Effect of Isopropanol Mixed Solvent on Interaction of Cetyltrimethylammonium Bromide with Bromocresol Green: A Conductometric Study

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In present work, the interaction of an anionic dye, bromocresol green (BCG) with a cationic surfactant, cetyltrimethylammonium bromide (CTAB), was studied using conductometric method. The effect of alteration of solvent media from water to cosolvent isopropanol and the effect of elevation in experimental temperature on the association behaviour of BCG-CTAB system were studied. The observed CMC and ΔG_m° values indicate disfavored micellization of CTAB system in isopropanol. Whereas micellization of CTAB is favoured in the presence of BCG as additive. For BCG-CTAB system micellization becomes more feasible in presence of isopropanol. The observed value of ΔH_m° and ΔS_m° predicts micellization of CTAB is endothermic and entropy driven in aqueous solution, whereas, in the presence of BCG it becomes exothermic and enthalpy driven. The micellization process of BCG-CTAB system is exothermic and enthalpy driven in isopropanol. The calculated thermodynamic parameters of transfer for the BCG-CTAB system from water to water-isopropanol media at various temperatures ($\Delta G_{m,tr}^\circ$, $\Delta H_{m,tr}^\circ$, $\Delta S_{m,tr}^\circ$) also supports the entropy-enthalpy mutual act in the micellization process of BCG-CTAB system. Present study also reveals that a compensation phenomenon is operative between the enthalpy and entropy of micellization in case of association process involving the CTAB and the BCG-CTAB systems. The hydrophobic stabilization results to increase in spontaneity of micellization of BCG-CTAB system in water while there is a decrease in hydrophobic stabilization in the presence of isopropanol and a decrease in spontaneity of micellization.

Keywords: Cationic surfactant, Bromocresol green dye, Micelles, Cetyltrimethylammonium bromide, Thermodynamic parameters.

INTRODUCTION

Surfactants, being an amphiphile, when dissolved in aqueous medium at a particular concentration, are known to from clustered molecules called the micelle. The concentration of surfactant molecules at which the micelle formation begins known as the critical micelle concentration (CMC). The structure of the micelle in aqueous medium is such that the non-polar hydrocarbon chains of the surfactant molecules are oriented away from the aqueous phase and the polar head groups remains dissolved in aqueous medium. Due to this micro-heterogenous construction, surfactant micelles can offer non-polar spherical nanocavities within its structure and hydrophobic and water insoluble/sparingly soluble dye molecules can be incorporated in it [1,2]. The study of the solubility of dye molecule in surfactant micelle is of vital importance in textile industry and as well as in the wastewater treatment plants [2]. Removal of dye from wastewater requires well understanding of the dye-surfactant interactions and are typically discussed under the three condi-

tions of the solubilities of the surfactant in water *i.e.* (i) at low concentration of surfactant, when surfactants are adsorbed preferentially at the interface of the air-water (pre-micellar region), (ii) at critical micelle concentration (CMC), when surfactants begin to form micelle and (iii) after CMC (post-micellar region) [3-6]. Solubility of dye molecules in surfactants also depends on the features of the dye molecule itself. It has been reported earlier that, in the pre-micellar region, where surfactant acts like normal electrolyte, dye-surfactant ion-association complex is formed [6-8]. At CMC, dye enters the outermost Gouy-Chapman layer of the micelle or may move to inner Stern layer of the micelle. Usage of surfactant concentration above CMC greatly increases the solubility of the dye in water, as in this situation dye may penetrate deep into the innermost hydrocarbon core of the micelle. Dye-surfactant interactions arises due to the (i) hydrophobic interactions, (ii) electrostatic interactions, (iii) hydrogen bonds, (iv) p-stacking and (v) van der Waals forces, *etc.* [6-8].

Presence of cosolvent like alcohol with water results to the changes in the CMC value of the surfactant. It has been reported that the use of cosolvents like ethanol either increases the solubility of surfactant in water or influence the hydrophobicity and/or hydrophilicity of the surfactant and thus changes the surface properties of surfactants. As a result, in the mixed solvent, the extent of dye-surfactant interactions also changes [8-11].

Temperature plays an important role in dye-surfactant interactions, it has been reported that, typically, the CMC of the surfactant increases with the rise in temperature, both in the aqueous solution as well as in the binary mixture of water and alcohol. Sometimes though, CMC of surfactant deceases first with the initial increase in temperature and at the high temperature region the CMC starts increasing. On increase in the temperature two cases may come up, *e.g.* (i) the degree of hydration of hydrophilic group may decrease, which favour micellization and (ii) the disruptions of water structure surrounding the hydrophobic group may also happen, which is unfavourable to micellization. Usually, the second factor overpowers the first factor and increase in CMC is observed [8-11]. Increase in CMC with the increase in temperature is also explained based on the increase in kinetic motion of the surfactant and water molecules, which leads to the increase in repulsion between the hydrophobic head groups of the surfactants and thus increase in CMC is observed [12,13].

Cetyltrimethylammonium bromide (CTAB) is a quaternary ammonium surfactant having the structural formula $[(C_{16}H_{33})N-(CH_3)_3]Br$ and its hydrophilic group carrying a positive charge. It is also widely used for its antiseptic properties [14]. Bromocresol green (BCG) is a dye having the core structure of triphenylmethane dye group (sulfonephthalein). It is used as a pH indicator, as in the low pH (< 3.8) medium it deprotonates producing mono-anionic form of yellow in colour and in the high pH (> 5.6) region it deprotonates again to produce dianionic form of blue in colour. Dianionic form is more resonance stabilized, so, at neutral pH the ionization equilibrium of dye is tilted more towards the dianionic form and the solution of BCG appears to be blue in colour. Although BCG as a pH-responsive dye shows many potential applications, such as growth mediums for microorganisms and titrations, in the measurement of serum albumin concentration within mammalian blood samples, in the thin-layer chromatography as staining solutions to visualize acidic compounds, as dye in textile industry, *etc.* [15]. The smaller solubility of dye in aqueous medium remains a problem in its use in textile industry. Therefore, a thorough understanding of the dye-surfactant interactions employing BCG-surfactant complexes in aqueous medium and with cosolvent alcohol are in trend in current research. Recently, Islam *et al.* [3,4], on the influence of alcohols and diols in the modes of interaction of the mixture of anionic dye BCG and anionic surfactant sodium dodecyl sulphate (SDS) by conductometric study, revealed that the presence of BCG and alcohols have a profound effect on the micellization process of the SDS. Presence of BCG lowers the CMC value of SDS indicating micellization process is favourable in the BCG and SDS combined system. The work also reveals that by evaluating different thermodynamic parameters, presence of alcohols or diols eases the micellization process of BCG-SDS

system when the alcohols or diols are used as cosolvent in lower percentage, but as the percent of additive increases the CMC value of BCG-SDS system rises indicating hindrance in the process of micellization.

