

Article

Interaction of cetyltrimethylammonium bromide with drug in aqueous/electrolyte solution: A combined conductometric and molecular dynamics method study

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ABSTRACT

Interaction between beta-lactum antibiotic drug ciprofloxacin hydrochloride (CFH) and cationic surfactant cetyltrimethylammonium bromide (CTAB) was performed conductometrically in aqueous as well as in the occurrence of different salts (NaCl, KCl as well as NH_4Cl) over the temperature range of 298.15–323.15 K at the regular interval of 5 K. CFH drug has been suggested for the treatment of bacterial infections such as urinary tract infections and acute sinusitis. A clear critical micelle concentration (CMC) was obtained for pure CTAB as well as (CFH + CTAB) mixed systems. The decrease in CMC values of CTAB caused by the addition of CFH reveals the existence of the interaction between the components and therefore it is the indication of micelle formation at lower concentration of CTAB and their CMC values further decrease in attendance of salts. A nonlinear behavior in the CMC versus T plot was observed in all the cases. The ΔG_m^0 values are found to be negative in present study systems demonstrated the stability of the solution. The values of ΔH_m^0 and ΔS_m^0 reveal the existence of hydrophobic and electrostatic interactions between CFH and CTAB. The thermodynamic properties of transfer for the micellization were also evaluated and discussed in detail. Molecular dynamic simulation disclosed that environment of water and salts have impact on the hydrophobic interaction between CFH and CTAB. In water and salts, CTAB adopts spherical micelle in which charged hydrophilic groups are interacted with waters whereas hydrophobic tails form the core of the micelle. This hydrophobic core region is highly conserved and protected. In addition, micelle formation is more favorable in aqueous NaCl solution than other solutions.

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1. Introduction

Many researchers have paid attention to surfactants (cationic/anionic/nonionic) extensively not only for their broad application in regularly utilized products for example fabric softeners, cosmetics, antimicrobial agents and in mining as well as in paper manufacturing [1–5] but also for their leniency to eyes, skin and clothes along with their biodegradability. The interaction of surfactants with various types of pharmaceutical excipients is crucial for wide range of biological, pharmacological and clinical points of view. The interactions between drugs and surfactants have been studying with considerable attention in recent years since surfactants are extensively used in drug delivery [1–3]. In pharmaceutical industries surfactants are extensively used as solubility enhancer, emulsifier, diluents, stabilizer *etc.* These applications of surfac-

tants are mainly dependent on the complex formation behavior of surfactants with solutes such as drugs, dyes, organic molecules *etc.* as well as the micelle formation of surfactant at a critical concentration which is known as critical micelle concentration (CMC) [1,4–6].

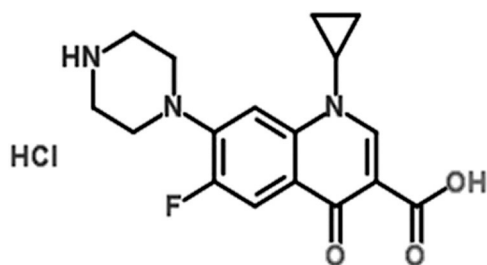
Micelles have found diverse benefits over other choices, concerning their task as drug carriers [6]. Micelles can enhance the bioavailability of hydrophobic drugs by solubilizing [7], they have the capability of staying in blood for extended period along with micelles which afford slow gathering in the particular area. The size of micelles is moderately sufficient for their amassing in body areas with permeable vasculature [8] and also they can be simply prepared on huge amount.

Amphiphile mixed systems are well accounted in the literature, being of key interest in order to advance their self-assembly and convenient applications [1,4–8].

Ciprofloxacin hydrochloride (CFH) [Scheme 1], is a broad spectrum antibiotic drugs belongs to quinolone group which has been suggested for use in the treatment of bacterial infections such as urinary tract

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Scheme 1. Molecular structure of ciprofloxacin hydrochloride (CFH).

infections, acute sinusitis, uncomplicated cervical and inhalational anthrax, sinuses, skin, lungs, ears, bones, in addition to joints attributable to susceptible bacteria [9].

