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Benzalkonium Chloride Micellization: Salt and Temperature Dependence (Conductivity, Surface Tension)

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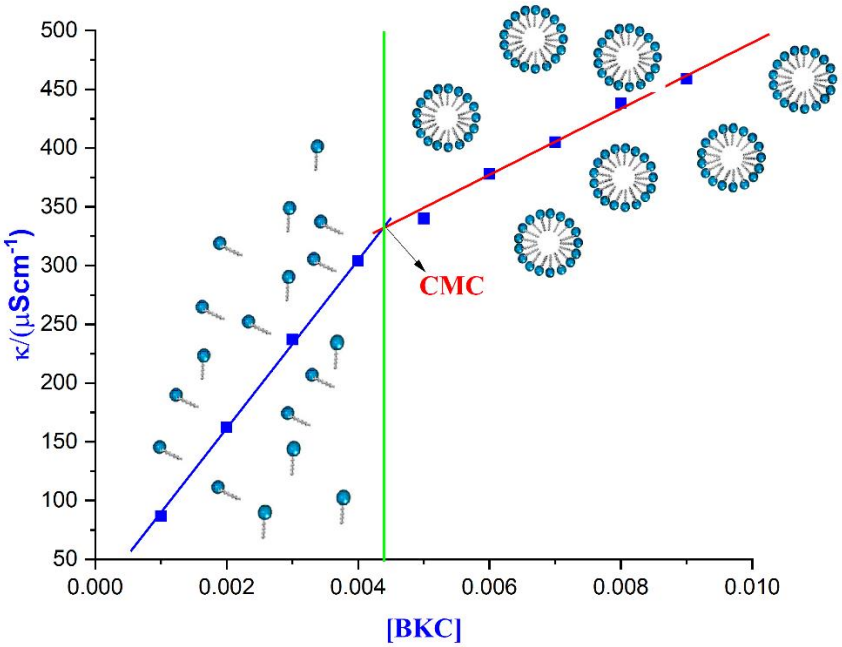

Abstract: The aggregation behavior of cationic surfactant (Benzalkonium chloride (BKC)), in the absence and presence of KCl and $MgSO_4$ in aqueous media, was investigated at room temperature by surface tension measurements and at different temperatures by conductivity measurements. Critical micelle concentration (CMC), micelle ionization degree (α), the thermodynamic parameters (standard Gibb's energy of micellization (ΔG^o_{mic}), enthalpy of micellization (ΔH^o_{mic}), and entropy of micellization (ΔS^o_{mic})), and interfacial parameters were determined. In addition, the geometry of formed micelles was investigated. The effect of magnesium sulfate on BKC

micellization was more pronounced compared to potassium chloride. At all temperatures, BKC's CMC values were lower with magnesium sulfate than with potassium chloride. Similarly, the CMC and α values were directly proportional to temperature.

Keywords: Benzalkonium chloride, Micellization, Thermodynamic parameters, Micelle geometry

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Introduction

Surfactants are very important compounds because they have amphiphilic properties and are used in widely varied fields of technology and biological systems [1]. One of the important applications of surfactants is their use as drug delivery systems [2,3]. Depending on the specific solution conditions, ionic surfactant micelles are aggregates of surfactant molecules with varying sizes and shapes that develop in aqueous mediums. A micelle of ionic surfactants is made up of a less compressive surface structure encircling a compressive core. Furthermore, counter ions are attached to the surface of the micelle.

Cationic surfactants have some additional advantages over other categories of surfactants [4]. cationic surfactants are used for many industrial processes. Some important usages of cationic surfactants are fabric softeners for the textile industry and anti-caking agents for fertilizers, corrosion inhibitors for metal surfaces, pigment dispersants, and show antibacterial properties [4,5]. Benzalkonium chloride (BKC, Fig. 1) is a cationic surfactant because its head groups carry a positive charge.

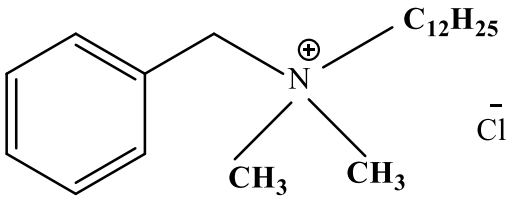

Figure 1. Structure of Benzalkonium chloride

Due to the amphiphilic properties of surfactants molecules, the aggregation of surfactants in the aqueous phase is possible.[6] This aggregation takes place at a certain concentration, which is known as critical micelle concentration (CMC) [6].

Water is the main common solvent with high surface tension value that arises wetting problem. Surfactants diminish the surface and interfacial tension with respect to the neighboring surface, and hence it is recognized as the heart of interfacial chemistry [7].

Examining BKC's conductivity behavior in comparison to CMC may provide information about their micellar structure, aggregation behavior, and ion transport properties. Through examining the differences in conductivity at various concentrations, especially in the vicinity of the CMC, scientists may learn a great deal about micelle stability [8].

The investigations of the salt's effect on the micelle formation, notably the CMC, show that adding salt to surfactant solution changes the interaction and helps micelle formation [9,10].

The effect of salt on the micellar behavior of ionic surfactant depends essentially on the counter ions. However, the salt decreases the electrostatic repulsion between the polar head groups and reduce the CMC value [9,10].

