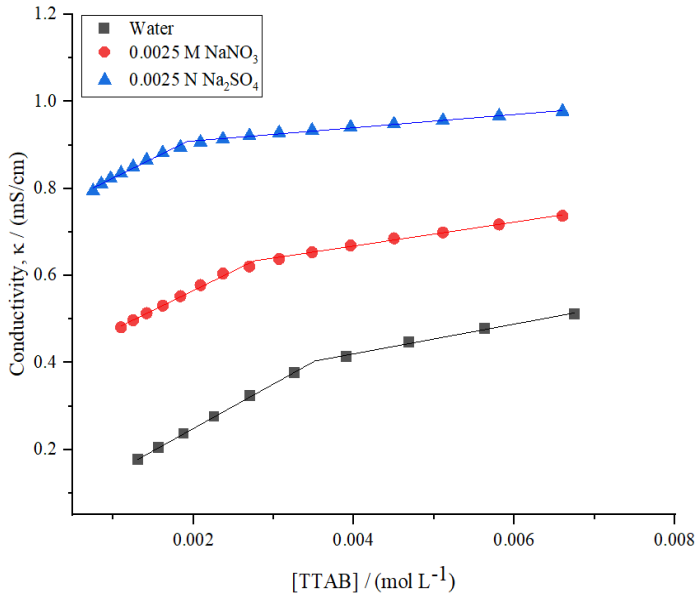

Fig. 3. Plot of conductivity against [TTAB] solution in the absence and presence of inorganic salts at 298.15 K and 1 atm pressure.

The decrease in CMC of TTAB on the addition of inorganic salts $NaNO_3$ and Na_2SO_4 to the solutions is due to the shielding or screening of the electrostatic repulsion between positively charged polar head groups TTA^+ ions (Sharker et al., 2017). The Shielding effect helps the TTA^+ ions to easily fit together more closely in the micelle, and that helps the micelle formation at lower concentrations of the surfactants (Islam et al., 2015). More stronger kosmotropic SO_4^{2-} ion decreases the CMC more effectively than a weaker kosmotropic NO_3^- ion because of more efficiency in promoting hydrophobic interactions of TTA^+ ions (Alam et al., 2019). The results are in agreement with the effects reported by the anions of the Hofmeister series on micellization of cationic surfactants. The Hofmeister series provides qualitative order of ions, which was based on their capacity to salting out or salting in proteins and other macromolecules from aqueous solutions, so providing insightful knowledge into the influence of ions on surfactant behaviors (Łuczak et al., 2011). The interactions of NO_3^- and SO_4^{2-} separately with the cationic head of TTA^+ ions can change the surface charge, which stabilizes the polar heads, and therefore decrease in CMC of TTAB by the addition of $NaNO_3$ and Na_2SO_4 (Gerola et al., 2017). The effectiveness of CMC reduction is different for the counter ions NO_3^- and SO_4^{2-} is more for divalent counter SO_4^{2-} than for monovalent counter NO_3^- ions, showing the weaker effect of monovalent counter-ions compared to the stronger ability of multivalent counter-ions to neutralize the charge of cationic head groups in the study (Alam et al., 2019).

Degree of dissociation and CMC

The observed value of the degree of dissociation (α) of TTAB in aqueous solution was 0.33, and the value is in agreement with the reported literature value of 0.31. The value of α increases with increase in temperature (Islam et al., 2015). The increase in temperature helps to decrease the charge density of micelles, and that results in more dissociation of counter-ions of TTAB molecules (Islam et al., 2015; Maiti et al., 2007). Furthermore, in the present work, the value of α decreases in the presence of both the salts $NaNO_3$ and Na_2SO_4 than in the absence of the salts in the solution. The counter-ions from added salts bind with the charged micellar surface and decrease electrostatic repulsion between polar heads, thus helping in lowering the degree of dissociation (Tagashira et al., 2009). The effect of lowering the degree of dissociation is more by Na_2SO_4 than by $NaNO_3$. The SO_4^{2-} ions have more charge density than NO_3^- ions, so SO_4^{2-}ions neutralize the charge on the surfactants' polar head more effectively than NO_3^- ions, resulting in more lowering of degree of ionization (Paria & Yuet, 2006). Additionally, the order of reduction of the degree of dissociation of TTAB in different salt solutions was in the order: 0.0025 M $NaNO_3$ < 0.005 M $NaNO_3$ < 0.0025 M Na_2SO_4, i.e., the value of the degree of dissociation of TTAB was lowest in 0.0025 M Na_2SO_4 at all the temperatures investigated.

Table 2. Values of pre-micellar slope (S_1) and post micellar slope (S_2) from plot of conductivity vs. concentration, degree of counter ion dissociation , CMC, ionic strength (I), and slopes of curves obtained from plot of CMC against ionic strength (I) of the TTAB solutions in presence and absence of inorganic salts at various temperatures and 1 atm pressure.