In our previous papers, interaction of different drugs and amino acids with ionic surfactants such as hexadecyltrimethylammonium bromide (HDTAB), dodecyltrimethyl-ammonium bromide (DTAB) and cetyltrimethylammonium bromide (CTMAB) in aqueous solution as well as in occurrence of different salts was earlier accounted [10–14]. Srivastava *et al.* [15] determined the critical micelle concentrations by examining the interaction between tetracaine hydrochloride and sodium deoxycholate mixture and found the synergism behavior (attractive interaction) between the components. Yang *et al.* [16] have studied the interaction of CFH with different surfactants using fluorescence spectroscopic method. They observed the change of fluorescence intensity and described the existence of hydrophobic interaction between CFH and surfactants. Chauhan *et al.* [17,18] have studied the micellization behavior of sodium dodecyl sulfate (SDS) in the presence of furosemide (cardiovascular drug) and dimethylsulfoxide (DMSO)/salts at different temperatures. They found that micellization behavior of SDS in aqueous electrolyte solutions in the presence of DMSO arises from counterion-/solvent (DMSO) and intermolecular interactions. Addition of DMSO has a profound influence on the micellar properties of SDS and it leads to the formation of charged complex between DMSO and furosemide preferentially due to the solubilization of drugs in the micellar core.

Interaction between surfactants and various types of amphiphiles together with drugs is already accounted earlier [3–8,11–15] but still very less experiment has been performed so far regarding the interaction between CFH and CTAB using conductometric method therefore in present study we have evaluated the CFH and CTAB mixture interaction in the absence and attendance of various salts (NaCl, KCl as well as NH_4Cl). The addition of various additives into aggregates of an amphiphiles will affect its physicochemical properties such as degree of ionization, reaction rates and clouding/phase separation [19–22]. The sodium and potassium ions are among the most important metal ions in biology. Sodium is the chief positive ion in fluid outside of cells. Potassium is the chief positive ion obtained inside of cells. The concentration of these ions is controlled by intricate control systems, such as the sodium/potassium pump, which also plays a significant role in transmitting nerve signals [23]. Salts support micelle growth by withdrawing the electrostatic interaction among the head groups. Salts reduce the critical micelle concentration (CMC) which means that it enhances the aggregation number (N_{agg}) [24]. At higher salt

concentration the shape of spherical micelles changes into non-spherical by reducing electrostatic repulsion between the polar head groups along with the migration of the hydrophobic groups apart from the aqueous surroundings that are credited to micelle growth. The various physiochemical parameters associated with the interaction of CFH–CTAB mixture in aqueous and in attendance of salts at different temperatures. The properties of mixed systems, obtained by mixing of different amphiphiles, can be altered according to the properties required for a particular application. In addition, to disclose the molecular level interpretation of the non-bonding interactions between CFH and CTAB, molecular dynamics are performed in water, aqueous NaCl and KCl solutions.

2. Experimental and Computational

2.1. Materials and conductivity technique

All materials used were of analytical grade and used as received. Table 1 shows details about the compounds used in the present study. The stock solutions of CFH as well as CTAB (the attendance/absence of NaCl, KCl or NH_4Cl) were prepared in molar concentration unit using double distilled–deionized water having specific conductivity $1.5\text{--}2.0\ \mu\text{S}\cdot\text{cm}^{-1}$ (over the temperature range $298.15\text{--}318.15\ \text{K}$). Electric balance (Mettler Toledo) was used for weight measurement of samples. An aqueous solution $25\ \text{mmol}\cdot\text{L}^{-1}$ CTAB (the attendance/absence of NaCl, KCl or NH_4Cl) was regularly placed to 20 ml of known concentration of CFH solution in the absence/attendance of salt at a fixed temperature followed by measurements of conductivity of the resultant mixture solution. The determination of the specific conductivity of (CFH + CTAB) mixed system was done by means of a 4510 conductivity meter (Jenway, UK) having a dip cell of cell constant $0.97\ \text{cm}^{-1}$ (the value is provided by manufacturer) and with alternating current (AC) voltage source at frequency of 60 Hz [5–8,11–14,25,26]. Conductivity meter was calibrated with KCl solution with appropriate concentration range. The error in conductance measurements is around $\pm 0.5\%$. The required temperature was controlled with the help of RM6 Lauda thermostated bath with accuracy of $\pm 0.2\ \text{K}$. To view the outcome of salt, all solutions were prepared in attendance of NaCl, KCl or NH_4Cl . Critical micelle concentration (CMC) values were determined from the abrupt changes in specific conductance values of CTAB in water/(drug + water) mixed system with the increase of concentration of CTAB.