In present study, the different modes of dye-surfactant interaction of anionic dye BCG (at pH~7.0), in its dianionic form under the different conditions of surfactant concentrations, *e.g.* at pre-CMC, CMC and post-CMC concentrations, were investigated using the conductometric and spectrophotometric analysis. Also, the studies involving variation in the solvent media, which was achieved by using isopropanol as an additive (cosolvent) and the effect of alteration in temperature were performed. Different thermodynamic parameters pertaining to the micellization process involved in BCG-CTAB collective system were computed from the conductometric and spectrophotometric data under various experimental conditions. These studies may help to comprehend the nature of different intermolecular interactions responsible for BCG-CTAB complex formation taking in to account that BCG and CTAB have the opposite charges.

EXPERIMENTAL

Cetyltrimethylammonium bromide (CTAB, molar mass 364.45 g/mol), bromocresol green (BCG) sodium salt, (molar mass 720.02 g/mol) and isopropanol solvent, AR grade purchased from Merck Ltd. India, were used. Entire solutions were prepared by employing deionized water having conductivity less than 3.00×10^{-6} μS.

Conductometric measurements: A digital conductivity metre (Systronics-304) with a resolution level of ± 0.1 μS was used to measure the conductivity of the studied systems. The conductivity metre was calibrated prior using by 0.1 M and 0.01 M KCl solutions. The temperature of the experimental system was maintained by employing a Thermostat bath (Borosil-WLC, temperature range ambient 5 ºC to 95 ºC, uniformity ± 0.5 ºC).

To prepare the experimental solutions, initially stock solutions of CTAB in water and CTAB in 10% v/v of isopropanol in water were prepared (1×10^{-2} M), Similarly, the stock solutions of BCG (1×10^{-3} M) in water and in 10% v/v of isopropanol in water were prepared. Then, from the stock solutions, the desired range of solutions of CTAB (0.05 mM to 4 mM) and BCG were prepared by proper mixing and positioned in water bath to attain the experimental temperature. Conductivity of the solutions were measured after the attainment of the desired temperature in water bath. All graphs and calculations were performed using MS Excel 2010 software.

RESULTS AND DISCUSSION

Variation in specific conductance of solution of CTAB with its concentration: The plot of specific conductance of CTAB with varying concentration of CTAB in water (Fig. 1) can be linearly fitted with two straight lines, representing pre-CMC and post-CMC regions of surfactant respectively, having different slopes and the point of intersection of these two straight lines gives the CMC value (Table-1).
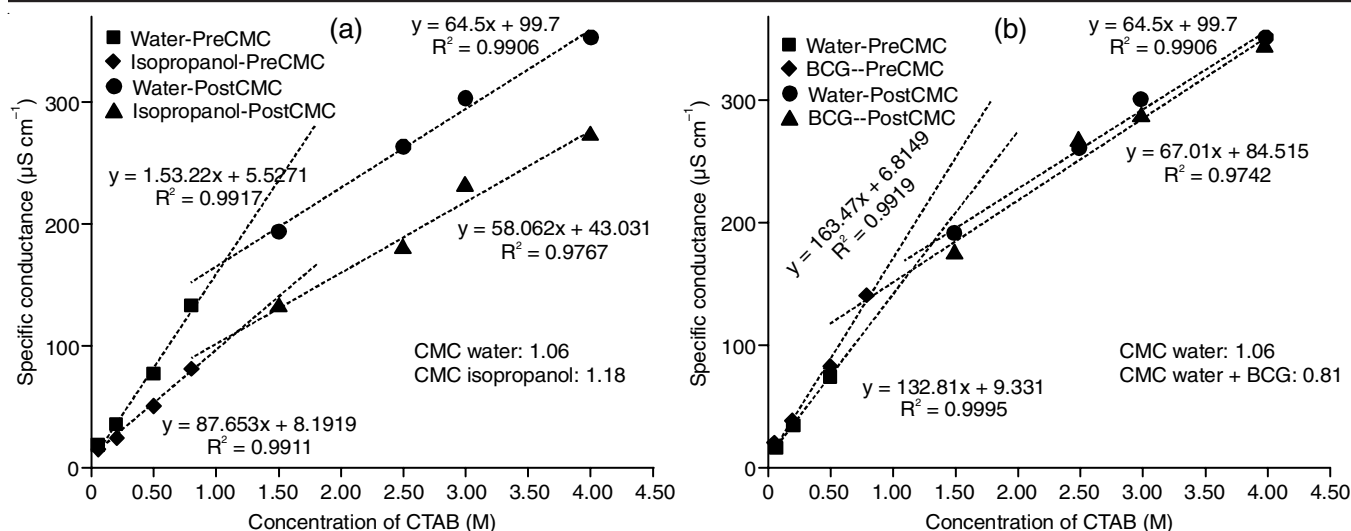
Fig. 1. Plot of specific conductance (mS cm^{-1}) of CTAB (range-0.05 mM to 4 mM) at 303 K: (a) in pure water and in mixed solvent with 10% isopropanol, (b) in pure water and in presence of 0.01 mM of BCG

TABLE-1
CMC, DEGREE OF MICELLAR IONIZATION (α), ΔG°_m, ΔH°_m and ΔS°_m ASSOCIATED WITH THE
MICELLIZATION OF CTAB IN THE COMPLEX OF BCG-CTAB AT VARIOUS TEMPERATURES

