Effects of Selected Metal Chlorides on the Micellization Parameters of Cetrimonium Bromide at Different Temperatures

[1]Sumbal Saeed, [1]Arif Hussain, [2]M. Faizan Nazar, [3]Hameed Ullah, [4]Afzal Shah
[4]Syed Sakhawat Shah and [1]Asad Muhammad Khan*
[1]*Department of Chemistry, COMSATS University Islamabad, Abbottabad Campus, 22060 Abbottabad.*
[2]*Division of Science and Technology, Department of Chemistry, University of Education,*
Multan Campus, Multan, Pakistan.
[3]*Department of Chemistry, Islamia College University, Peshawar, Pakistan.*
[4]*Department of Chemistry, Quaid-i-Azam University, Islamabad, 45320, Pakistan.*
amk.qau@gmail.com; amkhan@cuiatd.edu.pk

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Summary: The pre-modification of surfactant counterions using transition metal salts provides a means to activate the interface using corresponding properties of metal ions. In this work, a cationic surfactant cetyltrimethylammonium bromide (CTAB) was modified by pre-mixing metal chlorides ($FeCl_3$, $CuCl_2$ and $ZnCl_2$) and CTAB in 1:1 molar ratio using methanol as solvent. As a result, $FeCl_3$, $CuCl_2$ and $ZnCl_2$ were added as $[FeCl_3Br]^{-1}$, $[CuCl_2Br]^{-1}$ and $[ZnCl_2Br]^{-1}$ respectively acting as counter anions (CAs) instead of bromide anion. Hence CTAB was called CTAF, CTAC and CTAZ in order of added CAs i.e., $[FeCl_3Br]^{-1}$, $[CuCl_2Br]^{-1}$ and $[ZnCl_2Br]^{-1}$ respectively. The effect of these metal chlorides on the micellar behaviour of CTAB was investigated using conductivities of their different solutions. Furthermore, the critical micelle concentration (CMC) as well as the degree of counterion binding (β) were considered at 25.0, 30.0, 35.0, 40.0 and 45.0 °C ±0.1 °C. The analysis of results revealed that incorporation of metal cations reduces the CMC values in the order CTAF< CTAZ~CTAC<CTAB. Change in entropy (ΔS), enthalpy (ΔH) and free energy (ΔG) were calculated to understand the thermodynamics of micellization under the circumstances. The aim of this study is to improve the understanding regarding the presence of transition metals in micellization process as well as the possibility of their interactions with Bromide counterions and possibility of the formation of complex counter-anions.

Keywords: Surfactant; Micelles; Counterions; Binding; Thermodynamics; Conductivity.

Introduction

Surfactants are amphiphilic chemicals having plenty of industrial and household applications. The study of surfactant interaction with organic molecules such as dyes[1, 2] and drugs[3-6] remained area of interest for many decades and still occupies central place in colloidal research. Typically, ionic surfactants, an important group of surfactants, are composed of a hydrophilic part known as head and a hydrophobic part as tail. They have strong ability to adsorb at interfaces and surfaces [7-9].

An important parameter of surfactant in solution is its critical micelle concentration (CMC). A smaller value of CMC indicates lower concentration of surfactant required for micelle formation. Micelles can solubilize several hydrophobic species like drugs [10-12], dyes, and different biomolecules[9]. Micelles generally have an anisotropic water distribution inside their structures. The concentration of water tends to decrease from surface to core of the micelle, with a completely hydrophobic core. As a result, the particular position of a molecule within the micelle will depend on its polarity *i.e.,* nonpolar molecules will tend to solubilize in the core of micelle and those, which have intermediate polarity will move toward the surfactant molecules in definite intermediate positions [13]. Hence the extent of solubilization depends on degree of hydrophobicity and electrostatic interaction between surfactant and different kinds of additives.

Solubilization is actually an important property of micelle, which means “enhancement in the solubility of sparingly soluble molecules” [14]. In that context, it can be defined as “dissolution of a substance spontaneously by reversible interaction with micelle to form isotropic solution having reasonable stability with minimum thermodynamic activity”. Generally, if sparingly soluble substance is plotted against surfactant concentration, then value of solubility is very low before CMC appears. However, after the CMC, solubility rises linearly with surfactant concentration, which indicates that solubilization is directly dependent on micellization [13].

