RESEARCH ARTICLE

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Micellisation of Cetyltrimethyl Ammonium Bromide in Aqueous-Organic Media

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Abstract
The micellisation behaviour of cetyltrimethylammonium bromide (CTABr) in different mass fraction (17–47) of ethylene glycol (EG), dimethylsulfoxide (DMSO), and dimethylformamide (DMF)–water mixed solvents, was investigated using electrical conductivity measurement at different temperatures (293.1–313.1 k). The critical micelle concentration and degree of counterion dissociation (α) values increased with increase in the amount of EG, DMSO, and DMF but micellisation was found to be unfavourable in the presence of the co-solvents. The results of the thermodynamic analysis showed that addition of organic solvents, which are principally located in the bulk phase made the micellisation process less spontaneous. The London-dispersion interaction represented the major attraction force for micellisation and micellisation proceeded via an exothermic process. The difference in the magnitude of $\Delta S_{\mathrm{m}}^{\mathrm{o}}$ value between the CTAB–water and CTAB–water-co-solvent medium is a pointer to the fact that the micellisation in CTAB–water-co-solvent system is favoured by entropy gain. This indicated that the solvents still controlled the three-dimensional water matrix and the micellisation process of the studied surfactant is exothermic though the positive values of $\Delta S_{\mathrm{m}}^{\mathrm{o}}$, are due to the melting of flickering cluster around hydrocarbon ends of the surfactant monomer and increased the randomness of the hydrocarbon chains in the micelle core.

Keywords: Co-solvent; micellisation; hydrophobic; dielectric constant; counterion.

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1. Introduction

Solvent has a great role to play in controlling the micellisation of surfactants [1, 2]. Micellisation phenomenon of surfactants (amphiphiles) in non-aqueous media has been the scope of many researchers [3, 4] due to the increasing use of these materials in applications, which require water-free or water-poor media. The different association behaviours of surfactants in water and other solvents have stimulated the interest to elucidate how the solvent properties influence aggregation. These investigations have focused mainly on two essential aspects: the nature of the interactions implied in the process of micellar formation, and the structure of the aggregates formed. Evans *et al.* [5] established that the specific properties of water are not indispensable to promote surfactant self-assembly. In a given medium (usually, water or binary mixtures of either two non-aqueous solvents or non-aqueous solvent with water), amphiphilic molecules self-aggregate together to minimize the unfavourable interaction with the solvent medium and form different types of aggregates.

Hydrophobic or, more generally, solvophobic interactions play an important role in raising the above situation and, therefore, several studies have been made by altering the medium(water) properties either by the incorporation of additives [1, 6–8] or by mixing with polar/non-polar non-aqueous solvents [9–12]. The importance of studying micellisation behaviour of surfactants in water–organic mixed-solvent systems is driven by both fundamental and practical considerations [13].

Cationic surfactants possess valuable characteristic such as emulsification, wetting, water proofing, repellence and spreading, etc., used in detergent, food industries , pharmaceutical, enhanced oil recovery [14–16], metallurgical process for ore concentration, and solubilisation of water insoluble dyes [17]. In many of these applications, quaternary surfactants are usually employed because of their superior properties, which include the insensitivity of their cations to pH variations and their high substantivity, which encompasses the uptake of surfactants from solution onto the surface of negatively charged surfaces such as fibres, proteins, wool, metals, and pigments [18].

Investigations of micellisation in non-aqueous polar solvents, such as ethylene glycol (EG), glycerol, and dimethylformamide, which have properties resembling that of water, have shown that a solvent requires three conditions to induce surfactant aggregation which include: (i) a high cohesive energy, (ii) a high dielectric constant, and (iii) a high hydrogen-bonding ability. It has been proposed [19] that the capability of hydrogen bond formation is one of the most necessary conditions for the self-assembly of surfactants. Addition of polar organic solvents to aqueous micellar solutions will alter the tendency of amphiphile molecules to avoid contact with the solvent, and therefore, it is expected to affect the value of surfactant concentration at which micellisation occurs, i.e. critical micelle concentration (CMC), as well as micelles characteristics such as the counter ion dissociation constant.

A temperature of maximum stability for protein native structure and a temperature of minimum for the CMC of ionic surfactants [20] are widely reported in the literature. It is reasonable to think that these effects correspond to variations with temperature of the hydration of hydrophobic groups and hydrophobic interactions. While hydrophobic interactions were thought for a long time a major contribution to the micellisation, major emphasis in recent studies has been placed on London-dispersion interactions. Arguments for the relative importance of the various interactions on the micellisation process can only be obtained from comprehensive studies of thermodynamic properties of the complicated process of micellisation in which surfactant alkyl chains, surfactant head groups, counterions, and surrounding medium all play important role. In particular, micellisation parameters related to micellar conductance at different temperature need more attention.