2.2. Molecular dynamics study

The initial structure of CFH and CTAB structure was optimized by Universal Force Field (UFF) [27] using Gaussian 09 program [28]. Molecular dynamic (MD) simulation was performed on CFH–CTAB system in water, NaCl + H_2O and KCl + H_2O . The initial optimized CTAB surfactants are assembled together through continuous minimization. 16 CTAB molecules are considered and one drug molecule is randomly placed in each system. For considering salt containing surfactant–drug system, 1% of NaCl and KCl were used. All molecular dynamic simulations were conducted using AMBER14 force field [29] in the suite of YASARA Dynamic program [30]. A cut-off radius of 0.8 nm was used for short-range van der Waals and Coulomb

Table 1
Provenance, purity and CAS of the materials studied

Chemical	Source	Mass fraction ^① purity	CAS number	MW $\times 10^{-3}/\text{kg}\cdot\text{mol}^{-1}$	Specific conductance/ $\mu\text{S}\cdot\text{cm}^{-1}$
CTAB	Aldrich, USA	>0.99	57-09-0	364.46	
CFH	The Acme Laboratories, BD	0.98	93107-08-5	367.80	
NaCl	BDH, England	0.995	7647-14-5	58.44	
KCl	BDH, England	0.995	7447-40-7	74.55	
NH_4Cl	Merck, Germany	0.995	12125-02-9	53.49	
H_2O	Distilled–deionized				1.5–2

^① Purity of materials as declared by the supplier.

interactions. The particle-mesh Ewald method [31] was applied to calculate the long-range electrostatic interactions. Periodic boundary condition (cell box of $5.4 \text{ nm} \times 5.4 \text{ nm} \times 5.4 \text{ nm}$) and temperature of 298°C were considered for all simulations. Time step of 1.25 fs was used and simulation snapshots were captured at every 100 ps . 1036 water molecules were added to keep the solvent density of $1 \text{ g} \cdot \text{ml}^{-1}$ for both systems. A total of ~ 16500 atoms were present in these systems. The systems were minimized and equilibrated with the default protocols of the YASARA dynamic. Finally, 2000 ps non-constrained MD simulation was performed for each system.

3. Results and Discussion

3.1. Critical micelle concentration (CMC) and fraction of counter ion binding (β) of the micellization of pure CTAB and (CFH + CTAB) mixed system

Fig. 1 illustrates the variation of specific conductance (κ) with surfactant concentration of CTAB (c_{CTAB}) in water/(drug + water) mixed system at 303.15 K . The conductivity of surfactant solution was linearly changed with the concentration in the pre- as well as post-micellar regions. In the plot of κ versus c_{CTAB} a sharp break point was observed for pure CTAB and CTAB-drug mixed system in the absence and presence of salt. The surfactant concentration analogous to the break point was considered as the CMC for the system [3,11–14]. At low surfactant concentrations (below the CMC), the initial increase of specific conductance values was due to the contributions from the free CTA^+ and Br^- ions. Above the CMC, the incremental increase of specific conductance values becomes smaller because of the formation of CTAB micelles and also due to the condensation of the Br^- ions with CTAB micelles to form the Helmholtz layer which maintain the associated amphiphile system through surface charge neutralization therefore, lessening in intermolecular repulsion potential takes place [32]. Thus the micelles have poorer mobility than the free ions of CTAB. The literature values of CMC for pure CTAB in water at 303.15 K are in the range of $0.8\text{--}1.1 \text{ mmol} \cdot \text{L}^{-1}$ which are in good agreement with our observed values [4,11].

Degree of ionization (α) of micelles was evaluated as of the ratio of the slopes of the straight lines analogous to the above and below CMC [4,25,26,33]. If S_1 and S_2 are the slopes above and below CMC, α can be calculated from the ratios S_2/S_1 , therefore, fraction of counter ion binding (β) at CMC was computed by deducting the value of α from 1 i.e., $\beta = (1 - \alpha)$.