Although, the surfactants, which are currently being used are quite efficient i.e., they have

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[*] To whom all correspondence should be addressed.

low toxicity and exhibit excellent solubilizations but there is still a room for improving micellar solubilization at higher dilution factors [15]. Hence, there is a need to find ways to overcome this shortcoming by playing with surfactant chemistry at molecular level. In this connection, modification of counterion environment in surfactant solution can play an important role [16]. Furthermore, it is well established that counterions are responsible for two different functions in a surfactant system i.e., they adsorb on the micelle surface after micelle formation and secondly, they contribute to the conductivity of the surfactant solution. Since they adsorb at the micelle surface, therefore it is observed that in ionic surfactants, the increase in conductivity after micellization is not that much prominent after the formation of micelles take place.

Among the various newly designed amphiphiles with improved and customized properties, metal-surfactant complexes are exciting due to combination of inherent interfacial action of surfactants *i.e.,* surface activity [3, 17] and self-assembly etc., with properties shown by metal ions such as optical shown by “Ho(III)” or magnetic responses shown by Fe(III), Ho(III) and Gd(III) etc and redox properties [18-20]. Therefore, introducing transition metals in to counterions can be responsible for surfactant systems, which have differentiating as well as controlled properties, when compared to conventional surfactants [3, 16, 20, 21]. The presence of transition metal ions can result in new applications of surfactant based solutions [22] e.g., the metal ions could be present on the polar head [23], on tail and or as the counter ion [24] of surfactants. However, in the case of counterions modifications, the alkyl chain and surfactant head group remain intact and therefore there are no hardcore changes in the surfactant structure itself, which make it an easy process. In other words, the nature of surfactant remains same but counterions are manipulated in such a way to induce a tailored response depending upon the kind of modifications carried out in counterions.

Here, in this study we explored the modified forms of CTAB i.e., containing metal ions as part of counter ion. The use of metal halides offers this unique opportunity due to the already present halogen counter-anion in CTAB i.e., bromide ion and hence ensures formation of complex metal-based counter anions. Therefore, it can be expected that modifying counter ions, different properties like stability [25] aggregation behaviour [26] and critical micelle concentration of surfactant [27] can be altered. Moreover, the presence of metal ions as part of counter ion may provide many additional features e.g., applications in anticancer treatment by hindering replication of DNA [28], catalysis [20, 29], drug delivery [30], magnetic resonance imaging [31], interaction with different proteins and nanoparticles etc [18].

With the development of several proven possibilities of using counterions modifications as a path for the synthesis of materials with tailored responses [19, 32-34], it is now envisaged that deeper understanding of complex counterions, their stabilities and dissociations in surfactant-based systems can be handy in designing new materials. Furthermore, it is a well-known fact that changing individual counterions affect aggregation behaviours of corresponding ionic surfactants. This effect can be explained in terms of so called kosmotropes (higher charge density) and chaotropes (relatively lower charge density), which plays a prominent role in structuring of water molecules around ions and thus effect hydration or dehydration mechanism. In this study, modifications in counterions are studied where a relatively small size counter anion, a bromide ion is modified by including a metal chloride thus making it larger counter-anion and with obviously different charge size. It must be kept in mind that when compared with Chloride (structure maker) and Iodide (structure breaker), Br^- doesn’t show much structuring effect on water [35].

Although, both types of ionic surfactants i.e., cationic and anionic with different metal ions can be synthesized, but we choose cationic CTAB due to ease of modification and non-invasive manipulation of physiochemical properties [36]. Furthermore, by changing the counter ion from alkali/alkaline metals to transition metals, certain changes in the interfacial properties such as aggregation [26], micellization [37] and counter ion binding *etc.*, can be achieved. Moreover, the number of studies where CTAB is used for such manipulations are appreciably larger and therefore it is relatively easier to relate different properties. As already discussed, the use of transition metals as part of counterions is not uncommon [19, 32-34, 38-42]. However, there is still a need to completely understand their existence in surfactant solutions in pre and post micellar concentration ranges [43]. It can be easily hypothesized that counterion binding will be much different in case of complex metal based modified counterions and their stabilities can be tricky in micellar and premicellar solutions.

Experimental

Cetyltrimethylammonium bromide (CTAB,98%), metallic salts including zinc chloride ($ZnCl_2$,98%), ferric chloride ($FeCl_3$,97 %), cupric chloride ($CuCl_2$,97%) and methanol of analytical grade were used without any further purification. All the chemicals used were of analytical grade and were purchased from Dae-Jung Korea Chemicals and Metals. Doubly distilled and deionized water was used for all experiments. The conductivity of water used was ≤1 μS/cm. The solutions of CTAB and its modified forms were used in the concentration range from pre-micellar to post-micellar range. All the observations were made at room temperature if not mentioned otherwise.