Since the majority of the work reported in the mixed-solvent systems was done only at a few selected compositions of the organic solvents, a study in which the compositions of the mixed systems are varied and thermodynamic parameters studies shall be investigated conductiometrically in mixed EG + water, DMSO + water, and DMF + water. This will give an insight about the selection of mixed-solvent systems for their use in enhanced oil recovery, pharmaceutical and cosmetic applications, washings, and chemical reactions.

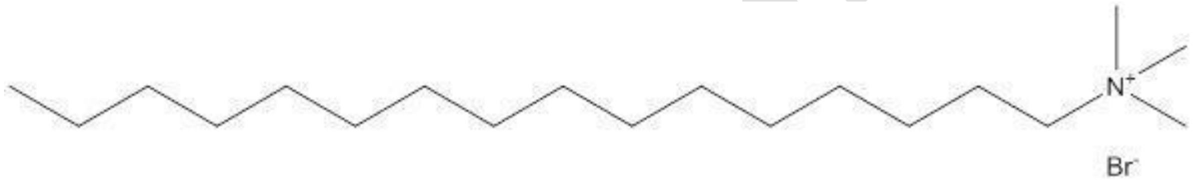

Figure 1: Schematic representation of CTABr molecular structure.

2. Methods

2.1. Materials

Cetyltrimethylammonium bromide (CTABr) was procured from Sigma. All the solvents used (EG, DMSO, and DMF) were obtained from Central Drug House (Bombay, India) and were of highest purity (99.9%), used without further purification.

2.2. Determination of critical micelle concentration (CMC)

Conductometric measurements were carried out with a digital systronics conductivity meter (306) model connected to a water flow thermostat at a frequency of 200 Hz using a dip-type cell of cell constant 1.0 cm^{-1}. The cell was calibrated with KCl solutions in the approximate concentration range. Initially, 10 mL of the reference solution (i.e., water) or an appropriate amount of each additive in water was taken in the conductivity cell and equilibrated at specified temperature for 1 hr before starting the experiment. A known concentration of CTABr, made with the same reference solution, was then added from a micropipette and equilibrated until the conductivity value became constant. In this way, the precise conductance of CTABr in EG + Water, DMSO + Water, and DMF + Water, mass fraction were determined. The error in the conductance measurements was ±0.5%.

2.3. Theoretical background

The standard states are defined for the free surfactant and the micelle state. For the free surfactant, the unit activity is taken as the standard state. While for micelle surfactant, the micelle state is considered as the standard state. The free surfactants in solution are assumed to be in equilibrium with the surfactants in the micelle phase. Thus, μ_s is the chemical potential of the free surfactants and μ_m, is the chemical potential of the surfactants in the micelle. Since the chemical potential for the free surfactant in solution and the chemical potential in micellar phase are in equilibrium.

Then

$$\mu_{\mathrm{s}} = \mu_{\mathrm{m}} \quad (1)$$

If the solution is ideal, the chemical potential for the free surfactant in solution at fixed temperature and pressure is given by

$$\mu_{\mathrm{s}} = \mu_{\mathrm{s}}^{\mathrm{o}} + RT \ln a_{\mathrm{s}} \quad (2)$$

For surfactant in the micellar phase, the chemical potential is equivalent to the standard thermodynamic properties ($\mu_{\mathrm{m}}^{\mathrm{o}}$) at equilibrium. Therefore

$$\mu_{\mathrm{m}} = \mu_{\mathrm{m}}^{\mathrm{o}} \quad (3)$$

At equilibrium,

$$\mu_{\mathrm{s}}^{\mathrm{o}} + RT \ln a_{\mathrm{s}} = \mu_{\mathrm{m}}^{\mathrm{o}} \quad (4)$$

and

$$\Delta G_{\mathrm{m}}^{\mathrm{o}} = \mu_{\mathrm{m}}^{\mathrm{o}} - \mu_{\mathrm{s}}^{\mathrm{o}} = RT \ln a_{\mathrm{s}} \quad (5)$$

where $\Delta G_{\mathrm{m}}^{\mathrm{o}}$ is the Gibb's energy of micellisation and a_{s} is the activity of the free surfactant in solution, *R* is the gas constant and *T*, the temperature.