Critical micelle concentration (CMC) with its mole fractional values (X_{CMC}) and fraction of counterion binding (β) of pure CTAB and (CFH + CTAB) in water at 303.15 K is shown in Table 2. The values of CMC or

Table 2

Values of critical micelle concentration (CMC), mole fraction of critical micelle concentration (X_{CMC}), counter ion binding (β) and free energy change (ΔG_m^0) for CTAB and (CFH + CTAB) systems at 303.15 K having different concentrations of CFH^①

Systems	$c_{\text{drug}}/\text{mmol} \cdot \text{L}^{-1}$	$\text{CMC}/\text{mmol} \cdot \text{L}^{-1}$	$X_{\text{CMC}}/10^{-5}$	β	$\Delta G_m^0/\text{kJ} \cdot \text{mol}^{-1}$
CTAB	0.000	0.99	1.78	0.73	−47.87
(CFH + CTAB)	0.502	0.95	1.71	0.78	−50.23
	1.002	0.91	1.64	0.81	−49.50
	2.023	0.83	1.49	0.80	−50.48
	3.033	0.76	1.37	0.82	−52.20

^① Relative standard uncertainties (u_r) are $u_r(\text{CMC}) = \pm 3\%$, $u_r(\beta) = \pm 4\%$ and $u_r(\Delta G_m^0) = \pm 3\%$.

X_{CMC} for (CFH + CTAB) mixed system in water are obtained to be lower in comparison to pure CTAB. This result reveals that the addition of CFH favors the micellization of CTAB. At 303.15 K , the alteration in the CMC or X_{CMC} values is observed for (CFH + CTAB) mixture by means of the change in concentrations of CFH showing the interaction between CFH and CTAB. The result reveals that the adding of CFH favors the aggregation of CTAB. Larger negative free energy (ΔG_m^0) for CTAB and drug mixed systems for all the cases also support the interaction between the components.

The values of CMC or X_{CMC} and β for (CFH + CTAB) mixture at 303.15 K in the attendance of salts, are presented in Table 3. Some types of salts are attained in the human being and their amount in the body may change with time whereas their occurrence along with concentration may influence the interaction propensity of amphiphile mixtures. Therefore, it is important to have knowledge of surfactant as well as drug-surfactant mixed systems association behavior with temperature as well as the presence of electrolytes. The CMC or X_{CMC} values of (CFH + CTAB) mixed system at 303.15 K temperature in occurrence of salt were achieved to be less in comparison to their absence and value further decreases with enhancement of the ionic strength of salts. The CMC or X_{CMC} values of (CFH + CTAB) mixed system in attendance of salts at 303.15 K and at ionic strength, $I = 0.50 \text{ mmol} \cdot \text{L}^{-1}$ followed the order: $\text{CMC}_{\text{NaCl}} < \text{CMC}_{\text{KCl}} < \text{CMC}_{\text{NH}_4\text{Cl}}$ (Table 3). This change of CMC values may be due to the presence of different cations in the salts containing identical anion (Cl^-). By way of adding salt in the solution of pure as well as mixed amphiphiles, decrease in CMC values was also observed earlier [11–14,34,35]. The cationic/anionic amphiphiles form charged monolayer/mixed monolayer at the interfacial surface, on adding of salt in the solution the lowering of the thickness and potential of the electric double layer occurs [36]. Consequently, it lessens the electrostatic repulsion between the polar head groups and makes the