The study of temperature effect on the CMC is very important in the field of surfactant applications [11]. Due to the absence of a universal model applicable to all surfactant classes, temperature plays a critical role in micellization behavior. The effect of temperature on the critical micelle concentration (CMC) has been extensively studied, revealing a complex and surfactant-specific dependence [11]. It is helpful to get various thermodynamic characteristics at various temperatures in order to comprehend the principles that drive micelle production. Since they establish the relative significance of hydrophobic interactions, surfactant water contact, and head-group repulsions in the case of ionic surfactants, micelle thermodynamic characteristics in aqueous and non-aqueous settings are more significant [10].

The effect of molecular composition of head group and temperature on micellar properties of ionic surfactant with C12 alkyl chain was reported by Oremusová et al. [12]. El-Aila disclosed Conductometry and Thermodynamics Study of Metal Dioctylsulfosuccinate in Aqueous Solution [13]. Rafique et al. Reported the Micellar structure and transformations in sodium alkylbenzenesulfonate (NaLAS) aqueous solutions: effects of concentration, temperature, and salt [14]. The influences of NaCl and Na_2SO_4 on the micellization behavior of the mixture of cetylpyridinium chloride + polyvinyl pyrrolidone at several temperatures was reported by Ahmed et al. [15]. More studies are still to understand the effect of salt and temperature on the micellization and geometry of the surfactant micelles. By considering the previous studies and application of surfactant micelles in both with and without salt, in the current study, we used the conductivity and surface tension measurements to investigate the effect of KCl and $MgSO_4$ on the micellization process in the temperature range (298.15-333.15 K). The several micellization parameters, including CMC, degree of micelle dissociation (α), interfacial parameters (ΠCMC, Γmax, Amin, Gomin), related thermodynamic parameters of micellization (ΔG^o_m, ΔG^o_{ads}, , ΔH^o_m, and ΔS^o_m) as well as size, shape, molar mass, and aggregation number have been determined.

Experimental

Chemicals

All materials were used as received without further purification. Benzalkonium chloride (BKC) was obtained from Sigma-Aldrich (St. Louis, MO, USA), while potassium chloride and magnesium sulfate have been supplied by Merck, Germany. Ultra-pure water with specific conductivity 2×10^{-6} Scm^{-1} was used for solution preparation. The salt-free stock solution (1×10^{-2} mol dm^{-3}) of BKC was prepared by dissolving the required quantity of surfactant in distilled water. Also, the same concentration of benzalkonium chloride was prepared in the presence of 0.01 M potassium chloride once and in the presence of 0.01 M magnesium sulfate another time.

Dilute Solutions

The native solutions of BKC were used to prepare a series of dilute solutions (1×10^{-3} to 9×10^{-3} mol dm^{-3}) by adding the required volumes of distilled water to different volumes of native solutions.

Conductivity measurements

A Mettler Toledo 226 conductivity meter (Switzerland), fitted with a cell constant of 0.726 cm^{-1}, was used to measure the conductivity in the temperature range (298.15-333.15 K). The temperature was controlled using a thermostatic water bath. Prior to testing the experimental samples, the conductivity meter was calibrated using 0.01M and 0.1M KCl [16].

Surface tension measurements

Surface tension measurements of the experimental samples were conducted at 25°C using the drop weight method with a Wasser Tropfzahl F. stalagmometer. Prior to each measurement, the instrument was calibrated using double-distilled water. The stalagmometer was thoroughly cleaned by sequential rinsing with hot water, ethanol, and chromic acid, followed by multiple rinses with double-distilled water. It was then dried by placing it in a tilted position in a clean environment, allowing residual moisture to evaporate naturally.
About 20 drops of the given liquid are received from the drop-pipette in a weighing bottle and weighed. Thus, weight of one drop is found.

Results and discussion

Critical micelle concentration

Conductivity and surface tension measurements have been used to determine the critical micelle concentration (CMC) of a surfactant in the absence and presence of salts. CMC is a certain concentration of surfactant molecules at which surfactant ions aggregate and get self -assembled or micelle [17,18]. The CMC value of BKC decrease in the presence of salts as shown in Table 1. The values of the obtained CMC in this study were consistent with previous studies [19-21].

Table 1. Critical micelle concentration (CMC) of BKC in the absence and presence KCl and $MgSO_4$ electrolytes at 25°C.

Media	CMC (mM)	
	Cond.	S.T.
H_2O	4.39	4.00±10
0.01M KCl	3.59	3.65±0.6
0.01M $MgSO_4$	3.27	3.17±0.7

Conductivity study

The conductivity measurements have been used to determine CMC and micelle ionization degree (α) of BKC in the absence and presence of KCl and $MgSO_4$ electrolytes [8,22]. The importance of this technique is that it gives accurate values for the CMC [8,22]. Where CMC values are determined from the break point at each plot, which arises due to each conductivity curve having two straight lines with different slopes pre- and post-micellization process [8,18,21].

Figures 2, 3, and 4 represent the conductivity graphs of BKC at different temperatures in H_2O, KCl, and $MgSO_4$ media, respectively. We can observe a direct relationship between conductivity and surfactant concentration in all systems. The increase in conductivity with increasing surfactant concentration can be explained as a result of the increase in the number of surfactant ions in the solution, and the difference in the rate of increase in conductivity before and after micelle formation can also be explained as a result of the difference in mobility between a single molecule and a micelle.

The micelle ionization degree (α) which as an indicator for the micelle formation was calculated by the following simple relation Equation (1) [22]:

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

where S_1 and S_2 represent the pre-micellar slope and post-micellar slope of the conductivity curve.