Surfactant Modification

CTAB with modified counterions were obtained by mixing surfactant CTAB and metal chlorides $FeCl_3$, $ZnCl_2$ and $CuCl_2$ in equimolar quantities (1:1) in presence of methanol as solvent by following well established methods [20]. The mixture was stirred overnight at room temperature. The solvent was removed using rotary evaporator followed by drying at 105ºC. This resulted in brown, white and black solid for complexes of CTAB with $FeCl_3$, $ZnCl_2$ and $CuCl_2$ respectively [44] and were designated CATF, CTAZ and CTAC in the same order.

Conductometric studies

The conductometric study was performed by preparing a post micellar solution of surfactants using dilution method for finding out the CMCs of CTAB and its modified forms by using WTW conductometer model Cond7110 with serial no. 16010879. The conductivity cell used was TetraCon 325 with a cell constant of 0.475 cm^{-1} and conductivity measuring range of 1μS/cm to 2 S/cm and resolution of 1μS/cm with a measuring accuracy of ≤0.5%±0.1 of the measured value. The internal temperature was also noted with the help of same probe with an accuracy of ≤0.1°C ±0.1.

All the conductivity measurements were performed in doubly distilled deionized water with conductivity of ≤1μS/cm. The temperature of solutions was maintained using temperature regulated water bath from Daihan Scientific Model WB22 and with ambient temperature range of +5°C to 100°C, ±0.1°C.

The CMC was later calculated by applying linear regression to the data obtained from conductivities of various solutions. The intersection of two straight lines from pre- and post-micellar region was used to calculate CMC.

Results and Discussion

Conductometry is rapid, simple, inexpensive, and currently applied method in literature. The additional benefits of accurate control of temperature of the measuring vessel with minimum effort is unparalleled and most reliable when compared to any other technique, especially when it comes to ionic surfactants. Due to these reasons, conductivity was chosen as a method of choice for carrying out these experiments.

The conductivity measurements were performed for cationic surfactant CTAB at 25.0, 30.0, 35.0, 40.0 and 45.0 °C ±0.1 °C and at all temperatures increase in CTAB concentration resulted in increased conductivity for both pre- and post-micelle regions with slope being greater for pre-micelle than for post micelle region and is shown in Fig 1.

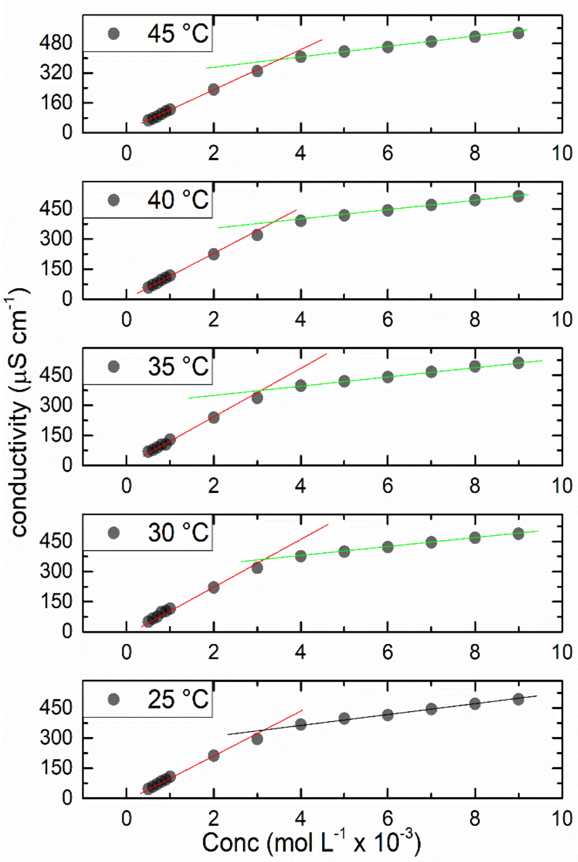

Fig. 1: Effect of temperature on the CMC of CTAB using conductometry. Measuring accuracy is ≤0.5%±0.1 of last digit.

The results for changes in CTAF conductivities with variation in concentrations at different temperatures are shown in Fig 2.