	Temp. (K)	CMC (mM)	β	ΔG°_m (kJ mol^{-1})	ΔH°_m (kJ mol^{-1})	ΔS°_m (kJ mol^{-1} K^{-1})	ΔC°_m (kJ mol^{-1} K^{-1})
Aqueous solution of CTAB*	303	1.06	0.58	-43.22	10.73	0.178	
	311	1.27	0.52	-41.98	5.01	0.151	-0.72
	319	1.58	0.42	-39.42	-0.84	0.121	
Aqueous solution of CTAB + BCG**	303	0.81	0.59	-44.62	-10.56	0.112	
	311	0.92	0.34	-42.83	-30.86	0.029	-2.59
	319	1.22	0.33	-39.92	-52.03	-0.044	
CTAB in cosolvent isopropanol***	303	1.18	0.46	-36.26	-14.80	0.071	
	311	1.52	0.30	-35.17	-1.77	0.107	-1.67
	319	1.78	0.27	-34.93	11.95	0.147	
CTAB + BCG in cosolvent isopropanol***	303	0.76	0.61	-45.46	-73.74	-0.093	
	311	1.06	0.55	-43.67	-35.36	0.027	4.88
	319	1.15	0.52	-43.47	4.36	0.150	

*Aqueous solution of CTAB (range-0.05 mM to 4 mM), **in presence of 0.01 mM solution of BCG, ***in presence of 10% v/v isopropanol in water.

In pre-CMC region, the surfactant monomers ionize and behaves as strong electrolyte, whereas in post-CMC region, surfactant molecules aggregate to form micelles and micelles are partially ionized and less conducting. Thus, slope of the line representing pre-CMC region was always found to be greater than that for the post-CMC region. The reason for lower conductance of post-micellar solutions was elaborated by several researchers as follows; within the micelle there are two ions of opposite charges, *i.e.* the long-chain headgroup ions of the surfactant and its counterions. In micelle, the long chain headgroup ions bind with the counterions by coulombic attractions, thus within the micelle inter headgroup ionic repulsion decreases and the micelle becomes stabilized. As a result of strong binding between the ionic head groups and counter ions, total surface charge of micelle decreases. Due to this lessening of the total surface charge in micelle and because of the lower mobility of large micelles, overall reduction in conductance is observed [3-8].

Effect of addition of 10% isopropanol to aqueous CTAB solutions: Fig. 1 also shows the variation in specific conductance of aqueous solution of CTAB with its increasing concentration in 10% v/v isopropanol. It was observed that specific conductance of CTAB decreases in the presence of isopropanol, which was reported by several researchers [3-8] as the effect of lessening of dielectric constant of the mixed solvent medium compared to that of pure water. Therefore, the slope of both pre-CMC and post-CMC lines of CTAB, in mixed solvent of isopropanol in water was observed to be less than that found in pure water.

Effect of addition of BCG to aqueous CTAB solutions: In presence of BCG solution, the slope of linear curve of pre-CMC region of CTAB-BCG complex was found to be greater than that for pure CTAB in water. In post-CMC region, the slope of linear curve of BCG-CTAB complex was found to be less than that for pure CTAB in water. This difference in slopes leads to a decrease in CMC of CTAB + BCG complex in water compared to CMC of aqueous solution of CTAB (Table-1). In post-CMC region, BCG probably starts forming stronger complex with the CTAB micelle and BCG-CTAB system, thus shows lower values of conductance.

Effect of addition of BCG to CTAB solutions in cosolvent isopropanol: When isopropanol was added to the BCG-CTAB aqueous solutions, the conductance value of mixed solutions (Fig. 2a) decreases in both pre-CMC and post-CMC regions.

Effect of variation of temperature: With increase in temperature, the conductance values of CTAB solutions increases progressively with the gradual increase in temperature irrespective of the presence or absence of BCG (Fig. 3). Similar increase in temperature results to increase in conductance values of BCG-CTAB system in cosolvent isopropanol. Higher conductance values of surfactant solutions were observed probably due to greater kinetic (thermal) energy of the charged species [3-11].

Thermodynamic parameters: Different thermodynamic parameters related to the micellization of pure surfactants (CTAB and SDS) and surfactant-dye complexes (CTAB + BCG) were calculated from the conductometric data [3-11] and presented in Table-2.

CMC: From the plot of specific conductance (mS cm^{-1}) values of CTAB solutions against their concentrations (mM)-point of intersection of two straight lines representing pre-CMC and post-CMC regions.

Degree of micellar ionization (α): Given by S_2/S_1, where S_2 is the post micellar slope, S_1 is the premicellar slope of plot of specific conductance (mS cm^{-1}) values of surfactant solutions.

Degree of micellar counter ion binding (β): Within the micelle two oppositely charged ions, the long chain ions and the counterions, binds together. The percentage of counterions in relation to the number of long-chain ions in the micelle, is called the fraction of micellar charge neutralized, and given by:

$$\beta = 1 - \alpha \qquad (1)$$

Changes in free energy (ΔG_m°) is given by:

$$\Delta G_m^\circ = (1 + \beta) \, RT \ln X_{CMC} \qquad (2)$$

where X_{CMC} indicates the mole fraction of CMC. The values of X_{CMC} were evaluated from the ratio of the number of moles
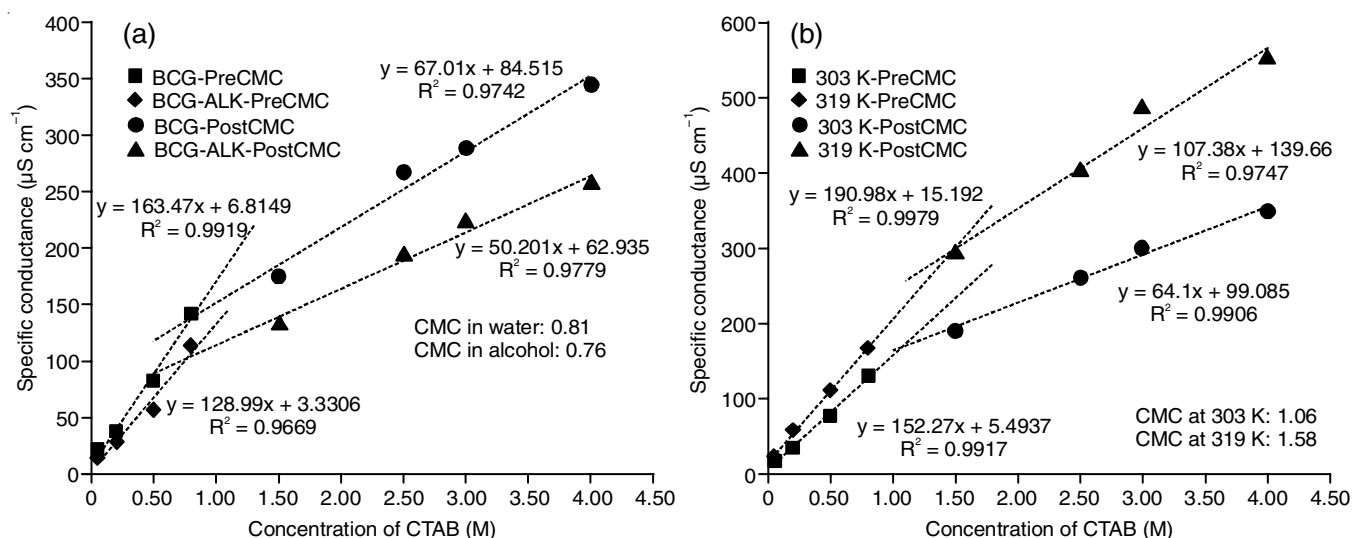

Fig. 2. Plot of specific conductance (mS cm^{-1}) of aqueous solution of CTAB (range-0.05 mM to 4 mM) (a) in presence of 0.01 mM of BCG in cosolvent isopropanol at 303 K (b) at 303 K and at 319 K
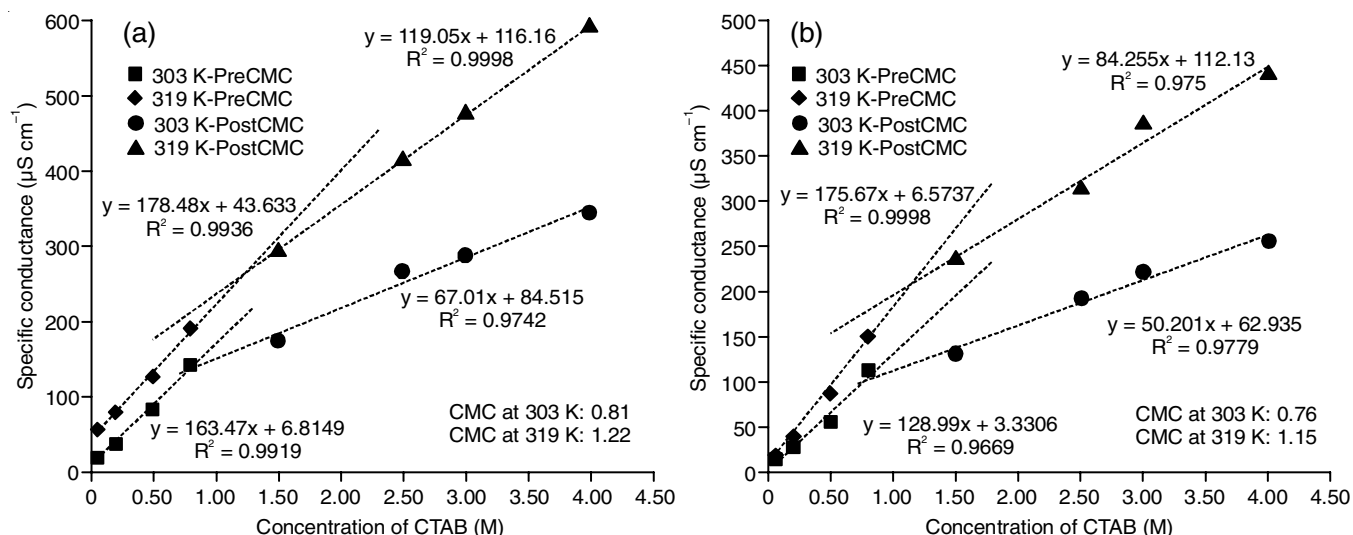

Fig. 3. Plot of specific conductance (mS cm^{-1}) of solution of CTAB (range-0.05 mM to 4 mM) in presence of 0.01 mM of BCG at 303 K and at 319 K (a) in aqueous solution (b) in cosolvent isopropanol

TABLE-2
INTERPLAY BETWEEN ENTHALPY AND ENTROPY FACTOR ON THE PROCESS OF MICELLIZATION

System	Medium	ΔH°_m (sign and magnitude with rise in temperature)	ΔS°_m (sign and magnitude with rise in temperature)	Predicted micellization
CTAB	Water	Positive and reduces to low negative	Positive and reduces	Endothermic and changes to low exothermic at high temperature and entropy driven
	Isopropanol (10% v/v)	High negative and rises to high positive	Positive and rises	Exothermic and changes to endothermic at high temperature and entropy driven
BCG-CTAB	Water	Negative and rises to more negative	Positive and changes to negative	Exothermic and exothermicity raises with temperature and enthalpy driven
	Isopropanol (10% v/v)	Negative and reduces	Negative and changes to positive value	Exothermic and enthalpy driven

corresponds to CMC and the total number of moles present in the solution contributed by CTAB (at CMC), BCG and H_2O or H_2O + EtOH. The moles of H_2O have been calculated from the ratio 1000/18.02 where 18.02 g mol^{-1} is the mol. wt. of H_2O.