Based on the phase separation model for ionic surfactant, for the calculated $\Delta G_{\mathrm{m}}^{\mathrm{o}}$, it is necessary to consider not only the transfer of surfactant molecules but also the transfer of moles of counterions (1 - α), where α is the degree of counterions dissociation.
Therefore, at equilibrium

$$\Delta G_{\mathrm{m}}^{\mathrm{o}} = RT \ln a_{\mathrm{s}} + (1-\alpha) RT \ln a_{\mathrm{Br}} \quad (6)$$

where a_{Br} is the activity of the counterions. Then, equation (6) can be written as

$$\Delta G_{\mathrm{m}}^{\mathrm{o}} = (2-\alpha) RT \ln a_{\pm\mathrm{cmc}} \quad (7)$$

where $a_{\pm\mathrm{cmc}}$ is the mean activity of the counterions at the CMC.

For most thermodynamic studies on the micellisation of ionic surfactants $a_{\pm\mathrm{cmc}}$ has been replaced by X_{cmc}. As given in the following equation.

$$\Delta G_{\mathrm{m}}^{\mathrm{o}} = (2-\alpha) RT \ln X_{\mathrm{cmc}} \quad (8)$$

where $\ln X_{\mathrm{cmc}} \approx [\mathrm{cmc}]/\mathrm{c}$, and C is the mole of the solvent per dm^3.

The enthalpy of micellisation can be obtained from the temperature dependence of the CMC by applying the Gibbs–Helmholtz equation [23].

$$\Delta H_{\mathrm{m}}^{\mathrm{o}} = -\frac{T^2 \partial(\Delta G_{\mathrm{m}}^{\mathrm{o}}/T)}{\partial T} \quad (9)$$

In order to do this, the $\ln X_{\mathrm{cmc}}$ and the α values are fitted to the polynomial equations (10) and (11) as presented below.

$$\ln X_{\mathrm{cmc}}(T) = a + b(T/K) + c(T/K)^2 \quad (10)$$

$$\alpha(T) = d + e(T/K) \quad (11)$$

In the above equations a, b, c, d and e are determined by least square regression analysis. $\Delta H_{\mathrm{m}}^{\mathrm{o}}$ is then calculated numerically by substituting equations (10) and (11) into equation (9). Once the Gibbs–free energy and the enthalpy of micelle formation are obtained, then the entropy of micelle formation can be determined using the equation below.

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$$\Delta S_{\mathrm{m}}^{\mathrm{o}} = \frac{1}{T}(\Delta \mathrm{H}_{\mathrm{m}}^{\mathrm{o}} - \Delta G_{\mathrm{m}}^{\mathrm{o}}) \quad (12)$$

3. Results and Discussion

The profile of the conductance reading versus the varying concentration of CTABr gave a curve with two different slopes. The data above and below the region, in which there is a rapid change of slope, were fixed by linear regression and the CMC was taken as the point of intersection. The degree of counterion dissociation (α) was obtained from the ratio of the slope in post-micelle (S_2) and that of the pre-micelle region (S_1) [21]. The CMC of CTABr in water increased with increase in temperature from 8.63 x 10^{-4} at 293.1 K to 1.22 x 10^{-3} mol dm^{-3} at 313.1 K. Addition of different mass fraction of co-solvent (17–47) to water at different temperature also increased the value of CMC as shown in Table 1.

Table 1: The CMC for CTABr in different aqueous-organic media at various temperatures.

$10^{-2.}$ ω_s Co-solvent	**Temperature (K)**				
	293.1	298.1	303.1	308.1	313.1
	Critical Micelle Concentration (mol dm^{-3}) ± 0.50				
Water	8.63 x 10^{-4}	9.50 x 10^{-4}	1.07 x 10^{-3}	1.14 x 10^{-3}	1.22 x 10^{-3}
EG–Water					
17	1.08 x 10^{-3}	1.27 x 10^{-3}	1.35 x 10^{-3}	1.47 x 10^{-3}	1.63 x 10^{-3}
27	1.57 x 10^{-3}	1.67 x 10^{-3}	1.74 x 10^{-3}	1.95 x 10^{-3}	2.25 x 10^{-3}
37	1.61 x 10^{-3}	1.75 x 10^{-3}	1.87 x 10^{-3}	2.15 x 10^{-3}	2.40 x 10^{-3}
47	2.53 x 10^{-3}	2.61 x 10^{-3}	2.70 x 10^{-3}	2.90 x 10^{-3}	3.12 x 10^{-3}
DMSO–Water					
17	1.32 x 10^{-3}	1.53 x 10^{-3}	1.68 x 10^{-3}	1.86 x 10^{-3}	1.97 x 10^{-3}
27	1.92 x 10^{-3}	1.98 x 10^{-3}	2.20 x 10^{-3}	2.38 x 10^{-3}	2.42 x 10^{-3}
37	2.80 x 10^{-3}	2.98 x 10^{-3}	3.18 x 10^{-3}	3.24 x 10^{-3}	3.52 x 10^{-3}
47	3.73 x 10^{-3}	4.00 x 10^{-3}	4.26 x 10^{-3}	4.58 x 10^{-3}	4.88 x 10^{-3}
DMF–Water					
17	2.20 x 10^{-3}	2.45 x 10^{-3}	2.63 x 10^{-3}	3.00 x 10^{-3}	3.25 x 10^{-3}
27	3.93 x 10^{-3}	4.20 x 10^{-3}	4.55 x 10^{-3}	5.15 x 10^{-3}	5.45 x 10^{-3}
37	5.55 x 10^{-3}	6.00 x 10^{-3}	7.53 x 10^{-3}	8.92 x 10^{-3}	1.02 x 10^{-2}
47	1.35 x 10^{-2}	1.55 x 10^{-2}	1.75 x 10^{-2}	1.97 x 10^{-2}	