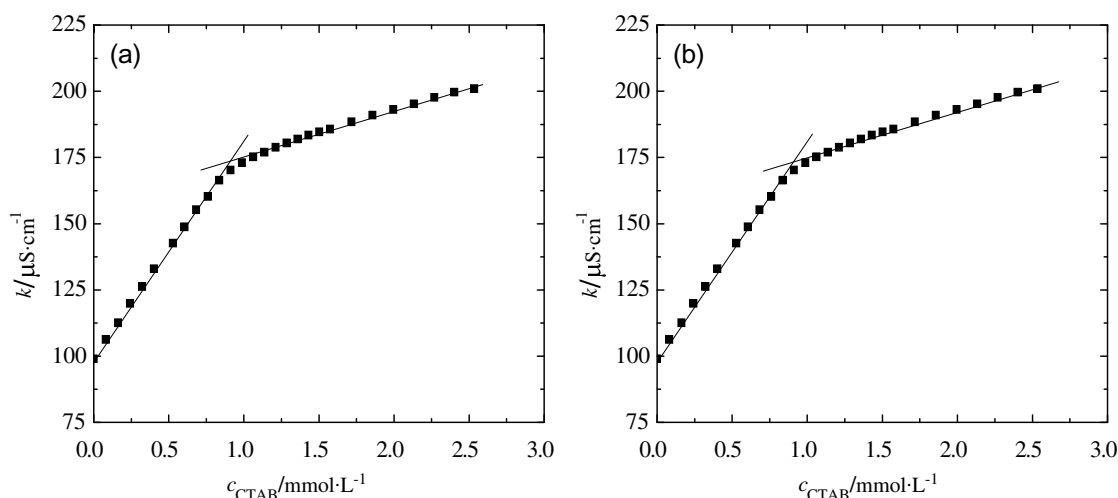


Fig. 1. Specific conductance (κ) versus concentration of CTAB for (a) pure CTAB in water and (b) (CFH + CTAB) mixed system containing $1.002 \text{ mmol} \cdot \text{L}^{-1}$ CFH in water at 303.15 K .

Table 3

Values of critical micelle concentration (CMC), mole fraction of critical micelle concentration (X_{CMC}), and counter ion binding (β) for pure CTAB and (CFH + CTAB) mixed system containing $1.002 \text{ mmol} \cdot \text{L}^{-1}$ CFH drug in pure water and in aqueous solutions of different salts at various temperatures^①

Medium	$C_{\text{salt}}/\text{mmol} \cdot \text{L}^{-1}$	T/K	$CMC/\text{mmol} \cdot \text{L}^{-1}$	$X_{\text{CMC}} \times 10^{-5}$	β
<i>CFH + CTAB</i>					
Water	0.00	303.15	0.91	1.64	0.78
NaCl + H ₂ O	0.501	303.15	0.78	1.40	0.77
	1.002	303.15	0.71	1.28	0.74
	2.032	303.15	0.68	1.22	0.75
	3.013	303.15	0.59	1.06	0.73
KCl + H ₂ O	0.505	303.15	0.83	1.49	0.72
	1.067	303.15	0.74	1.33	0.73
	2.035	303.15	0.70	1.26	0.75
	3.013	303.15	0.61	1.10	0.76
NH ₄ Cl + H ₂ O	0.506	303.15	0.85	1.53	0.72
	1.078	303.15	0.77	1.39	0.74
	2.038	303.15	0.72	1.30	0.71
	3.087	303.15	0.64	1.15	0.68
<i>CTAB</i>					
H ₂ O	0.00	298.15	1.01	1.82	0.73
		303.15	0.99	1.78	0.72
		308.15	1.05	1.89	0.71
		313.15	1.16	2.09	0.70
		318.15	1.23	2.21	0.70
		323.15	1.33	2.39	0.69
<i>CFH + CTAB</i>					
H ₂ O	0.00	298.15	0.93	1.67	0.75
		303.15	0.91	1.64	0.74
		308.15	0.98	1.76	0.74
		313.15	1.04	1.87	0.73
		318.15	1.11	2.00	0.72

^① Relative standard uncertainties (u_r) are $u_r(CMC) = \pm 3\%$ and $u_r(\beta) = \pm 4\%$.

amphiphiles effectively more hydrophobic leading to considerably lesser CMC value in contrast to aqueous solution. The repulsion among amphiphiles head groups is main cause for delaying aggregation.

The values of CMC or X_{CMC} and β for pure CTAB and (CFH + CTAB) mixed system at various temperatures in water are shown in Table 3 and in the presence of salts above values are given in Tables TS1–TS3 (Supplementary material). The values of CMC or X_{CMC} for (CFH + CTAB) mixed system at different temperatures in water and in the presence of salts are shown in Fig. 2 and in Figs. S1–S2 (Supplementary material). In all the cases the CMC or X_{CMC} values for pure CTAB and (CFH + CTAB) mixed system decrease equal to assure temperature, pass a lowest value and afterward the values have a tendency to raise by means of additional enhance in temperature. In Fig. 2 and in Figs. S1–S2, a nonlinearity behavior was observed in the X_{CMC} versus T plots. Such observation of nonlinearity/minimum position in the CMC versus T plots is also reported in the literature for different ionic amphiphiles in the absence and attendance of solutes [11]. The change of values of CMC by means of temperature can be elucidated through the change of the type of hydration neighboring the CTAB monomers and CTAB micelles. If an amphiphile is in monomeric condition in solution then hydrophobic as well as hydrophilic hydrations are feasible together while only hydrophilic hydration is achievable in case of micellized CTAB. Hydrophilic as well as hydration hydrations are probable to be decreased with rise of temperature. De-solvation of ionic/polar head group of CTAB/CFH (decrease in hydrophilic hydration) favors the micelle formation i.e. CMC values decrease while interruption of the structured water molecules and breaking of hydrogen bonds surrounding nonpolar parts of CTAB/CFH (decrease of hydrophobic dehydration) with the increase of temperature disfavors the micelle formation i.e. CMC values increase [4,11,12,37,38]. Therefore the magnitude of above both aspects determines that the values of CMC enhance or reduce over a distinct range of temperatures. Generally the first factor dominates at lower temperature range and after a certain temperature,