Change in enthalpy (ΔH°_m):

$$\Delta H^{\circ}_m = -(1+\beta)RT^2 \left(\frac{\partial \ln(X_{CMC})}{\partial T} \right) \quad (3)$$

To compute ΔH°_m, ln (X_{CMC}) is plotted against temperature (T in K) and the curve is fitted with a polynomial as:

$$\ln (X_{CMC}) = aT^2 + bT + c \quad (4)$$

a, b and c are the constants (polynomial regression coefficients), their values were acquired from the second order polynomial fitting (Fig. 4).
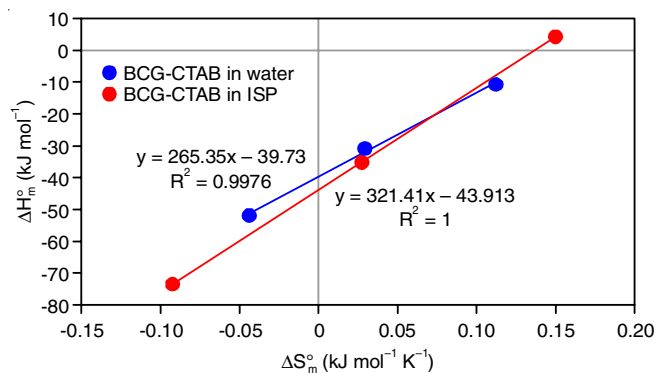

Fig. 4. Plot of enthalpy-entropy compensation for BCG-CTAB system in water and in isopropanol

Thus, the modified vant Hoff equation become:

$$\Delta H^{\circ}_m = -(1+\beta) RT^2 (2aT + b) \quad (5)$$

Change in entropy (ΔS°_m) is given by:

$$\Delta S^{\circ}_m = \frac{(\Delta H^{\circ}_m - \Delta G^{\circ}_m)}{T} \quad (6)$$

Comparative study of the BCG-CTAB interactions in different solvent media: Dye-surfactant interactions are mainly classified as under electrostatic, hydrogen bonding, hydrophilic, hydrophobic and ion-dipole/dipole–dipole interactions. From the obtained data (Table-1) under different conditions, the following observations were made to determine which of the different kinds of interactions influenced the extent of micelle formation in the BCG-CTAB system.

(A) CMC values and free energy of micellization ($-\Delta G^{\circ}_m$) of CTAB in absence of BCG, at a particular temperature, follows the general trend: CMC (water) < CMC (10% v/v isopropanol) and $-\Delta G^{\circ}_m$ (water) > $-\Delta H^{\circ}_m$ (10% v/v isopropanol):

(i) Alcohols break the hydrogen bonded cluster of water molecules and frees more water molecules in medium [3-6]. Thus, an increase in the solubilization of CTAB in cosolvent medium results and increase in CMC values of CTAB in the presence of isopropanol is observed.

(ii) Stability of micelle is a result of the coulombic attracting force between the counter ions with the ionic head groups of the surfactants. Presence of alcohols decreases the dielectric constant of solvent medium. Because of this, the counter ion binding tendency of ionic head groups decreases in the presence of alcohols, thus, the electrostatic repulsive interaction between the micelle forming ionic head groups increases and the micelle become unstable [3-6]. Thus, in presence of isopropanol as a cosolvent, an increase in CMC value of aqueous solution of CTAB was observed.

(iii) Extent of increase in CMC of the surfactant in presence of alcohol depends on the alkyl chain length of alcohols used as well as on the percent composition of alcohol in water [3-11]. The cross section of any Micelle can be subdivided into three layers: (a) the Gouy-Chapman layer- it is the outermost layer, which is hydrophilic in nature and where loosely bound counterions in the pool of water is found; (b) the Stern layer, which is the middle layer and is less hydrophilic and the presence of strongly bound counterions with a small number of water molecules are found there, and (c) hydrocarbon core, which is the innermost layer and hydrophobic in nature. Alcohols with lower alkyl chain length (methanol), probably positions and binds itself by at the junction of the outermost Gouy-Chapman Layer and the middle layer called the Stern layer of micelle. This would result to lessening in the electrostatic repulsion between the similarly charged head groups and hence micellization becomes favored and CMC lowers. With the increase in the percentile composition of alcohol in water, alcohol penetrates the middle layer (Stern layer) of micelle and replaces the counter ions present there. This would lead to the increase in the electrostatic repulsion between the alike charged head groups, and hence micellization becomes less favored and CMC increases. Alcohols with higher alkyl chain length (propanol) are reported to shows similar effect of increasing the CMC even at the lower percentile composition. This is because of the more penetrating

power of the higher alkyl chain length alcohols [3-11]. Thus, in present study, increase in CMC of aqueous solution of CTAB was observed in the presence of cosolvent isopropanol.

(B) In presence of BCG at a particular temperature, the CMC values decreases and negative free energy of micellization (ΔG_m°) of CTAB increases: There is electrostatic attractive interaction present between the anionic dye BCG and cationic surfactant CTAB, thus, these two ionic entities bind with each other greatly. In case, if BCG binds itself at the junction of the outermost Gouy-Chapman layer and the middle layer called the Stern layer of micelle, it would result in lessening of the electrostatic repulsion between the similarly charged head groups. Hence, micellization becomes favoured and thus, in the present study lowering in CMC of the BCG-CTAB system was observed. To learn more on the location of BCG in CTAB micelle and the extent of binding between these two oppositely charged moieties, spectrophotometric studies had been carried out and are discussed in the latter section of this article.

(C) Cosolvent isopropanol has little effect on the CMC values of CTAB + BCG complexes. If we consider a binary immiscible solvent phase system composed by water and isopropanol together forming as one solvent phase and the micelle of CTAB as another phase, then, BCG molecules have a choice of partitioning itself into the binary phase. As the BCG-CTAB forms a strong association by columbic attraction between the two oppositely charged moieties, so, it is likely that BCG will partition more in to the CTAB micelle compared to water + isopropanol cosolvent media. Also, BCG have three non-polar benzene rings attached to each other in its structure, which enhances the chance of inclusion of BCG into the micellar non-polar cavity. Probably, due to this intrinsic nature of BCG to form strong complexes with CTAB the process of micellization of CTAB becomes more feasible in the presence of BCG.