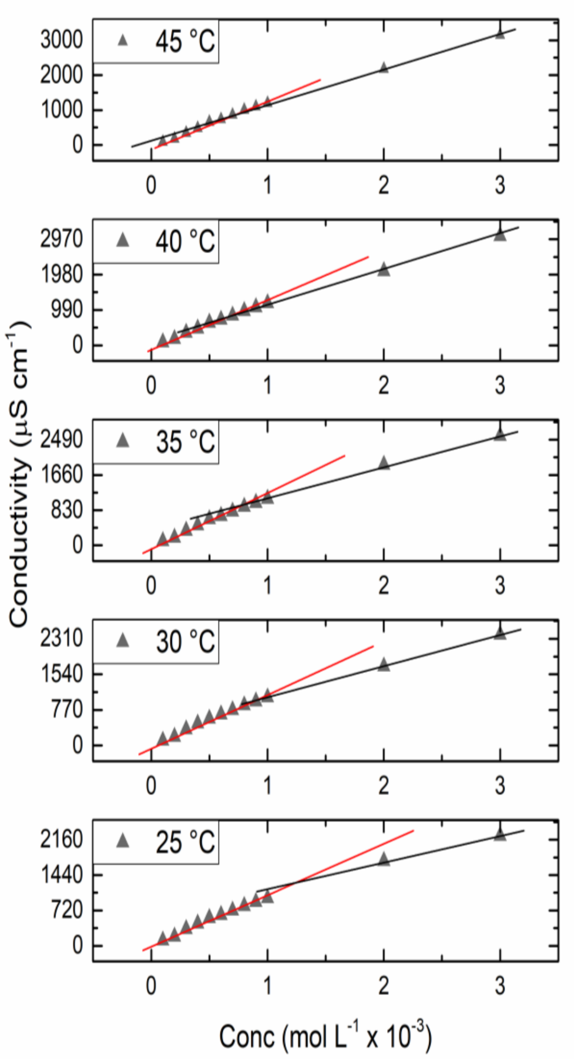

Fig. 2: Changes in the conductivity of CTAF at various temperatures. Measuring accuracy is ≤0.5%±0.1 of last digit.

The higher conductivity values for CTAF with variation in concentration at different temperatures, can be attributed to the dissociation of CTAF surfactant (Fig 2). The increase in the conductivity is uniform when compared to CTAB in Fig 1 and therefore, the break point in the conductivity profile is not as prominent as is in the case of CTAB.

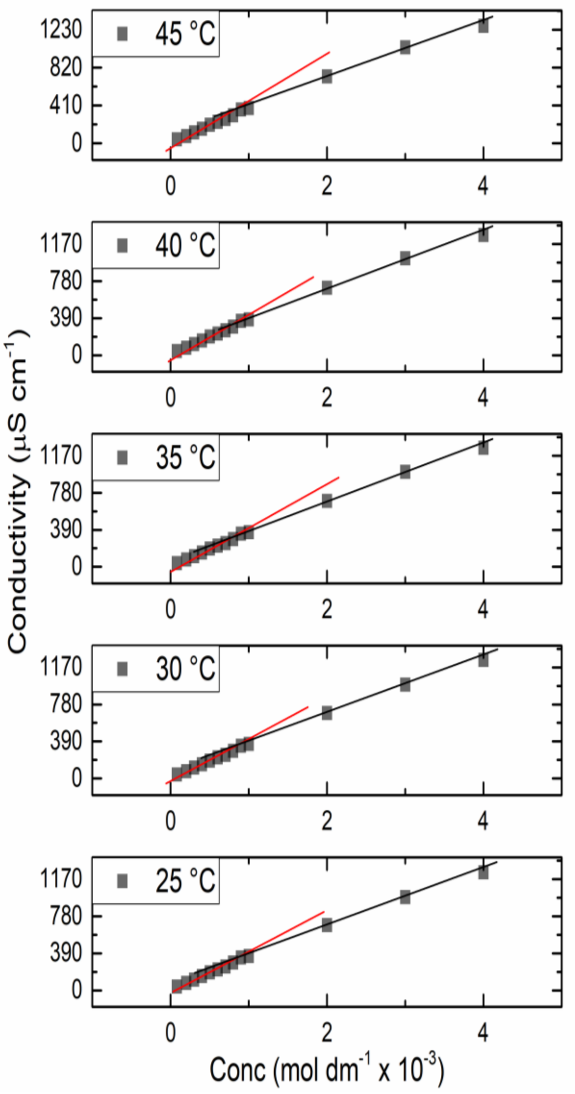

Fig. 3: The dependence of different concentrations of CTAC conductivities on temperature. Measuring accuracy is ≤0.5%±0.1 of last digit.

In case of CTAC, as shown in Fig 3, the increase in conductivities was not as high as was observed for CTAF. For temperatures ranging from 25 °C up to 40 °C, the conductivities levelled at similar value but at 45 °C, the conductivity was higher than other temperatures observed. However, the conductivity was higher when compared to CTAB. The break in conductivity was not very prominent as was the case for CTAF.