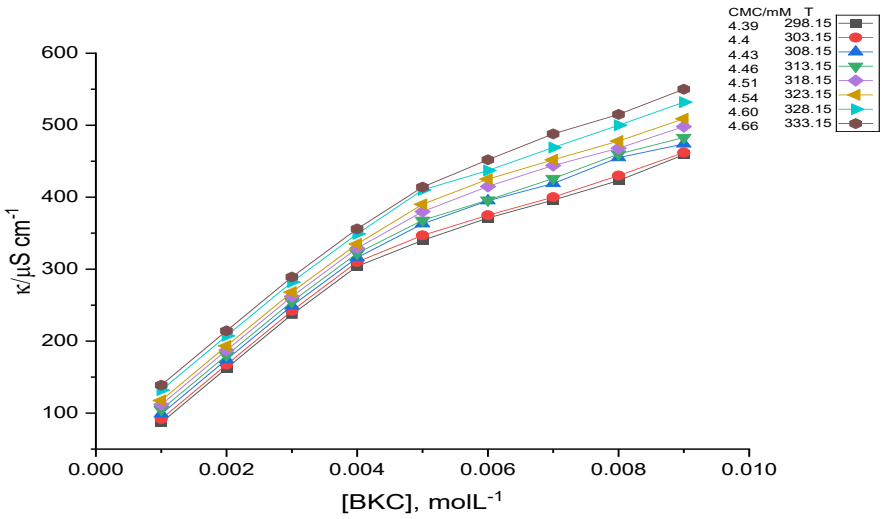

Figure 2. Conductivity versus [BKC] in aqueous solution at temperature range (298.15K -333.15K).

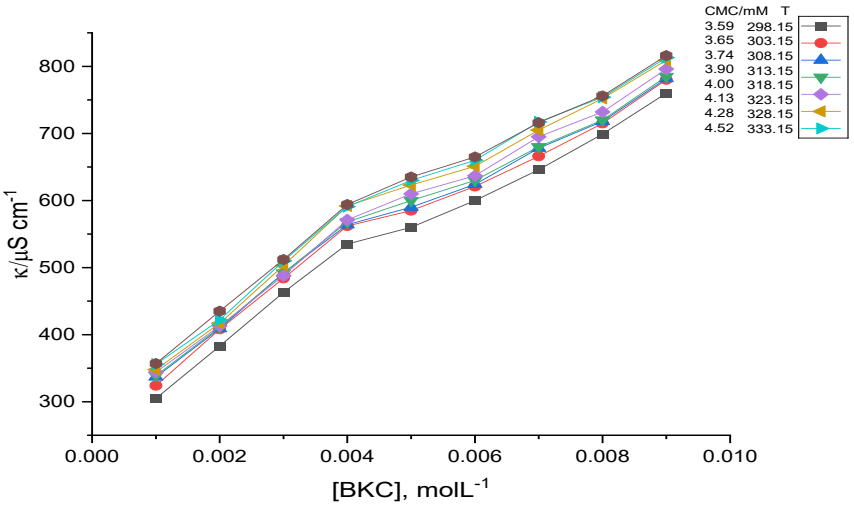

Figure 3. Conductivity versus [BKC] in 0.01M KCl solution at temperature range (298.15K -333.15K).

The values of CMC and α of benzalkonium chloride at different temperatures in aqueous, 0.01MKCl, and 0.01M $MgSO_4$ media are listed in Table 2.

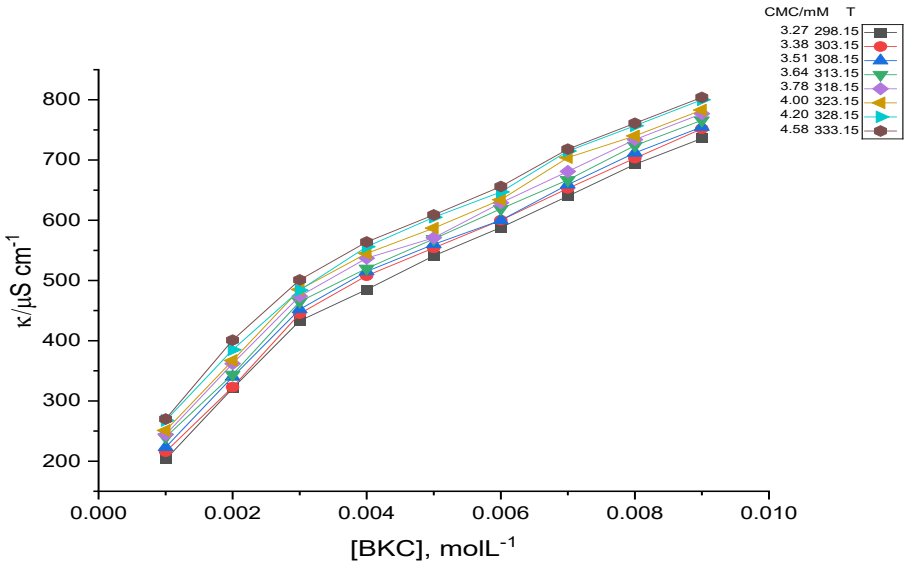

Figure 4. Conductivity versus [BKC] in 0.01M $MgSO_4$ solution at temperature range (298.15K - 333.15K).