This showed that the value of CMC increased with increase in temperature within the temperature range investigated. The effect of temperature on the CMC of surfactant in aqueous solution has been analysed in terms of two opposing factors. First, as the temperature increases, the degree of hydration of the hydrophilic group decreases, which favours micellisation, however, an increase in temperature also causes the disruptions of the water structure surrounding the hydrophobic group and this is unfavourable to micellisation [22]. The results presented in Table 1 revealed that second effect predominated within the temperature range studied. Also that micellisation is unfavourable in the presence of EG, DMSO, and DMF. EG being a water structure breaker decreases the hydrophobic interaction due to the decrease in cohesive energy and dielectric constant. These properties of EG enabled it to increase the solubility of the hydrocarbon chain of the CTABr monomer which made it difficult for the hydrocarbon chain to aggregate and the fewer hydrocarbons aggregated occurred at higher concentration of CTABr. The same trend was observed in the case of DMSO–water and DMF–water. The delay in micellisation in the case of DMSO and DMF can be justified by taking into consideration the increased structuring of the H_2O–DMSO and H_2O–DMF liquid system. Both DMSO and DMF are known to form stoichiometric hydrate with water of the type DMSO.H_2O and DMF.H_2O. The hydrate formation substantially restricted the motion of the surfactant molecule, which ultimately leads to reduction in

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hydrophobic interaction and an increase in CMC. It is noteworthy that the dielectric constant of DMSO and DMF are 48.9 and 36.7 respectively, and this played a prominent role in the micellisation of CTABr. Addition of more DMSO and DMF to the binary system decreased the dielectric constant of the medium further and since solvent with low dielectric constant, i.e., polarity usually solubilised organic molecules more easily [23] than those with high polarity, the mutual repulsion between ionic head in the micelle increased, hence an increase in the magnitude of CMC. Representative plot of the dependence of CMC on the co-solvent mass fraction at varying temperature is shown in Figure 2.