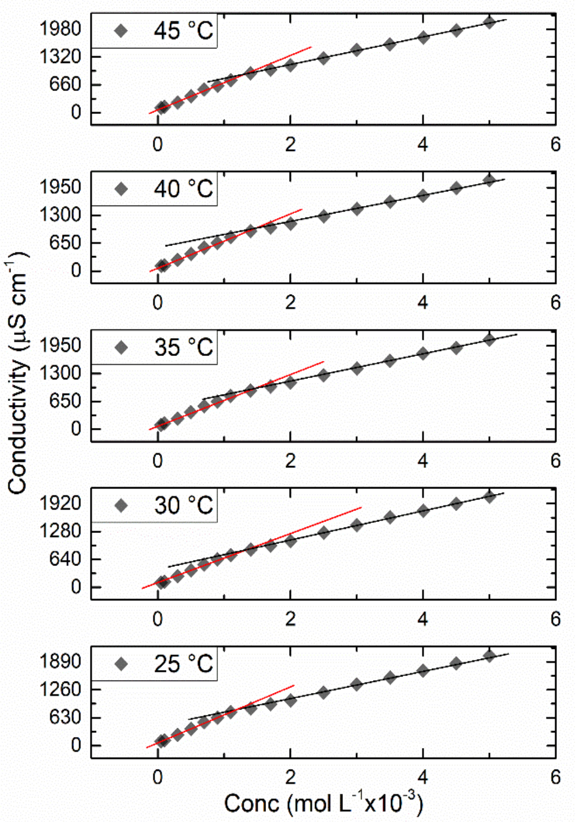

Fig. 4: Changes in conductivities of CTAZ concentrations at different temperatures. Measuring accuracy is ≤0.5%±0.1 of last digit.

In Fig 2, 3 and 4, larger slopes in premicellar regions can be attributed to the availability of large number of free surfactant monomers with positively charged head groups and complex counter-anions (CAs), when compared to post-micellar concentrations. Furthermore, “surfactants with modified counter ions” (SMCs) shown significantly higher conductivities as shown in Figs 2-4, when compared to CTAB (Fig 1). The order in which different surfactant solutions shown conductivities were noted are as CTAF> CTAZ>CTAC>CTAB. The difference in conductivities can be attributed to the presence of complex anions and their possible dissociation in their diluted form. Dilute solutions of transition metal chlorides are highly dissociated, and there are numerous papers reporting the kinetics of inner and outer sphere complex formation with chlorides. The reported conductivity of CTAB is around 200 $\mu S\cdot cm^{-1}$ at 2×10^{-3} $mol\cdot L^{-1}$ (below the CMC) and rises to around 500 $\mu S\cdot cm^{-1}$ at 10×10^{-3} $mol\cdot L^{-1}$ (Fig 1). However, at 2×10^{-3} $mol\cdot L^{-1}$ the conductivities for the other solutions are ca~ 2000 $\mu S\cdot cm^{-1}$ for CTAF (Fig 2), 500 $\mu S\cdot cm^{-1}$ for CTAC (Fig 3) and 1000 $\mu S\cdot cm^{-1}$ for CTAZ (Fig 4). Since the mobilities of the complex $(MX_4)^-$ anions can’t possibly be substantially larger than that of bromide (Br^-). These large conductivities have to reflect the dissociation of the anions in water.

Support for this comes from the orders of the conductivities and CMC values. Thus, higher conductivity reflects greater number of ions present in the solution (greater dissociation) and lower CMC through the normal mechanism of surface charge neutralization. The conductivities decrease in the order: CTAF > CTAZ > CTAC and the CMC values increase in the same order: CTAF < CTAZ < CTAC.

Nonetheless, in post-micellar concentration range, some counter-anion may adsorb on the positively charged micellar surface. As is known, among the halides, bromide ion (Br^-) show lower counterion binding when compared to fluoride (F^-) and chloride (Cl^-) counteranion (CAs) and therefore higher CMC for the same alkyl chain and quaternary ammonium head group. The decrease in CMC of SMCs can be attributed to similar effect. The CAs in this study are based on metal chlorides. The presence of Cl^- in addition to Br^-may change over all degree of counterion binding as is shown in Table 1 and therefore go in favour of lower CMC values.

It is well-known fact that surfactants behave differently in pre-micellar and post-micellar concentration ranges. In pre-micellar concentration ranges, the monomers are free to move and are still in process of forming monolayers on the air/water interface. Meanwhile, the CAs are not bound to monomers and may dissociate upon dilution and provide extra charge mobilities in solutions.