Effect of salts

The micellization behavior of BKC is modified in the presence of KCl and $MgSO_4$ electrolytes, which is mainly due to the reducing electrostatic repulsion among the hydrophilic parts of the surfactant by the shielding effect of the ions. At low concentrations of these electrolytes as used in this research, the shielding enhances the micellization process by facilitating the aggregation of cationic surfactant molecules, and this effect leads to a decrease in the CMC value as shown in Table 2 [21,23,24]. While at a high concentration of $MgSO_4$, the micellization process may be inhibited due to hydration shell interactions (Table 2) [21,23,24].

Table 2. Critical micelle concentration (CMC) and micelle ionization degree (α) of BKC in aqueous, 0.01M KCl and 0.01M $MgSO_4$ media at temperature range (298.15- 333.15 K).

T/K	Media					
	H_2O		KCl		$MgSO_4$	
	CMC/mM	α	CMC/mM	α	CMC/mM	α
298.15	4.39	0.388	3.59	0.283	3.27	0.278
303.15	4.40	0.391	3.65	0.288	3.38	0.284
308.15	4.43	0.397	3.74	0.294	3.51	0.291
313.15	4.46	0.398	3.90	0.296	3.64	0.294
318.15	4.50	0.400	4.00	0.299	3.78	0.295
323.15	4.54	0.405	4.13	0.302	4.00	0.300
328.15	4.60	0.423	4.28	0.311	4.20	0.306
333.15	4.66	0.461	4.52	0.324	4.58	0.315

In addition, the CMC and α value of BKC in the presence of $MgSO_4$ are less than their values in the presence of KCl. This is attributed to the divalent cations Mg^{2+} stabilizing the micellar structure more than monovalent cations K^+ and being a monovalent salt, has a weaker effect on reducing the electrostatic repulsion between the surfactant head groups (Table 2) [21.23].

Effect of temperature

The effect of temperature on the critical micelle concentration (CMC) of surfactants in aqueous media is intricate. Initially, the CMC decreases with rising temperature, reaching a minimum point, before increasing as the temperature continues to rise [25]. Higher temperatures reduce hydration of the hydrophilic groups, promoting micellization. Conversely, increased temperatures also disrupt the structured water around hydrophobic groups, hindering micellization [4,25]. The balance between these opposing effects dictates whether the CMC rises or falls within a specific temperature range. As shown in Figure 5 and Table 2, the CMC values rise with increasing temperature in the studied range, which indicates they are formed at higher surfactant concentrations. Similarly, the degree of ionization (α) also increases with temperature, likely due to a reduction in charge density at the micellar surface caused by a lower aggregation number in the micelles [4].

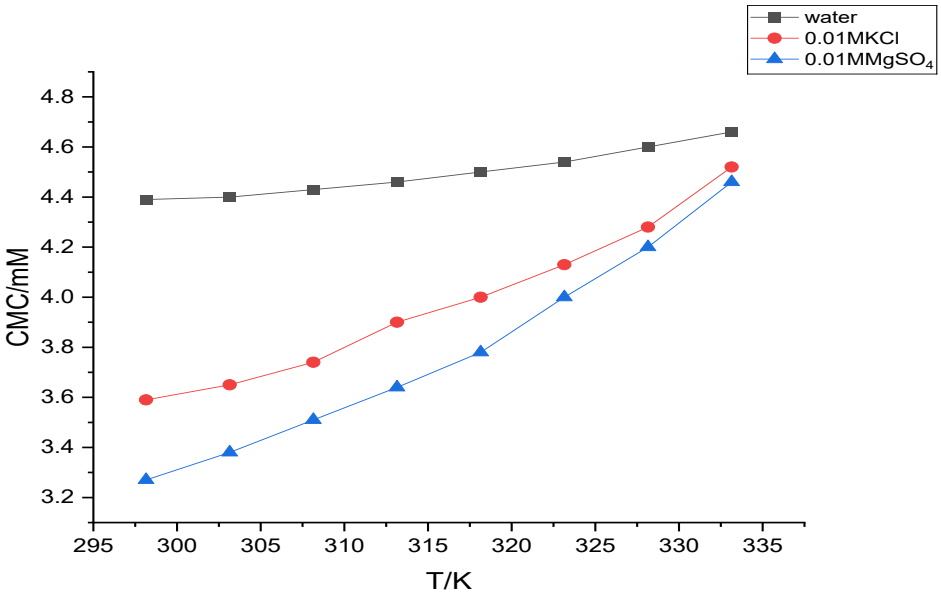

Figure 5. The CMC values of BKC in H2O, KCl and $MgSO_4$ at different temperatures.

3. 5. Surface tension study

One of the most important properties of surfactants is their ability to reduce the surface tension of liquids [22]. The CMC and surface activity of BKC in water, 0.01 M KCl, and

0.01M $MgSO_4$ at 25oC were computed by surface tension measurements. The surface tension (γ), can be calculated by Equation (2) [26]:

$$\gamma_2 = \frac{\gamma_1 m_2}{m_1} \quad (2)$$

where γ_1 and γ_2 are surface tension for reference liquid and surfactant solution, respectively, m_1 and m_2 are mass of one drop of reference liquid and surfactant solution respectively.

Measuring the surface tension is one of the simple and reliable methods for estimating the CMC of surfactant solutions [8,26]. The CMC values of the BKC solution in the absence and presence of KCl and $MgSO_4$ were recorded in Table 1. By plotting surface tension values (γ) versus concentration (Figure 6).