The formation of strong ionic complex between the BCG-CTAB system also hinders the replacement of BCG molecules by the alcohol molecules from the Stern layer (middle layer) of micelle. Hence, the electrostatic repulsion between the head group-head group of the CTAB micelle, which could result in instability of the micelle, are prevented. Thus, in the BCG-CTAB system a retention of the CMC-values in presence of isopropanol were observed compared to that in the aqueous solution.

(D) Increasing the temperature results in increase in the CMC of CTAB. The reasons are due to (i) stabilization of CTAB micelle also depends on the solvent molecules/counterions adhered to the ionic head groups of CTAB micelle as solvent/counter ions diminishes the electrostatic repulsion between the ionic head groups. With the increase in temperature the thermal (kinetic) motion of the solvent molecules/counterions and the surfactant ionic headgroups increases, as a result these becomes more vibrating. Therefore, the head group-head group columbic repulsion will increase and the destabilization of micelle will take place [3-11]. Thus, systematic increase in CMC values of CTAB in all kinds of media were observed with gradual increase in temperature.

(ii) It is ideal for the stabilization of micelle that some solvent molecules be present in micelle core, as this will lead to hydrophobic interaction between the hydrocarbon tail group (hydrophobic group) and the water molecule [3-11]. This will result in tight binding between the hydrophobic tail groups forming the micelle and is called hydrophobic stabilization factor for the micellization. With an increase in temperature, number of water molecules from the core of micelle is dislocated, hydrophobic stabilization energy decreases which leads to weakening of micelle and increase in CMC. Increase in temperature can also lead to decrease in hydration number of the hydrophilic head groups and this will lead to less solubilization of the surfactant in water and thus, the CMC value may decrease in this case [3-11]. Thus, increase in temperature may results to two opposing effects (a) increase in hydrophobic interaction-increase in CMC and (b) decrease in hydration of the hydrophilic tail groups-increase in the solubilization of surfactant. A balance between these two opposing effects determines whether CMC will increase or decrease with increase in temperature [3-6]. In present study, increase in CMC of CTAB was observed with the rise in temperature in the all the medium (in pure water, in presence of BCG and in cosolvent isopropanol. So, it may be concluded that CMC increases in all these cases are due to domination in hydrophobic interaction as discussed earlier. Observed relationship between the spontaneity of micellization and degree of hydrophobic interaction between ionic head groups of micelles are summarized in Table-3.

TABLE-3
HYDROPHOBIC STABILIZATION AND
SPONTANEITY OF MICELLIZATION UNDER
DIFFERENT EXPERIMENTAL CONDITION

Experiment	Spontaneity of micellization	Hydrophobic stabilization
Presence of isopropanol	Decreases	Lowers
Presence of BCG	Increases	Rises
Increase in temperature	Decreases	Lowers

Enthalpy (ΔH_m°) and entropy (ΔS_m°) of micellization: The enthalpy of micellization (ΔH_m°) and the entropy of micellization (ΔS_m°) were calculated using eqns. 3-6 [3-5,16,17] (Fig. 4) and are presented in Table-2. The ΔH_m° and the ΔS_m° values obtained under different experimental conditions and with the rise in temperature (Table-2). The observations predicted that micellization of CTAB in aqueous medium is endothermic and entropy driven, whereas in BCG solution, it is exothermic and enthalpy driven. Higher negative values of ΔH_m° supports to the fact that the BCG and the CTAB forms a strong complex in the BCG-CTAB system and BCG enters in to the micelle inner hydrocarbon core and stabilizes the micelle. In presence of isopropanol, the ΔH_m° values are initially negative indicating the process is exothermic but increases to a positive value (indicating the process is becoming more endothermic) with the rise in temperature. Progressive rise in entropy was observed with gradual rise in temperature in isopropanol cosolvent media. This validates to the fact that isopropanol increases the columbic repulsion between the micelle ionic headgroups by replacing the counterions attached to the ionic headgroups. Thus, to overcome this effect, and to bring the surfactant molecules from the aqueous medium to the micelle, supply of energy is needed.

Another way to effect micellization is to use of the fact that entropy of the system increases during the micellization process [3,4,18-28]. Thus, in presence of the cosolvent isopropanol the micellization is both enthalpy and entropy driven.

The higher negative ΔH_m° values of BCG-CTAB system in cosolvent isopropanol (Table-2) indicates BCG partition itself more in the micelle core compared to that in alcohol-water mixture, facilitating the formation of micelle by reducing hydrophobic repulsion between the ionic head groups. Table-2 also reflects the smaller value of ΔS_m° verifying the fact that in isopropanol medium, BCG probably do not replace much the hydration sphere surrounding the hydrophobic groups. Thus, in the cosolvent isopropanol the micellization of BCG-CTAB system becomes basically enthalpy driven. With increase in temperature ΔH_m° values becomes positive and an increase in ΔS_m° values is observed. To compensate the energy required to effect micellization, increase in entropy is observed with rise in temperature. Increase in entropy can take place by following two methods: (1) when the CTAB monomers forms micelle in aqueous solution it removes water molecules attached to its solvation sphere and (2) removal of water of hydration from the ionic head groups of micelle or hydrocarbon tails of the micelle by any alcohol or dye molecule (adduct) forming complexation with the micelle or with the increase in temperature [3,29-36]. In the BCG-CTAB system in presence of isopropanol, an increase in entropy with gradual increase in temperature probably is the effect of the release of water of hydration surrounding the ionic head groups and or hydrocarbon tails of the micelle and or release of BCG itself from the binding with the micelle. This destabilizes the micelle and increase in CMC value with the rise in temperature was observed.

The molar specific energy (ΔC_m°) for CTAB micellization process can be expressed as [37-39]:

$$\Delta C_m^\circ = \frac{\delta H_m^\circ}{\delta T} \qquad (7)$$

The ΔH_m° values at different temperatures were plotted against the temperature and the slope of the curve so obtained gives the ΔC_m° (Table-2). The calculated ΔC_m° value for BCG-CTAB system is negative in aqueous medium but it becomes positive in presence of cosolvent isopropanol. The positive specific energy may indicate structural phase change of the CTAB micelle is taking place while it binds with the BCG in presence of isopropanol.