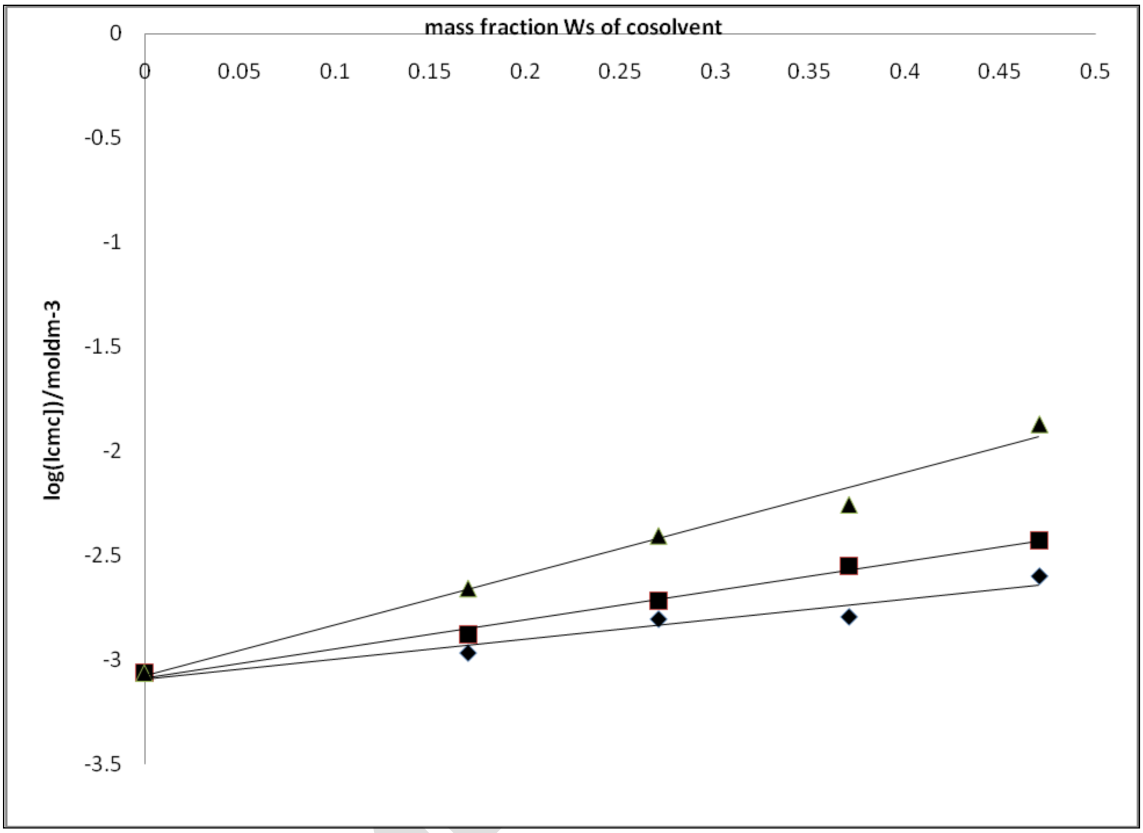

Figure 2: Plot of log([cmc]/moldm^{-3}) against the mass fraction (ω_s) of the organic solvent at 293.1 K (♦ = EG + Water, ■ = DMSO + Water, ▲ = DMF + Water).

A linear relationship between log [(CMC)]/mol dm^{-3} versus mass fraction of the co-solvent was observed. This finding was in agreement with the data presented by other workers [21, 24, 25]. This relationship is represented by the following equation:

$$\log([(\mathrm{CMC}]_{\mathrm{mix}} / \mathrm{mol\,dm}^{-3}) = \log([\mathrm{CMC}]_{\mathrm{aq}} / \mathrm{mol\,dm}^{-3}) + KW_{\mathrm{s}} \quad (13)$$

where the subscript, mix, represents the value of log ([CMC]/mol dm^{-3}) in co-solvent free medium; W_s, is the mass fraction of the co-solvent and K is a constant which is a measure of the hydrophobic character of the co-solvent [21]. The values of counterion dissociation (α) obtained at different mass fraction of co-solvent at varying temperature are presented in Table 2.

This increase in the value of α as mentioned above could be attributed to the columbic and thermal forces [26]. The former force attracts surfactant head groups while the latter disperses the surfactant head groups. The thermal forces predominated the columbic forces, and this led to an increase in the separation between the counterions and the head groups, hence increased α value. Increase in the values of CMC and α, as the mass fraction of co-solvent EG, DMSO, and DMF increased can be explained by considering the solvent-dependent contributions to the free energy of micellisation (6) viz. (i) the aggregate core–solvent interfacial energy, (ii) the head group interactions Gibbs energy, and (iii) the surfactant tail transfer Gibbs energy, which gives rise to solvophobic effect. The magnitude of the surfactant tail transfer Gibbs energy is smaller for EG, DMSO, and DMF when compared with that for water.

Table 2: Counterions dissociation (α) for CTABr in aqueous-organic media at different temperatures.

$10^{-2}\ \omega_s$ Co-solvent	Temperature (K)				
	293.1	298.1	303.1	308.1	313.1
Degree of Counterions dissociation (α)					
Water	0.328	0.336	0.348	0.363	0.383
EG–Water					
17	0.355	0.360	0.369	0.376	0.381
27	0.420	0.419	0.426	0.433	0.443
37	0.330	0.340	0.351	0.370	0.383
47	0.451	0.470	0.507	0.526	0.560
DMSO–Water					
17	0.304	0.307	0.310	0.317	0.322
27	0.300	0.309	0.330	0.350	0.365
37	0.290	0.341	0.364	0.411	0.441
47	0.432	0.480	0.523	0.592	0.630
DMF–Water					
17	0.323	0.348	0.371	0.392	0.422
27	0.374	0.420	0.451	0.491	0.543
37	0.671	0.681	0.714	0.743	0.762
47	0.700	0.741	0.793	0.811	-

The (α) value increased as the temperature increased (Figure 3).