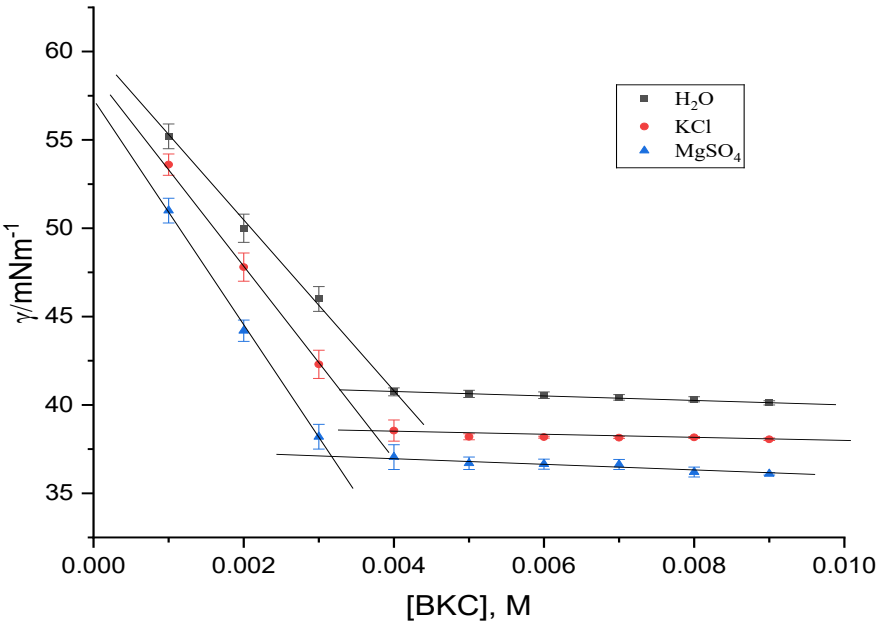

Figure 6. The surface tension (γ) versus concentration of BKC in H_2O, KCl and $MgSO_4$ at 25°C.

When a surfactant is added, as seen in figure 6, the surface tension decreases because the surfactant displaces part of the water molecules [2]. With increasing surfactant concentration, the surface tension of BKC solutions declines linearly up to a certain point, after which it is seen to be almost constant [22]. Table 3 shows the BKC surface pressure value at CMC (π_{CMC}).

The enhanced adsorption of BKC at the air/solution interface in the presence of KCl and $MgSO_4$ indicates a reduction in the critical micelle concentration (CMC) compared to that in pure aqueous solution. This behavior is attributed to the ability of these electrolytes to reduce electrostatic repulsion between the positively charged quaternary ammonium

headgroups of BKC. As a result, closer packing of surfactant molecules at the interface is facilitated, leading to increased surface adsorption and more favorable micellization.

Interfacial parameters of BKC

The surface configuration and interfacial characteristics of surfactant molecules at the air/water contact are reflected in the interfacial parameters [2,22]. The surface tension measurements were used to determine the interfacial parameters of BKC in the absence and presence of KCl or MgSO4 at 25oC and calculated values are listed in Table 3.

Surface pressure at CMC

Equation (3) is used to calculate the surface pressure at CMC (π_{CMC}).

$$\pi_{CMC} = \gamma_o - \gamma_{CMC} \tag{3}$$

where, γ_o is the surface tension of distilled water, and γ_{CMC} is the surface tension at CMC.

Table 3 includes the calculated values of π_{CMC}. The calculations show that the π_{CMC} values increase in the presence of salts because salts reduce the electrostatic repulsion between charged surfactant head groups, allowing them to pack more tightly at the interface. This tighter packing increases surface pressure [27]. As well as the calculations show that the value of π_{CMC} for $MgSO_4$ is higher than for KCl which can be attributed to $MgSO_4$ having a stronger ability to reduce electrostatic repulsion between surfactant head groups.

Maximum surface excess concentration

Gibb's adsorption isotherm equation was used to calculate maximum surface excess ($\Gamma_{\max}$) at air/solution interface by using surface tension measurements. The Gibb's adsorption isotherm equation is represented by Equation (5) [8]:

$$\Gamma_{max} = -\frac{1}{2.303nRT}\left(\frac{d\gamma}{dlogC}\right) \tag{4}$$

where, R is the general gas constant (8.314 $JK^{-1}mol^{-1}$), T absolute temperature (298K), n is equal two in case of ionic surfactant, and C is surfactant concentration [22].

The calculated values of Γ_{max} are listed in Table 3. The obtained result show that Γ_{max} increase in the presence of KCl and $MgSO_4$ salts. The increasing Γ_{max} in presence of salts is due to: Salts reduce the electrostatic repulsion between charged surfactant head groups, allowing them to pack more densely at the interface. This leads to an increase in the number of surfactant molecules adsorbed per unit area, and ions from salts screen the charges on the surfactant molecules, stabilizing their adsorption at the interface and

enhancing surface coverage, as well as the presence of salts can lower the free energy of adsorption, making the process more favorable and increasing the maximum surface excess [28,29]. Furthermore Γ_{max} is higher in the presence of $MgSO_4$ than the presence of KCl because multivalent ions, can interact more strongly with surfactant head groups, promoting tighter packing and higher surface excess [30]. Thus the micelle formation of BKC has been enhanced when adding salts to surfactant solution.

A minimum area per molecule

The values of minimum area per molecule in square angstroms of BKC in the absence and presence of KCl and $MgSO_4$ are listed in Table 3. And calculated by Equation (5) [22]:

$$A_{min} = \frac{10^{20}}{N_A \Gamma_{max}} \quad (5)$$

where, N_A is Avogadro's number.