The $\Delta G_{m,tr}^\circ$ is a thermodynamic parameter, which compares spontaneity/feasibility of bringing CTAB molecules from water to the micelle core to that of bringing CTAB molecules from water in presence of any additive (BCG, isopropanol) to the respective micelle core and is given by [40-42]:

$$\Delta G_{m,tr}^\circ = \Delta G_m^\circ \text{ (aq. additive)} - \Delta G_m^\circ \text{ (aq.)} \qquad (8)$$

where ΔG_m° (aq) and ΔG_m° (aq. additive) represents standard Gibbs free energy of micellization for CTAB in aqueous medium and in presence of different additives (BCG, isopropanol). In present study, the $\Delta G_{m,tr}^\circ$ values were calculated and presented in Table-4. The negative $\Delta G_{m,tr}^\circ$ values in water + BCG medium (Table-4) confirms that the transfer of CTAB molecules from aqueous solution to CTAB-micelle core is more feasible in presence of

TABLE-4 THERMODYNAMIC PARAMETERS OF TRANSFER FOR THE BCG-CTAB SYSTEM FROM WATER TO WATER-ISOPROPANOL MEDIA AT VARIOUS TEMPERATURES				
	Temp. (K)	$\Delta G_{m,tr}^\circ$ (kJ mol^{-1})	$\Delta H_{m,tr}^\circ$ (kJ mol^{-1})	$\Delta S_{m,tr}^\circ$ (kJ mol^{-1} K^{-1})
Water + BCG	303	-1.40	-21.29	-0.066
	311	-0.85	-35.87	-0.122
	319	-0.50	-51.19	-0.165
Water + isopropanol	303	6.96	-25.53	-0.107
	311	6.81	-6.78	-0.044
	319	4.49	12.79	0.026
Water + isopropanol + BCG	303	-0.84	-63.18	-0.205
	311	-3.84	-4.50	-0.002
	319	-5.55	56.39	0.194

BCG than the transfer of CTAB molecules from aqueous solution to CTAB-micelle core in absence of BCG. Hence, the micelle formation becomes easier in the presence of BCG. In presence of cosolvent isopropanol and in absence of BCG, the $\Delta G_{m,tr}^\circ$ values were found to be positive (Table-4), indicating non-spontaneous transfer of CTAB molecule from the bulk mixed solvent to the micelle core. Thus, it is corroborated to fact that in isopropanol mixed solvent the CTAB micellization process is hindered. Addition of BCG to the CTAB solutions, in the presence of isopropanol cosolvent, results to negative $\Delta H_{m,tr}^\circ$ values, indicating spontaneous micellization of CTAB molecules.

The other thermodynamic parameters involving enthalpy and entropy were calculated as follows [40-42]:

$$\Delta H_{m,tr}^\circ = \Delta H_m^\circ \text{ (aq. additive)} - \Delta H_m^\circ \text{ (aq.)} \qquad (9)$$

$$\Delta S_{m,tr}^\circ = \Delta G_m^\circ \text{ (aq. additive)} - \Delta S_m^\circ \text{ (aq.)} \qquad (10)$$

The $\Delta H_{m,tr}^\circ$ values are all negative excepting at high temperature (Table-4) and negative values point to the high exothermic nature of micellization in these medium compared to that in water. The exothermicity of micellization in BCG medium compared to that in water increases with the increase in temperature. While in presence of isopropanol, with an increase in temperature, the relative exothermicity with respect to water medium decreases and at high temperature it becomes completely endothermic (positive $\Delta H_{m,tr}^\circ$, Table-4). In water + isopropanol + BCG mixed media the $\Delta H_{m,tr}^\circ$ shows the highest negative value at the lower range of temperature and at higher temperature it becomes positive relative to water + BCG mixed media.

The $\Delta S_{m,tr}^\circ$ values are all negative in presence of BCG and negative values increases with increase in temperature. In presence of isopropanol cosolvent the negative values of $\Delta S_{m,tr}^\circ$ decreases with the rise in temperature and ultimately reaches to appositive value at high temperature. Similar trend in $\Delta S_{m,tr}^\circ$ values are observed in BCG medium in presence of isopropanol.

Enthalpy entropy compensation (EEC) phenomenon: It was found that process of micellization of the BCG-CTAB system depends both upon enthalpy and entropy, thus, to find out if any correlation between the two is there, enthalpy entropy compensation (EEC) studies were performed. Similar processes are reported in the literature [43-51], where enthalpy (ΔH_m°) and entropy (ΔS_m°) of the process bears a linear correlation among them of the following type:

$$\Delta H_m^\circ = \Delta H_m^{\circ,*} + T_{comp}\,\Delta S_m^\circ \qquad (11)$$

Initiation of micellization involving surfactant molecules can be thought of taking place by two processes *viz.* (i) dehydration/desolvation of hydrophobic (hydrocarbon) tail groups and (ii) the aggregation of hydrophobic tail groups. The desolvation process is represented by the slope of EEC (eqn. 11, T_{comp}), where, T_{comp} is called the compensation temperature and characterized by the solute-solvent interactions. The intercept of the EEC (eqn. 11), $\Delta H_m^{\circ,*}$, is physically characterized by the solute-solute interactions [43-51]. The significance of $\Delta H_m^{\circ,*}$ is that it becomes equal the molar enthalpy change of micellization (ΔH_m°) when micellization process becomes independent of entropy effect ($\Delta S_m^\circ = 0$) [43-51].

Fig. 4 represents the linear regression plots between the enthalpy of micellization (ΔH_m°) and the entropy of micellization (ΔS_m°), for the BCG-CTAB system in presence and absence of isopropanol. The plots were shown to be best fitted linearly maintaining EEC relation (eqn. 11). The EEC parameters were obtained from the linear regression plots and are presented in Table-5.