Furthermore, in post-micellar concentrations, when micelles are formed, the free movement of surfactant monomers could decrease. During the formation of self-assembled structures called micelles, the monomers come together and provide an extra charged surface for adsorption to a portion of CAs in their un-dissociated form. This could be attribute to relatively lower increase in conductivities after CMCs of corresponding surfactants. However, when more surfactant is added, it increases conductivity but the change in conductivity is not as prominent as it was observed in pre-micellar concentrations. The intersection of two linear lines gives the CMC of CTAB solutions as shown in Fig. 1[45]. It was also observed that in case of SMCs, the breakpoint in conductivities was not as sharp as was shown by CTAB. The effect of temperature was evidently less pronounced in cases of CTAC and CTAZ. However, CTAF conductivities were clearly affected by temperature as shown in Fig. 2.

The observed value of CMC for CTAB was 3.4 $\times10^{-3}$ mol·L^{-1} (as shown in Fig. 1), while for CTAZ (Fig. 4), CTAF (Fig. 2) and CTAC (Fig. 3), it came out to be 0.8, 0.85 and 1.12 mol·L^{-1} respectively. Hence it can be inferred that modifying conventional surfactant with different metal chlorides can be a way to lower CMC value of cationic surfactants. The details of calculations are shown in Table 1 for CTAB, CTAZ, CTAC and CTAF.

The metal chlorides, when become part of counter ion of surfactants, reduce repulsions between ionic head groups acting as a screen [46]. Moreover, these co-ions enhance participation in competitive interaction of positively charged head group toward negatively charged chloride ions, which can cause more crowding at interfacial region and thus lead to early micelle formation [38]. The extent of this decrease in the CMC values depends on atomic radius of metal ions used to modify counterions. The reason for this change can be explained. It is well-known fact that when we move from Sc to Zn in periodic table, the atomic radius decreases along with the increased nuclear charge, which results in the increased polarity of metal ions leading to more interaction. The values of atomic radii are 1.42, 1.45 and 1.56 Å for zinc, copper and iron respectively, where $ZnCl_2$ has shown most pronounced effect over the CMC of CTAB resulting in 0.8 mM value [47].

However, this trend is not completely followed, and iron came second instead of copper. The behaviour shown by Iron based counter-anion is due to the reason that iron was employed in +3 oxidation state leading to more interaction with bromine group of surfactants and hence micellization process was initiated earlier than expected.

Effect of Temperature

To determine the CMC of SMCs at different temperatures, dependencies of their conductivities on changes in their concentrations were experimentally done using a thermostatic bath. Each experiment was independently carried out and the relevant uncertainties in CMC values are given in caption Fig. 5.

The conductivity values of three different surfactant CTAF, CTAZ and CTAC versus temperature as obtained in Fig. 1- Fig. 4 shows that when we increase temperature from 25°C (298 K) the values of CMC corresponding to each surfactant initially lowers till 40°C (313 K) and later it begins to rise again for all the surfactant system as is given in Table 1 and the trend can be explicitly observed in Fig. 5. This is because variation in CMC with change in temperature is due to presence of two opposing processes i.e., dehydration of hydrophilic and hydrophobic portions [48]. The dehydration of hydrophilic parts resists the micellization and leads to higher CMC value due to repulsions between ionic head groups of surfactant monomers. On the contrary, hydrophobic dehydration favours process of micellization and decreases CMC [49].

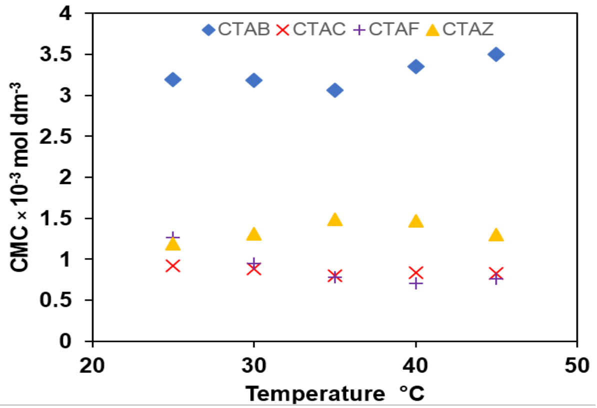

Fig. 5: CMC verses temperature for CTAB, CTAC, CTAZ, and CTAF. For individual measurement, the measuring accuracy was ≤0.5%±0.1 for last digit.