The presence of KCl and $MgSO_4$ reduces the minimum area per molecule (A_{min}) of BKC at the air/solution interface by screening electrostatic repulsion between the positively charged headgroups. This ionic screening facilitates tighter molecular packing and enhances surface adsorption. Notably, MgSO4exhibits a more pronounced effect due to its divalent Mg^{2+} ions, which interact more strongly with the cationic surfactant headgroups. As shown in Table 3, the A_{min} values decrease in the presence of both electrolytes, with a greater reduction observed for MgSO4 [30].

Table 3. Surface pressure at CMC ($\boldsymbol{\pi_{CMC}}$), maximum surface excess concentration ($\boldsymbol{\Gamma_{max}}$), and minimum area per molecule ($\boldsymbol{A_{min}}$) of BKC in water, KCl, and $MgSO_4$.

Media	π_{CMC}/mNm^{-1}	$10^6\Gamma_{max}$/m^{2}mol^{-1}	A_{min}/Å^2
H_2O	31.00	2.25	73.92
0.01M KCl	33.79	2.69	60.27
0.01M $MgSO_4$	34.90	2.81	58.10

Thermodynamic parameters of cationic surfactants

Determining thermodynamic parameters such as standard Gibb's free energy of micellization (ΔG_m^o), standard Gibb's free energy of adsorption (ΔG_{ads}^o), and free energy of surface at equilibrium (G_{min}) is very important to understand the micellization process of surfactants.

Standard Gibb's free energy of micellization

The standard Gibb's free energy of micellization can be used to identify a surfactant's ability to produce micelles. The standard Gibb's free energy of micellization of BKC in water, KCl, and MgSO4 at 25oC is listed in Table 4 and evaluated by Equation (6) [31]:

$$\Delta G_m^o = (2-\alpha)RTlnX_{CMC} \qquad (6)$$

where, XCMC is the CMC in mole fraction scale.

The values of ΔG_m^o were negative in all media, which indicates that the micellization process is thermodynamically favorable, and its negative value increases in the presence of KCl and $MgSO_4$ salts, which means that the micellization process is more spontaneous in the presence salts especially in the presence of $MgSO_4$ because $MgSO_4$, being a divalent salt, has a stronger effect on reducing the electrostatic repulsion between the surfactant head groups [17,31].

Table 4. Thermodynamic parameters of BKC in water, KCl, and $MgSO_4$ at 25°C.

Media	$\Delta G_m^o\ (kJ/mol)$	$\Delta G_{ads}^o(kJ/mol)$	$G_{min}(kJ/mol)$
H_2O	-37.72	-51.50	18.25
0.01M KCl	-41.03	-53.59	13.87
0.01M $MgSO_4$	-41.55	-53.97	12.98

Standard Gibb's free energy of adsorption

The Gibbs free energy of adsorption is a crucial thermodynamic parameter that provides insights into the adsorption process and is useful for understanding how molecules interact with surfaces, which is essential for applications [32]. The sign and magnitude of the standard Gibbs free energy of adsorption ($\Delta G°_{ads}$) provide critical insight into the adsorption behavior of molecules at the air/solution interface. A negative $\Delta G°_{ads}$ indicates that adsorption is thermodynamically spontaneous, while its magnitude reflects the strength of the interaction between the molecule and the interface. More negative values suggest stronger adsorption, which is indicative of efficient surface activity and a higher tendency for the formation of stable monolayers or micelles. The values of Gibb's free energy of adsorption of BKC in the absence and presence of KCl and $MgSO_4$ were listed in Table 4 and calculated by Equation (7) [17]:

$$\Delta G_{ads}^o = \Delta G_m^o - \frac{\pi_{CMC}}{\Gamma_{max}} \qquad (7)$$

The obtained value of ΔG_{ads}^o is negative in the absence and presence of salts, and its magnitude increases in the presence of salts and is more negative in the presence of $MgSO_4$ because the electrostatic repulsion between the surfactant head groups is more strongly reduced by MgSO4 a divalent salt [17,30].

Free energy of surface at equilibrium

The thermodynamic parameter of surface free energy at the air/water interface plays a central role in evaluating synergistic interactions in mixed monolayer formation at the air–solution interface. Synergism occurs when mixed surfactants pack more efficiently at the interface than individual components, resulting in a lower overall surface free energy. This enhanced molecular packing not only stabilizes the interfacial monolayer but also contributes to the stability of micelles in bulk solution. A decrease in surface free energy reflects stronger intermolecular interactions and improved compatibility between surfactant components, which promotes micellization and influences micelle size, structure, and aggregation behavior. Thus, interfacial synergism and bulk micelle stability are thermodynamically linked through their shared dependence on surface free energy and molecular interactions.[4] The values of $\mathrm{G_{min}}$ of BKC in the absence and presence of KCl and $MgSO_4$ are depicted in Table 4 and evaluated by the following Equation (8) [21]:

$$G_{min} = A_{min}.\gamma_{CMC}.N_A \quad (8)$$

The low values of G_{min} for BKC at 25°C in the absence and presence of salts indicate that thermodynamically stable surfaces are formed [3].