TABLE-5
ENTHALPY-ENTROPY COMPENSATION PARAMETERS

	$\Delta H_{m,tr}^{\circ,*}$ (kJ mol^{-1})	T_{comp} (K)
Aqueous solution of CTAB	-25.46	203
CTAB + BCG in water	-39.73	265
CTAB in isopropanol (10% v/v)	-39.65	351
CTAB + BCG in isopropanol (10% v/v)	-43.91	321

The magnitude of negative $\Delta H_m^{\circ,*}$ values for BCG-CTAB system in water was found to be greater than that in pure CTAB system in water (Table-5). During the micelle formation, the entropy effect (ΔS_m°) arises due to the dehydration/desolvation of the hydrophobic groups of surfactant molecules and the enthalpy effect (ΔH_m°) arises due to the association/interaction between the hydrophobic groups of surfactant molecules. The $\Delta H_m^{\circ,*}$ values reflects the enthalpy effect arising under the condition $\Delta S_m^\circ = 0$ and its negative value indicates the extent of stabilization of the micelle. Thus, higher negative values of $\Delta H_m^{\circ,*}$ of BCG-CTAB system in water compared to pure CTAB in water indicates the relative ease of formation of CTAB micelle in presence of BCG, even when there is no increase in entropy in the system due to desolvation of the hydrophilic groups ($\Delta S_m^\circ = 0$). Similarly, it is found that negative $\Delta H_m^{\circ,*}$ values (Table-5) of CTAB system in the presence of isopropanol as cosolvent of water is greater in magnitude compared to that in pure water. When BCG and isopropanol are used together as additives in aqueous solution, the $\Delta H_m^{\circ,*}$ values becomes more negative, indicating further stabilization of the micelle. Both the instances of augmentation in negative $\Delta H_m^{\circ,*}$ values support the fact that CTAB micellization is practically enthalpy driven process in the presence of BCG or isopropanol.

The T_{comp} characterizes the compensation effect, *i.e.* due to dehydration/desolvation of the hydrophobic groups, entropy of the system (ΔS_m°) increases and to compensate this enthalpy of the system (ΔH_m°) arising from the hydrophobic group-hydro-

phobic group interaction (association) also increases. So, T_{comp} represents the how the solute-solute and solute-solvent interaction results to a compensation effect between the entropy and enthalpy of the micellization process. In present study, it was found that T_{comp} is higher in magnitude in case of BCG-CTAB system compare to that in pure CTAB. It has been reported that the magnitude of T_{comp} is higher in case of non-ionic surfactants compared to that in ionic surfactants and this is due to the nature of the hydrophilic groups attached to the ionic and non-ionic surfactants [43-51]. So, it can be predicted that in the BCG-CTAB system due to the strong binding between the anionic BCG and cationic CTAB, the hydrophilic groups of BCG-CTAB system attain the character like hydrophilic groups of the non-ionic surfactants. In the presence of isopropanol, further augmentation in the T_{comp} was found (Table-5).

Conclusion

In present work, the interaction of an anionic dye, bromocresol green (BCG) with a cationic surfactant, CTAB, was studied using conductometric method. The effect of changes of solvent media from water to cosolvent isopropanol and the effect of elevation in experimental temperature on the association behaviour of BCG-CTAB system were studied. It was observed that CMC and $-\Delta G_m^\circ$ values of aqueous CTAB decreases in the presence of isopropanol as a cosolvent of water. Whereas addition of BCG increases spontaneity of micellization of aqueous CTAB. Elevation in temperature was found to hinder the micelle formation process under all experimental conditions studied. The observed value of ΔH_m° was found to be positive in aqueous CTAB solution, whereas, in presence of additives (BCG, isopropanol) ΔH_m° values were found to be negative. With the rise in temperature the positive ΔH_m° value of aqueous CTAB solution reduces to a negative value. In presence of isopropanol additive, the rise in temperature results to changes in ΔH_m° value from exothermic to endothermic one. The ΔH_m° value for the aqueous BCG-CTAB system shows a rising trend in its exothermic nature with elevating temperatures. Whereas in the presence of cosolvent isopropanol, the exothermic nature aqueous BCG-CTAB system decreases with rise in temperature. The observed ΔS_m° for all the systems were found to be positive, with a highest positive value for aqueous CTAB system, except for aqueous BCG-CTAB system in the cosolvent isopropanol where it was found to be negative. Rise in temperature results to decrease in ΔS_m° values for aqueous solution of CTAB and in presence of additive as BCG. The ΔS_m° values increases with rise in temperature for the aqueous CTAB and BCG-CTAB system in cosolvent isopropanol. The results indicated that although micellization of CTAB in the presence and the absence of cosolvent is entropy driven and in presence of BCG it is enthalpy driven, both entropy and enthalpy play a mutual act in the CTAB micellization process in these media. Thermodynamic parameters of transfer for the BCG-CTAB system from water to water-isopropanol media at various temperatures ($\Delta G_{m,tr}^\circ$, $\Delta H_{m,tr}^\circ$, $\Delta S_{m,tr}^\circ$) also supports the entropy-enthalpy mutual act in the micellization process of BCG-CTAB system. Present study also revealed that a compensation phenomenon is operative between the enthalpy and entropy of micellization

in case association process involving the CTAB and the BCG-CTAB systems. The specific heat of micellization (ΔC_m°) values were found to be negative for all the systems except for BCG-CTAB system in cosolvent isopropanol, indicating a probable change in phase structure of the CTAB micelle in this medium. Of all the various modes of interaction like electrostatic, ion-dipole, dipole-dipole, hydrophobic, hydrophilic, *etc*. the hydrophobic interaction was found to be the dominant mode of interaction between the anionic dye BCG and cationic surfactant CTAB during the micellization process. The BCG was predicted to decrease the hydrophobic interaction between ionic head groups of micelle-core of CTAB by forming complexation with CTAB, while isopropanol is found to increase the hydrophobic interaction between ionic head groups of micelle-core of CTAB by increasing electrostatic repulsion by replacing the counterions attached to it. This hydrophobic stabilization results to increase in spontaneity of micellization of BCG-CTAB system in water while there is a decrease in hydrophobic stabilization in the presence of cosolvent isopropanol and a decrease in spontaneity of micellization.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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