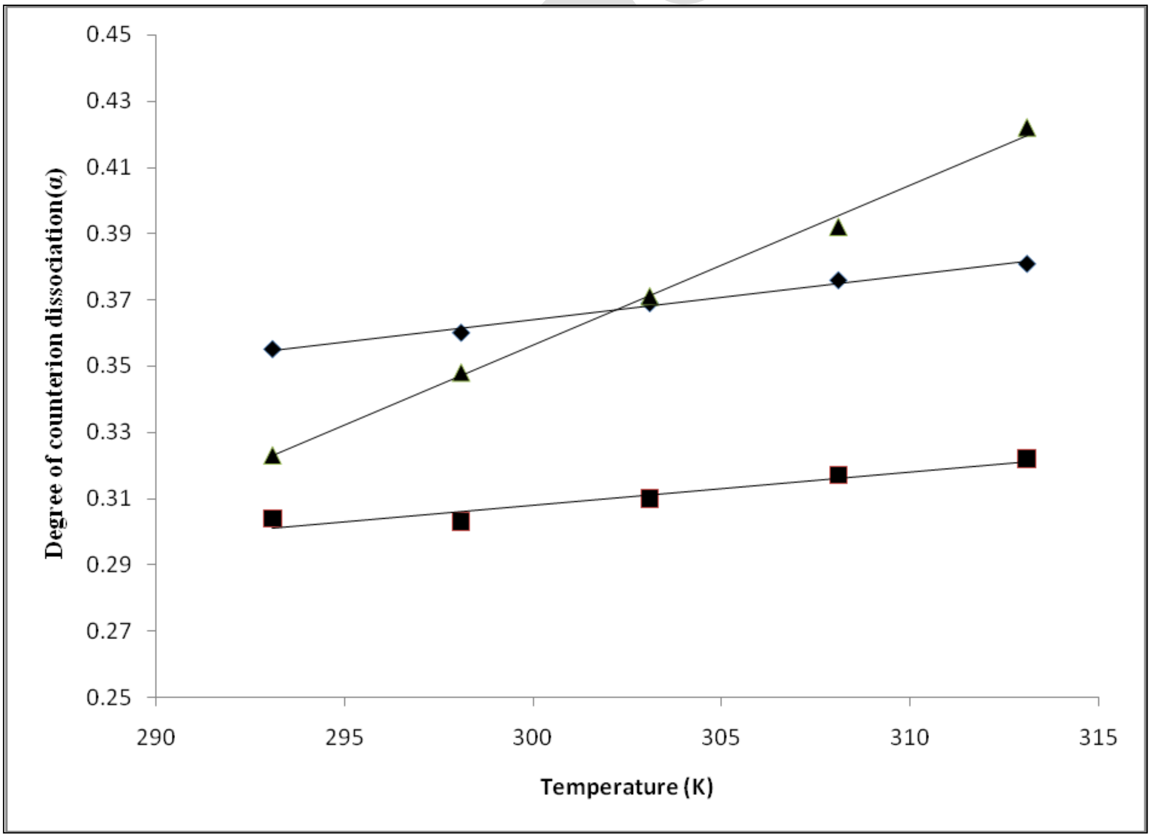

Figure 3: The plot of degree of counterions of dissociation (α) against temperature in 0.17 mass fraction (ω_s) of organic solvent (♦ = EG + Water, ■ = DMSO + Water, ▲ = DMF + Water).

3.1. Thermodynamics of micellisation

The dependence of CMC on solution temperature was used to evaluate the standard thermodynamic parameters of micellisation of CTABr in mixed-solvent systems. The change in the CMC value with temperature is generally analysed in terms of the phase separation or equilibrium model for micelle formation. Micellisation takes place where the energy of dissociation of hydrocarbon chain of the monomer is sufficient to overcome the electrical repulsion between the ionic head groups and the decrease in entropy accompanying the aggregation [27].

All the thermodynamic parameters of micellisation at 0.17, 0.27, 0.37, and 0.47 mass fraction of co-solvent are presented in Tables 3–5. The $\Delta G_{\mathrm{m}}^{\mathrm{o}}$ values are negative since thermodynamically stable micelle are formed spontaneously while the little change in thermodynamic parameter as temperature changes in the binary system signified that the process of micellisation was less spontaneous in nature.

The value of $\Delta G_{\mathrm{m}}^{\mathrm{o}}$ also varied with temperature as represented in Table 3 on addition of EG, DMSO, and DMF as co-solvent. However, the less negativity was observed in $\Delta G_{\mathrm{m}}^{\mathrm{o}}$ for CTABr upon addition of organic solvents is mainly determined by the increase in the CMC when the organic solvent content increases. This can be explained in terms of the transfer of the surfactant tail from the bulk phase into the micellar core and that of the alkyl chains in the head groups from the bulk phase into the micellar surface (or deeper if the chains are sufficiently long) are less spontaneous when the amount of organic solvent in the mixture increased. For this reason, and taking into account the $\Delta G_{\mathrm{m}}^{\mathrm{o}}$ values listed in Tables 3, one can infer that for CTABr, the addition of organic solvents which remain principally located in the bulk phase makes the micellisation process less spontaneous [28, 29].

Table 3: $\Delta G_{\mathrm{m}}^{\mathrm{o}}$ for CTABr in different aqueous-organic media at various temperatures.