Thermodynamic parameters of micellization

The thermodynamic parameters of micellization, including the standard Gibbs free energy change ($\Delta \mathrm{G_m^o}$), enthalpy change ($\Delta \mathrm{H_m^o}$), and entropy change ($\Delta \mathrm{S_m^o}$), were determined for benzalkonium chloride (BKC) in both the absence and presence of KCl and $MgSO_4$ over the temperature range of 298.15–333.15 K. These parameters were calculated using established thermodynamic equations as described in reference [17] (Equations 9 and 10) and ΔG_m^o determined by Equation (6).

$$\Delta H_m^o = -RT^2(2-\alpha)(dlnX_{CMC}/dT) \quad (9)$$

$$\Delta S_m^o = (\Delta H_m^o - \Delta G_m^o)/T \quad (10)$$

where, R is the general gas constant, T is the absolute temperature, α is the micelle ionization degree, and X_{CMC} is the mole fraction of BKC at CMC.

The value of X_{CMC} is calculated from the ratio of the moles of BKC to the moles of all components in the solution. The value of $(dlnX_{CMC}/dT)$ in Equation (9) was obtained by plotting lnXCMC versus T (Figure 7), and the values of ΔG_m^o, ΔH_m^o, ΔS_m^o, and lnX_{CMC} are displayed in Table 5.

The values of ΔG_m^o indicated the spontaneity of the micellization process in all media and at all temperatures used in this work, and that the spontaneity of micellization increased with the addition of salts, with a relative advantage for $MgSO_4$.

The magnitude of ΔG_m^o generally decreases with an increase in temperature. This is because micelle formation is driven by the hydrophobic effect, which becomes stronger at higher temperatures as water molecules gain more energy to exclude nonpolar surfactant tails. But in this study, we noted that its magnitude increases with temperature, which can be attributed to changes in the surfactant's solubility or other thermodynamic factors like entropy contributions. The precise behavior depends on the specific surfactant and solution conditions [33].

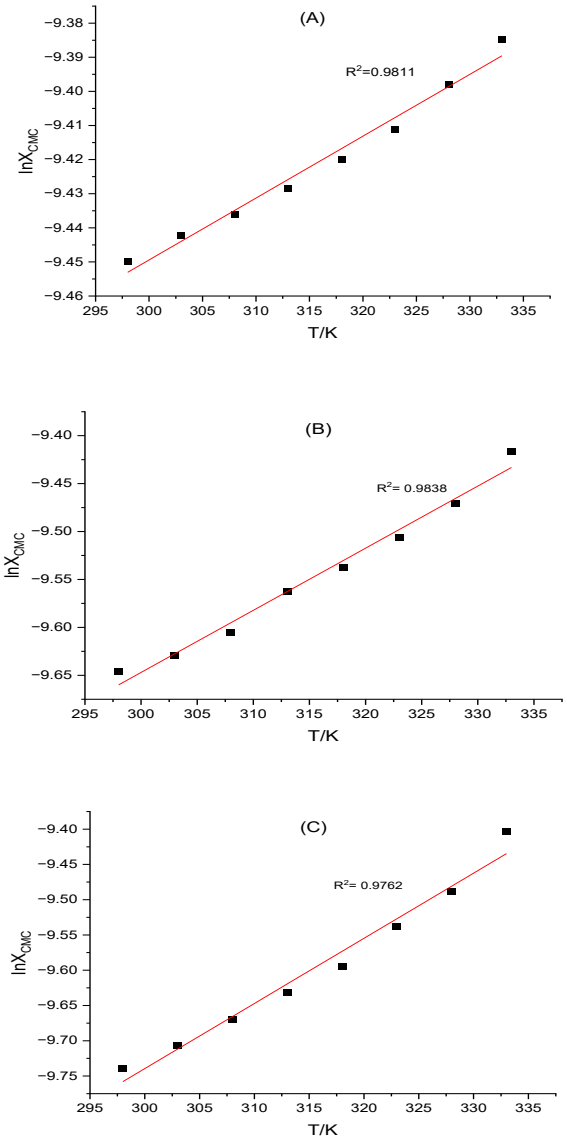

Figure 7. lnX_{CMC} vs. T for BKC in (a) aqueous medium, (b) 0.01MKCl and (C) 0.01M $MgSO_4$

Table 5. Values of lnXCMC and thermodynamic parameters of BKC in aqueous, 0.01MKCl, and 0.01M$MgSO_4$ media in the temperature range (298.15-333.15K)

Media	Temperature	ΔG_m^o (kJ/mol)	ΔH_m^o (kJ/mol)	ΔS_m^o $(J/K.mol)$	lnX_{CMC}
H_2O	298.15	-37.72	-2.15	119.35	-9.45
	303.15	-38.27	-2.22	118.98	-9.44
	308.15	-38.73	-2.29	118.33	-9.44
	313.15	-39.81	-2.36	119.63	-9.43
	318.15	-39.85	-2.43	117.65	-9.42
	323.15	-40.31	-2.50	117.05	-9.41
	328.15	-40.41	-2.55	115.43	-9.40
	333.15	-40.00	-2.57	112.37	-9.38
KCl	298.15	-41.03	-8.15	110.33	-9.65
	303.15	-41.53	-8.47	109.12	-9.63
	308.15	-41.96	-8.72	107.93	-9.60
	313.15	-42.40	-8.99	106.73	-9.56
	318.15	-42.89	-9.27	105.73	-9.54
	323.15	-43.35	-9.54	104.66	-9.51
	328.15	-43.62	-9.79	103.14	-9.47
	333.15	-43.69	-10.01	101.13	-9.42
$MgSO_4$	298.15	-41.55	-11.75	100.01	-9.74
	303.15	-41.96	-12.10	98.54	-9.71
	308.15	-42.31	-12.45	96.93	-9.67
	313.15	-42.75	-12.84	94.15	-9.63
	318.15	-43.25	-13.25	94.35	-9.59
	323.15	-43.54	-13.62	92.62	-9.54
	328.15	-43.83	-14.00	90.94	-9.49
	333.15	-43.86	-14.35	88.61	-9.40