Water						
$\frac{T}{(K)}$	S_1	S_2	$\frac{CMC}{(molL^{-1})}$	α	Ionic Strength (I)	Slope (Plot of ionic strength vs CMC)
298.15	102.46	34.15	0.0035	0.333	-	-
0.0025 M $NaNO_3$						
$\frac{T}{(K)}$	S_1	S_2	$\frac{CMC}{(molL^{-1})}$	α	Ionic Strength (I) due to $NaNO_3$	Slope (Plot of ionic strength vs CMC
298.15	96.82	28.96	0.0026	0.299	0.0025	-0.0014
308.15	114.19	39.33	0.0030	0.344	0.0025	-0.0016
318.15	135.37	51.82	0.0033	0.383	0.0025	-0.0018
0.005 M $NaNO_3$						
$\frac{T}{(K)}$	S_1	S_2	$\frac{CMC}{(molL^{-1})}$	α	Ionic Strength (I) due to $NaNO_3$	Slope (Plot of ionic strength vs CMC
298.15	90.90	26.31	0.0022	0.289	0.005	-0.0014
308.15	102.83	33.85	0.0024	0.329	0.005	-0.0016
318.15	123.52	42.63	0.0030	0.345	0.005	-0.0018
0.0025 M Na_2SO_4						
$\frac{T}{(K)}$	S_1	S_2	$\frac{CMC}{(molL^{-1})}$	α	Ionic Strength (I) due to Na_2SO_4	Slope (Plot of ionic strength vs CMC
298.15	91.26	15.19	0.0019	0.166	0.0075	-0.0014
308.15	97.853	21.250	0.0022	0.217	0.0075	-0.0016
318.15	125.06	34.23	0.0024	0.274	0.0075	-0.0018

Standard uncertainty in temperature is 0.03 K, error in the conductivity measurement is ±3%.

CMC and ionic strength

The ionic strength of a solution due to the presence of an electrolyte to a solution mainly depends on the concentration of the electrolyte and the valence of its ions. Ionic strength of an electrolytic solution can be determined using the equation below;

$$I = \frac{1}{2}\sum C_i Z_i^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots(i)$$

Where, I = ionic strength of the solution

C = molar concentrations of the ions

Z = valence of the ions

The ionic strength values of TTAB solutions due to the separate presence of $NaNO_3$ and Na_2SO_4 are given in Table 2. The ionic strength value of the solutions containing TTAB and salts increases in the following order: 0.0025 M $NaNO_3$ < 0.005 M $NaNO_3$ < 0.0025 M Na_2SO_4. The ionic strength contribution from the ions of TTAB is not taken into account for the calculation using equation (i), i.e., only the ionic strength due to the presence of inorganic salts is determined and tabulated in Table 2.

The increase in ionic strength lowers the CMC of TTAB, probably due to a greater reduction of repulsions among polar heads

of the TTA^+ ions because of more counter-ions from added salts. Furthermore, on discussing the CMC reduction efficiency of $NaNO_3$ and Na_2SO_4, the water molecules in the solution are localized around the water structure, making SO_4^{2-} ions, because of more charge density, which leads to more lowering of hydrophilic hydration and positively influences the hydrophobic interaction among the tails of the surfactant molecules than that of NO_3^- ions. Thus, Na_2SO_4 seems to be more efficient at lowering the CMC of the TTAB than $NaNO_3$ in the present study (Nishikido & Matuura, 1977). The effect of ionic strength on CMC is depicted in Figure 4. Figure 4 strongly supports the negative correlation of CMC with ionic strength of the solutions due to the presence of the inorganic salts used. In the present study, the minimum CMC noted was 0.0019 mol L^{-1} at 298.15 K in the presence of 0.0025 M Na_2SO_4 and water.

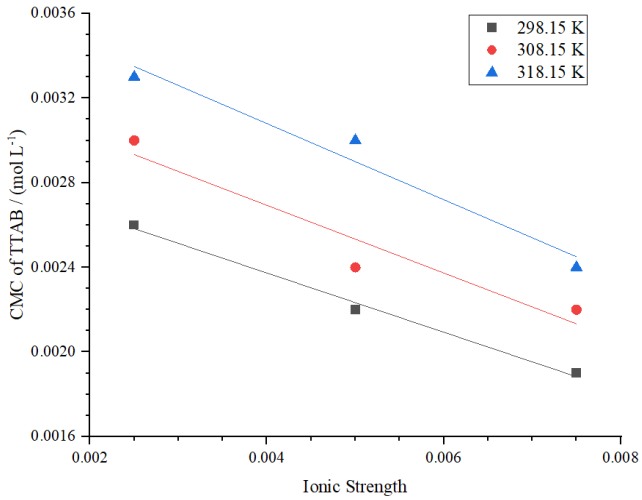

Fig. 4. Plot of CMC against ionic strength of TTAB solution due to the presence of 0.0025 M & 0.005 M $NaNO_3$ and Na_2SO_4 at 298.15 K, 308.15 K, and 318.15 K temperature and 1 atm pressure.