Therefore, changes in CMC values depends on relative magnitude of all factors discussed and not on a single factor. Hence, in this study hydrophobic dehydration effect prevails initially but after certain temperature, hydrophilic dehydration effect becomes dominant [50]. In general, the trend is different for CTAB, where a dip in CMC is visible at 35°C (308 K). There is also a striking similarity in CMC values trend for CTAF and CTAZ. The CMC values exhibited by CTAZ are visibly different although it lies next to Cu in periodic table.

The conductivity values at various temperatures and the CMC values determined at different temperatures help to calculate various parameters. One such parameter is β, which shows "the degree of counterion binding", which was obtained by taking ratios of the slopes of pre and post micellar concentrations of conductivities versus concentrations graph [51] as given in Fig 1-4.

$$\beta=1-(S_2/S_1) \qquad 1$$

where S_2 and S_1 are slopes of micellar and pre-micellar concentration range [35, 52]. The values of slope can be obtained from the equations shown for plots in Fig 1-4 of this paper.

Table-1: Variation of micellization parameters (CMC, degree of counter ion binding) of CTAB. Table also summarizes the slopes calculated from plots given in the Figs 1-4.

Surfactant	S2	S1	α=S2/S1	β=1-α	CMC±0.001 ×10^{-3} mol L^{-1}	Temp °C ± 0.1 °C
CTAB	24.18	98.92	0.24	0.76	3.191	25
	21.61	101.28	0.21	0.79	3.187	30
	24.39	100.11	0.24	0.76	3.062	35
	28.64	100.39	0.29	0.71	3.353	40
	30.46	102.46	0.30	0.70	3.497	45
CTAZ	329.14	647.65	0.51	0.49	1.187	25
	340.70	621.85	0.55	0.45	1.316	30
	328.61	651.96	0.50	0.50	1.491	35
	331.34	648.02	0.51	0.49	1.470	40
	335.06	637.92	0.53	0.47	1.300	45
CTAC	294.00	363.25	0.81	0.19	0.918	25
	297.10	368.10	0.81	0.19	0.887	30
	295.50	362.46	0.82	0.18	0.799	35
	297.50	378.21	0.79	0.21	0.838	40
	298.90	381.92	0.78	0.22	0.827	45
CTAF	650.96	1060.40	0.61	0.39	1.261	25
	716.91	1174.20	0.61	0.39	0.949	30
	760.34	1226.00	0.62	0.38	0.785	35
	951.87	1300.90	0.73	0.27	0.705	40
	974.78	1327.90	0.73	0.27	0.759	45

In Table 1, S2 is slope of the conductivity values from post-micellar concentrations and S1 is the slop of the values from premicellar concentration at the corresponding temperature.

β is degree of counterion binding; The R^2 value for all linear regressions used is 0.99 or more in both premicellar and post micellar concentrations.

These values are found to increase first, which means increase in electrostatic interaction ensuring large aggregation number thus reducing CMC. However further increase in the temperature leads to lower counter ion binding and hence low values of □ and increased CMC. Comparing the values of □ given in Table 1, it was found that □ is higher for CTAZ, and CTAC, but was less in the case for CTAF as compared to conventional CTAB. This is because of metal base complex counter ions lead to more charge density at the surface of micelle and increased stability of micellar charge by reducing repulsions. Among the three surfactants used, CTAZ has higher values of counter ion binding depending on the nuclear charge, which is highest for zinc among the transition elements.

On the other hand, the standard Free Energy of micellization (ΔG°_{m}) was calculated by using relation in Eq. 2 [53].

$$\Delta G^{\circ}_{m} = (2-\beta)\,RT\ \text{In}\ Xcmc \tag{2}$$

where T is the temperature in Kelvin, R is gas constant and its value is 8.31451 J·K^{-1}·mol^{-1}, β is degree of counter ion binding and in In X_{CMC}, CMC taken in mole fractions**.** This value gives us idea about micelle formation. Value of ΔG°_{m} is negative for all temperatures as shown in Table 2 and remains practically constant, which signifies that micellization is thermodynamically a spontaneous process. This is because of negative free energy change when single alkyl chain is transformed from monomer to micellar state. ΔG°_{m} values for ionic and amphoteric surfactants are found between -23 and -42 kJ/mol [54].The free energy values for all these metal based surfactants falls within this range, which means they show classical surfactant behaviour.

Similarly, the standard free enthalpy was calculated by using Eq. 3.

$$\Delta H^{\circ}_{m} = \frac{RT^{2}\,(2\text{-}\beta)\ \text{dlnXcmc}}{dT} \tag{3}$$

These values are negative as given in Table 2, and found to increase with increase in temperature throughout signifying the exothermic nature of process because there is release of water molecules due to relocation of hydrocarbon chain from the monomer to micelle form [53].