The micellization process of BKC is exothermic in these temperature and solvent environments, as evidenced by the fact that the values of ΔH_m^o for BKC were negative in all used conditions and its magnitude tended to increase with rising temperature [10]. The values of ΔS_m^o for BKC were positive in all cases and tended to decrease with rising temperature. In aqueous salt solutions of KCl and $MgSO_4$, the values of ΔS_m^o for BKC are lower than their value in the absence of salts, confirming that the micelles that are formed are more stable in the aqueous salt solutions. Consequently, entropy plays a significant role over that enthalpy, and the micellization is both enthalpy and entropy driven [10].

Morphology and aggregation number

The morphology and aggregation number of BKC were studied at 25°C. According to Tanford's suggestion, [6] the volume of the hydrophobic group (V_o) and the length of the hydrophobic group (lC) were determined by the following equation:

$$l_c = (1.54 + 1.265\ n)\text{Å} \tag{11}$$

$$V_o = (27.4 + 26.9\ n)\text{Å}^3 \tag{12}$$

From Equations (11 and 12), the values of l_C and V_o were 16.72 Å and 350.2 Å³ at 25°C, respectively. The shape of the micelle is determined by estimating the value of the packing parameter according to Equation (13) [34]:

$$P = \frac{V_o}{l_C A_{min}} \tag{13}$$

The P value is ≤ 0.33 for spherical micelles, 0.33 to 0.50 for cylindrical micelles, and 0.50 to 1.0 for lamellar micelles [25]. The values of P for a salt-free aqueous solution of BKC are found to be 0.283, which confirms a spherical shape. The aggregation number of spherical micelles of pure surfactant is determined by the following equations [12,35]:

$$N_{agg} = \frac{V}{V_o} = \frac{\frac{4}{3}\pi l_C^3}{V_o} \tag{14}$$

or

$$N_{agg} = \frac{4\pi l_C^2}{a_0} \tag{15}$$

where, Nagg is the aggregation number, V is the volume of the micelle, and a_o is the hydrophilic group area.

The hydrophobic group area of a spherical micelle is calculated by Equation (16) [12], and found to be 62.83 Å^2 for BKC at 25°C.

$$a_o = \frac{3V_o}{l_C} \tag{16}$$

The value of N_{agg} for salt free aqueous solution of BKC is found to be ≈ 56 particles.

In addition, the volume of the hydrocarbon core of the pure BKC micelles (V) and the molar mass of micelle (M) are calculated by Equations (17 and 18) [36]:

$$V = N_{agg}(27.4 + 26.9\ n)\ \text{Å}^3 \tag{17}$$

$$N_{agg} = \frac{M}{M_o} \tag{18}$$

where M and M_o are the molar mass of the monomer and micelle, respectively. From calculations, the V value was 19611Å^3 and the M value was 18452 gmol^{-1}.

The packing parameter of BKC in the presence of 0.01M KCl and 0.01M $MgSO_4$ is more than 0.33, and its value is found to be 0.344 and 0.360, respectively, which indicates a deviation of BKC from a spherical to a cylindrical shape in salt solutions.

Conclusion

This study provides a comprehensive analysis of the influence of electrolytes-specifically KCl and $MgSO_4$ on the micellization behavior of benzalkonium chloride (BKC) in aqueous solutions. Utilizing conductivity and surface tension measurements, we systematically characterized key micellar properties, including critical micelle concentration (CMC), thermodynamic parameters, and aggregate morphology. The addition of both monovalent (KCl) and divalent ($MgSO_4$) salts significantly reduced the CMC, with $MgSO_4$ exhibiting a more pronounced effect due to its superior electrostatic screening capacity and stronger ion–dipole interactions a trend consistent with established literature on ionic surfactants.

Temperature-dependent investigations revealed that micellization is governed by a delicate interplay between hydrophobic effects and electrostatic repulsions, with increasing temperature leading to higher CMC values and enhanced micelle ionization findings corroborated by previous studies on structurally similar cationic surfactants such as CTAB.[1,25,37] Thermodynamic analysis confirmed the spontaneous and exothermic nature of the process, as evidenced by negative standard Gibbs free energy values (ΔG^0_m = –37.72, –41.03, and –41.55 kJ/mol for BKC in H2O, 0.01 M KCl, and 0.01 M $MgSO_4$, respectively), aligning well with prior reports on quaternary ammonium surfactants in saline environments [38].

Furthermore, calculated packing parameters (P = 0.283, 0.344, and 0.360) indicate a morphological transition from spherical to cylindrical micelles upon salt addition, underscoring the role of ionic strength and counterion valency in modulating micellar geometry. This observation supports existing models of surfactant self-assembly under varying electrostatic conditions [25,35,39].

Collectively, these findings offer mechanistic insights into how environmental factors—particularly electrolyte composition and temperature—dictate the aggregation behavior and interfacial properties of cationic surfactants. These results hold significant implications for optimizing surfactant performance in pharmaceutical formulations, industrial processes, and environmental remediation technologies. Future work should extend to the investigation of mixed surfactant systems, broader salt types, and variable pH conditions to further elucidate the complex dynamics governing micellar assembly and interfacial activity.

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