Temperature and CMC of TTAB

Figure 5 shows the variation of conductivity against concentration of [TTAB] solution in the presence of 0.0025 M $NaNO_3$ at various temperatures and 1 atm pressure. The trend of CMC of TTAB on increase in temperature in the presence of $NaNO_3$ and Na_2SO_4 is presented in Table 2. The temperature of the solution significantly influences the micellization process, affecting the hydrophobic interactions, hydration forces, and the overall thermodynamics of micelle formation (Shaikh et al., 2021).

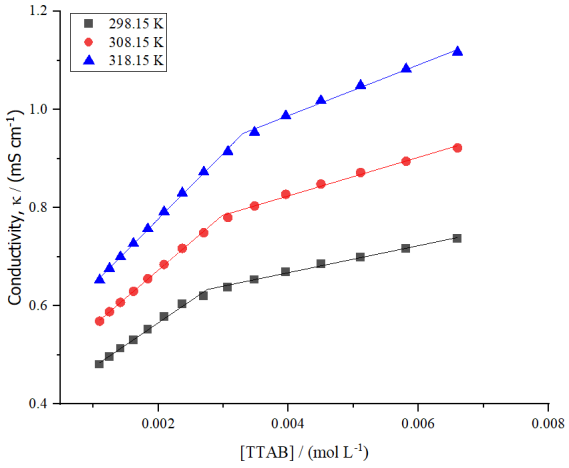

Fig. 5. Plot of conductivity vs. [TTAB] solution in the presence of 0.0025 M $NaNO_3$ at various temperatures and 1 atm pressure.

The observed effects of temperature on CMC for TTAB arise from a complex interplay of enthalpic and entropic assistance to the free energy of micellization (Kim & Lim, 2004). At higher temperatures, entropic effects become dominant for micelle formation. When the temperature of the solution rises, the counter-ions and surfactant molecules move faster, and this breaks

up the electrostatic interactions between the polar head with counter-ions of the TTAB molecules. This phenomenon will result in a weaker micellar structure and an increase in the CMC value of the TTAB (Alam et al., 2019). Furthermore, at higher temperatures, the greater solubility of TTAB (or TTA^+ ions) monomers in an aqueous phase helps to increase the CMC of ionic surfactants because of the need for a greater amount of surfactant to drive the self-assembly process (Alam et al., 2019).

Thermodynamics of micellization

An Investigation of the thermodynamic properties of the micellization process is very helpful to get valuable information related to the aggregation properties of surfactants. The thermodynamic properties studied here are the enthalpy of micellization (ΔH_m^0), free energy of micellization (ΔG_m^0), and entropy of micellization (ΔS_m^0). The equations below were used for the determination of the above-mentioned properties (Mukerjee, 1967; Sulthana et al., 1996; Phillips, 1955):

Free energy of micellization, $\Delta G_m^0 = (2-\alpha)RT\ ln\ cmc$ .....(v)

Enthalpy of micellization, $\Delta H_m^0 = -RT^2\left(\frac{dlnX_{cmc}}{dt}\right)$.....$(vi)$

and

Entropy of micellization, $\Delta S_m^0 = \frac{\Delta H_m^0 - \Delta G_m^0}{T}$ .....(vii)

where R is the gas constant (8.314 J mol^{-1} K^{-1}), α is the degree of dissociation of TTAB, T is the temperature in Kelvin scale, and X_{cmc} is the mole fraction of TTAB at CMC. Furthermore, $\left(\frac{dlnX_{cmc}}{dt}\right)$ is the slope obtained by plotting a graph of lnX_{cmc} versus T.

Table 3. Values of ΔH_m^0,ΔG_m^0, and ΔS_m^0 of TTAB in the presence of $NaNO_3$ & Na_2SO_4 at various temperatures and 1 atm pressure.