The standard entropy was calculated using Eq. 4.

$$\Delta S^{\circ}_{m} = \frac{\Delta H^{\circ} - \Delta G^{\circ}}{T} \tag{4}$$

In case of entropy, as temperature was increased, the ΔS°_{m} remained practically constant as shown in Table 2. It means that micelle formation is entropy controlled at low temperature [22].

Table-2: Variation of micellization parameters (Enthalpy, Gibbs free energy and Entropy) of CTAB.

Temp °C	ΔH°_{m} (kJ·mol^{-1})±0.01				ΔG°_{m} (kJ·mol^{-1}) ±0.01				ΔS°_{m} (kJ·mol^{-1} K^{-1}) ±0.01			
	CTAB	CTAZ	CTAF	CTAC	CTAB	CTAZ	CTAF	CTAC	CTAB	CTAZ	CTAF	CTAC
25	-2.20	-7.00	-4.30	-3.16	-42.09	-41.52	-38.07	-31.89	0.13	0.12	0.11	0.10
30	-2.14	-6.96	-4.49_{8}	-3.25	-43.57	-40.30	-51.72	-32.29	0.13	0.11	0.15	0.10
35	-2.35	-6.94	-4.57	-3.38	-43.68	-39.14	-39.75	-33.02	0.13	0.10	0.11	0.10
40	-2.37	-7.12	-4.72	-3.55	-43.04	-39.41	-37.15	-33.99	0.13	0.10	0.10	0.10
45	-2.43	-7.30	-4.47	-3.68	-43.42	-39.66	-37.28	-34.6	0.13	0.10	0.10	0.10

ΔH°_{m} were more negative for CTAZ when compared to CTAF, CTAC or CTAB. However, when compared to CTAB, the ΔH°_{m} values of all three modified CTABs were more negative. It was interesting to note that the most negative value for enthalpy was found for CTAZ at 45°C with no apparent reason. It was also observed that ΔH°_{m} decreased initially for CTAB and CTAZ followed by increase in its values. However, in case of CTAF, the trend was different and ΔH°_{m} consistently increased up to 40 °C and then dropped. In case of CTAC ΔH°_{m} increased with temperature for all values.

The reason could be stronger electrostatic interactions and weakening hydrophobic forces with increasing temperatures. Furthermore, the nature of counterions were different due to incorporation of transition metal cations of different metals, which may result in a difference in hydration and dehydration of micellar surface as well as different structuring of water molecules in surroundings.

ΔH°_{m} is the result of changes in enthalpies, which results from electrostatic interactions, hydrophobic interactions, hydration of polar moiety and degree of counter ion binding to micelles. A negative value of ΔH°_{m} was caused by hydration of the water molecules around hydrophilic heads groups dominancy over destruction of structure of water around hydrophobic portions of monomers [50].

The transfer of hydrophobic chains from aqueous regions to micellar systems leads to positive value of entropy [55]. Those water molecules lying in vicinity of hydrophobic chains have strong hydrogen bonding between them causing tightening of water structure, which may lead to restrictions on internal torsional vibration of chains. This naturally leads to decrease in entropy of system. So, the removal of the hydrophobic chains from aqueous regimes is entropically favourable [56]

Conclusion

Conductivity studies were successfully performed to investigate the effect of counterions on the CMC values of surfactants and it was observed that values have been reduced to 0.85 mM for CTAF, 0.80 mM for CTAZ and 1.12 mM for CTAC respectively as compared to CTAB, which exhibited a CMC value of 3.4 mM. The decrease in values follow the order CTAZ< CTAF< CTAC. This is because in hydrated form of metal base surfactant, counter ion of chlorine becomes closer to the metal co-ion because of its +2 charge. Hydration of metal ion also causes a change in colour. This in turn increased the size of layer having counter ion leading to reduction in repulsion between the cationic head groups and thus CMC is reduced [57]. Moreover, the effect of temperature on CMC profile shows that there is decrease in the value of CMC with increase in temperature up to 40°C (313 K) but as we further increased the temperature up to 45°C (318 K), the CMC begin to rise again depending upon the difference in hydration ability of co-ions. This effect of temperature is same on both modified and non-modified forms of surfactant [58]. Furthermore, it can be concluded that transition metal ions could be effective to tune surface aggregation properties of surfactants in solutions. However, more insight is needed to fully understand controlling factors manifested by modified counterions [59].

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