10^{-2} ω_s Co-solvent	**Temperature (K)**				
	293.1	298.1	303.1	308.1	313.1
$\Delta G_{\mathrm{m}}^{\mathrm{o}}$ Change in Gibb's Free Energy (KJ mol^{-1})					
Water	-45.36	-45.30	-45.25	-45.21	-45.16
EG–Water					
17	-44.90	-43.84	-43.24	-43.10	-42.37
27	-40.15	-39.80	-38.80	-38.42	-37.96
37	-41.99	-41.23	-41.10	-40.85	-40.72
47	-36.83	-36.20	-35.71	-35.13	-34.97
DMSO–Water					
17	-43.80	-43.53	-43.40	-43.20	-44.12
27	-42.64	-41.89	-41.58	-41.42	-41.24
37	-39.67	-38.86	-38.69	-38.13	-37.68
47	-34.70	-33.95	-33.31	-33.45	-31.43
DMF–Water					
17	-40.72	-40.36	-40.17	-39.17	-39.33
27	-36.65	-35.96	-35.54	-34.71	-33.84
37	-28.85	-28.35	-27.37	-26.65	-26.24
47	-23.85	-23.14	-22.43	-21.41	-

The negative $\Delta H_{\mathrm{m}}^{\mathrm{o}}$ values are evidence that London – dispersion interactions represents the major attractive force for micellisation and that micellisation proceeded via an exothermic process [30]. The $\Delta S_{\mathrm{m}}^{\mathrm{o}}$ value for CTABr–water-co-solvent system was positive, indicating that the micellisation process is favoured by entropy gain as observed in Table 5. Large positive value of entropy in the binary system dictated the randomness after micellisation and this clearly showed that the micellisation of CTABr in the binary system is

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governed mainly by hydrophobic interaction between the surfactant hydrophobic part and the organic molecule mixture resulting in the total breakdown of the water structure surrounding the hydrophobic group as they transfer from aqueous bulk phase to non-aqueous micellar interior.

Table 4: $\Delta H_{\mathrm{m}}^{\mathrm{o}}$ for CTABr in different aqueous-organic media at various temperatures.

10^{-2} ω_s **Co-solvent**	**Temperature (K)**				
	293.1	298.1	303.1	308.1	313.1
Change in Enthalpy of Micellisation ($\Delta H_{\mathrm{m}}^{\mathrm{o}}$) (KJ.Mol^{-1})± 0.50					
Water	-5.00	-1.00	-3.00	-7.00	-13.00
EG–Water					
17	-38.40	-35.90	-33.60	-30.60	-26.80
27	-9.00	-17.00	-25.00	-34.00	-45.00
37	-30.00	-37.00	-40.00	-46.00	-52.00
47	-45.00	-50.00	-56.00	-60.00	-63.00
DMSO–Water					
17	-38.10	-37.10	-36.20	-40.50	-39.90
27	-42.50	-41.80	-42.00	-42.00	-41.60
37	-67.34	-68.00	-68.00	-69.27	-70.00
47	-79.40	-81.50	-83.50	-85.70	-87.70
DMF–Water					
17	-58.00	-58.00	-60.00	-62.00	-63.00
27	-73.50	-75.40	-77.30	-79.00	-81.70
37	-88.50	-81.90	-84.30	-85.70	-67.00
47	-99.00	-95.00	-93.00	-90.00	-

Table 5: $\Delta S_{\mathrm{m}}^{\mathrm{o}}$ for CTABr in different aqueous-organic media at various temperatures.

10^{-2} ω_s **Co-solvent**	**Temperature (K)**				
	293.1	298.1	303.1	308.1	313.1
Change in Entropy of Micellisation $\Delta S_{\mathrm{m}}^{\mathrm{o}}$ (J Mol^{-1} K^{-1})					
Water	136.81	148.81	139.26	169.59	185.76
EG–Water					
17	15.35	23.28	31.24	41.03	52.92
27	103.54	76.48	49.92	19.96	38.45
37	37.50	13.75	4.06	16.72	36.06
47	31.29	46.29	60.34	80.72	89.52
DMSO–Water					
17	16.04	11.98	8.25	2.27	7.09
27	3.00	1.00	1.39	0.58	0.77
37	94.40	97.75	96.70	101.07	103.23
47	112.51	129.51	135.59	149.57	159.72
DMF–Water					
17	58.96	59.17	65.42	72.15	75.60
27	125.73	132.30	137.78	143.75	152.86
37	103.10	112.55	121.84	126.74	130.18
47	85.81	73.33	67.87	60.33	-

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The variation of $\Delta H_{\mathrm{m}}^{\mathrm{o}}$ values with temperature as shown in Figure 4 could be ascribed to change in the hydration of the head groups during micellisation.