Water			
$\frac{T}{(K)}$	$\frac{\Delta G_m^0}{(kJmol^{-1})}$	$\frac{\Delta H_m^0}{(kJmol^{-1})}$	$\frac{T\Delta S_m^0}{(kJmol^{-1})}$
298.15	-39.95	-	-
0.0025 M $NaNO_3$			
$\frac{T}{(K)}$	$\frac{\Delta G_m^0}{(kJmol^{-1})}$	$\frac{\Delta H_m^0}{(kJmol^{-1})}$	$\frac{T\Delta S_m^0}{(kJmol^{-1})}$
298.15	-42.02	-15.48	26.10
308.15	-41.66	-16.15	25.10
318.15	-41.58	-16.71	24.48
0.005 M $NaNO_3$			
$\frac{T}{(K)}$	$\frac{\Delta G_m^0}{(kJmol^{-1})}$	$\frac{\Delta H_m^0}{(kJmol^{-1})}$	$\frac{T\Delta S_m^0}{(kJmol^{-1})}$
298.15	-43.03	-21.05	21.62
308.15	-42.98	-21.10	21.54
318.15	-42.82	-23.04	19.47
0.0025 M Na_2SO_4			
$\frac{T}{(K)}$	$\frac{\Delta G_m^0}{(kJmol^{-1})}$	$\frac{\Delta H_m^0}{(kJmol^{-1})}$	$\frac{T\Delta S_m^0}{(kJmol^{-1})}$
298.15	-46.72	-15.97	30.24
308.15	-46.26	-16.79	29.01
318.15	-45.83	-17.90	27.50

Standard uncertainty in temperature is 0.03 K, error in the conductivity measurement is ±3%.

The negative value ΔG_m^0 indicated the spontaneity of micelle formation for TTAB in the given solvent systems (see Table

3). The ΔG_m^0 is less negative on increasing the temperature, indicating that the micellization process is less favorable or non-spontaneous in the range of temperature studied in the presence of both salts. The additions of $NaNO_3$ and Na_2SO_4 separately in the TTAB solutions make the ΔG_m^0 value more negative, indicating more spontaneity (Ren, 2014) in the micelle formation at a given temperature, and this is supported by decreases in CMC values of the TTAB in the study (see Table 2). The lowering of ΔG_m^0 is more observed in the presence of Na_2SO_4, indicating the greater influence of divalent counter-ions because of their charge density.

The thermodynamic parameter that reflects heat absorbed or released during micelle formation is the enthalpy of micellization (ΔH_m^0), and it offers insights into the driving forces governing micellization (Kumar et al., 2012). The ΔH_m^0 is more negative in the presence of both the salts $NaNO_3$ and Na_2SO_4 at a given temperature in the same solvent systems (see Table 3), which means the presence of salt favors micellization of TTAB. The negative ΔH_m^0 value may occur when hydration of water molecules around the hydrophilic charged head group becomes more pivotal than that of the destabilizing effects resulting from water structure around the hydrophobic chains of TTA^+ ions (Aktar et al., 2019). The ΔH_m^0 calculated values for all systems are negative, indicating the energetically favorable conditions for micellization of the TTAB. Moreover, temperature slightly makes ΔH_m^0 more negative as reported similar results in the literature (Islam et al., 2015), and the results explain the exothermic nature of micellization of TTAB in the presence of the salts.

Similarly, values of ΔS_m^0 were observed to be positive for TTAB in all solvent systems containing the salts and temperatures (see Table 3). The positive value of ΔS_m^0 indicates two important phenomena of micellization: one is the loss of hydrated hydrophobic tails from aqueous to hydrophobic (or non-polar) micelle core, and another is an increment of rotational degree of freedom of hydrophobic tails in a core of a micelle compared to an environment of water (Chen et al., 1998). The less ΔS_m^0 in increasing temperature may be due to more negative ΔH_m^0 due to stronger hydrophobic interactions, i.e., the disorder from increasing temperature is not enough to exceed the energy released from the aggregation of surfactant. In the presence of 0.0025 M $NaNO_3$, the micellization seems to be entropy driven, and in 0.005 M $NaNO_3$, it seems to be enthalpic-entropic driven, and the micellization is strongly entropy driven in 0.0025 M Na_2SO_4 (see Table 3). Strong binding tendency of divalent SO_4^{2-}ions can have a major impact on overall free energy change of micellization, with the entropic participation becoming the most important (Yamabe & Moroi, 1999).

Conclusions

The added $NaNO_3$ and Na_2SO_4 help minimize the CMC of TTAB in aqueous solutions at a given range of temperatures. The salts increase counter-ion dissociation of the surfactant. The increasing ionic strength due to the presence of the salts has a strong negative correlation with CMC, indicating their effectiveness in decreasing the CMC. The micellization process was found to be spontaneous in all solvent systems and provided temperature, as supported by a negative value of free energy of micellization. Furthermore, the change in enthalpy is also negative, and the change in entropy is positive for all solvent systems and the range of temperature investigated, and the values of enthalpy and entropy change contributed to the negative value of free energy of micellization. The negative value of enthalpy suggests the energetically favorable, and the positive value of entropy suggests the entropically favorable for micellization of the TTAB. Furthermore, the added salts have a positive contribution to the thermodynamics of micellization of the surfactant.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper

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