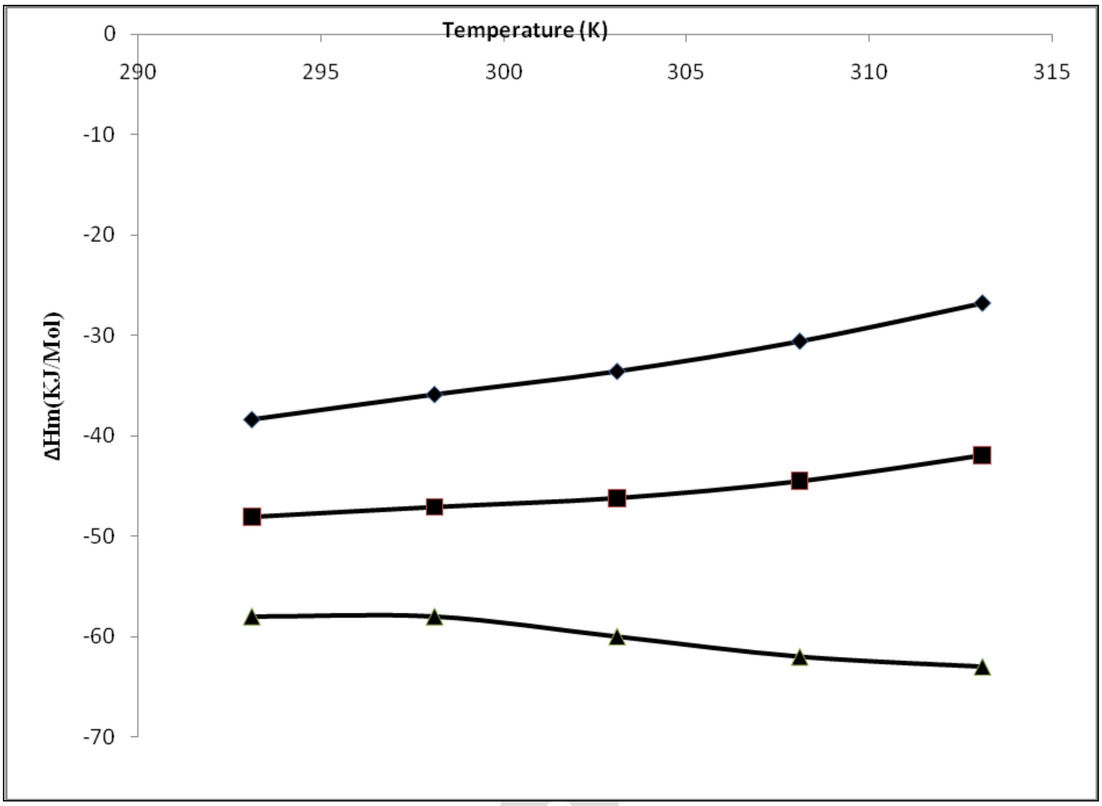

Figure 4: The change in enthalpy ($\Delta H_{\mathrm{m}}^{\mathrm{o}}$ KJ mol^{-1}) against temperature in 0.17 mass fraction (ω_{s}) of organic solvent (♦ = EG + Water, ■ = DMSO + Water; ▲ = DMF + Water).

The magnitude of $\Delta S_{\mathrm{m}}^{\mathrm{o}}$ is lower in the presence of co-solvent than in the absence of co-solvent. This suggested that the solvents still controlled the three-dimensional water matrix, indicating that the micellisation process of the studied surfactant is exothermic though the positive values of $\Delta S_{\mathrm{m}}^{\mathrm{o}}$, are due to the melting of flickering cluster" around hydrocarbon ends of the surfactant monomer and the increase randomness of the hydrocarbon chains in the micelle core. The amphiphilic monomers with a long hydrocarbon chain increased the orderliness of water by the formation of a Frank-Evan iceberg around the hydrocarbon chain which resulted in a decrease in the entropy of the system.

4. Conclusion

The micellisation of the cationic surfactant CTABr in EG, DMSO, and DMF binary mixture was investigated by conductivity measurement over temperature range of 298.1–313.1 K. The CMC and degree of counterion dissociation (α) values increased with increase in the amount of EG, DMSO, and DMF. Addition of organic solvents to the CTAB–water system made the micellisation process less spontaneous. The London-dispersion interaction represented the major attraction force for micellisation that proceeded via an exothermic process. The micellisation in CTAB–water-co-solvent system is favoured by entropy gain.

Competing Interests

Authors do not have any competing interests.

Authors' Contributions

SE developed, carried out and analysed data; NA, IA, and CO supervised the preparation of the manuscript; MO assisted with the preparation of the manuscript.

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