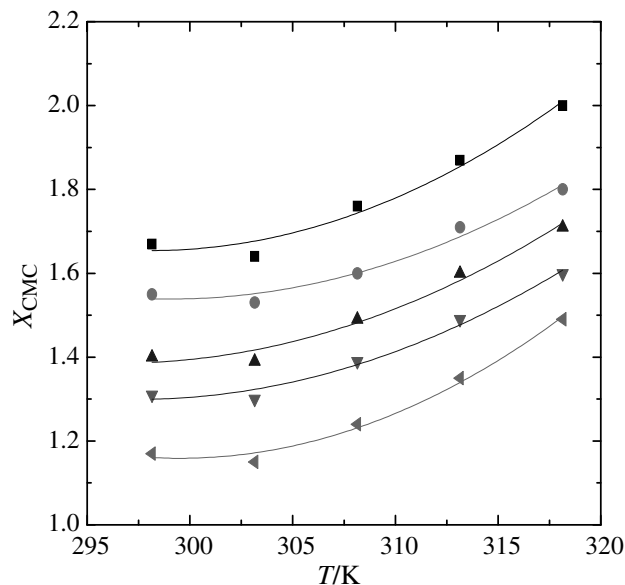


Fig. 2. Plot of X_{CMC} versus T for (CFH + CTAB) mixed system containing $1.002 \text{ mmol} \cdot \text{L}^{-1}$ CFH drug in water (■) and aqueous solution of $0.501 \text{ mmol} \cdot \text{L}^{-1}$ (●), $1.002 \text{ mmol} \cdot \text{L}^{-1}$ (▲), $2.032 \text{ mmol} \cdot \text{L}^{-1}$ (▼) and $3.013 \text{ mmol} \cdot \text{L}^{-1}$ (◄) NaCl.

the second factor initiates governing. The outcomes of temperature on trend of CMC of pure CTAB along with their mixed systems with drug are remaining the similar in the presence of inorganic salt but the magnitude of CMC is obtained to be less.

3.2. Thermodynamic parameters of micellization for pure CTAB and (CFH + CTAB) mixed system

The thermodynamic parameters are an effective tool to study the mode of interaction in the molecular level. By using the following equations, the thermodynamic parameters of (CFH + CTAB) mixed system enclosing 1:1 electrolyte amphiphile were evaluated [11–14,36,39–41]:

$$\Delta G_m^0 = (1 + \beta) RT \ln(CMC) \quad (1)$$

$$\Delta H_m^0 = -(1 + \beta) RT^2 (\partial \ln CMC / \partial T) \quad (2)$$

$$\Delta S_m^0 = (\Delta H_m^0 - \Delta G_m^0) / T \quad (3)$$

where the values of CMC were taken in the mole fraction unit. $\ln(CMC)$ versus T plot (Fig. 3) was found to be nonlinear. The plots were used to calculate ΔH_m^0 and slopes were drawn at each temperature which were considered as equivalent to value of $\partial \ln(CMC) / \partial T$ [11,36,39].

The ΔG_m^0 , ΔH_m^0 and ΔS_m^0 values for CTAB and drug–CTAB mixed systems in the absence and attendance of salts are summarized in Tables 4 and TS4–TS5 (Supplementary material). The values of ΔG_m^0 were found to be negative for pure CTAB and drug–CTAB mixed systems. We can see from the tables that the values of ΔG_m^0 for CTAB were found to be negative in the absence as well as attendance of drug/salts suggesting that the spontaneous formation of thermodynamically stable aggregates. In case of CTAB–drug mixtures, ΔG_m^0 achieved increasingly further negative with the increasing drug concentration signifying easiness of aggregation in mixed systems of CTAB and drug because drug supported CTAB micelles formation processes are thermodynamically spontaneous. The ΔG_m^0 values are all times additional negative in occurrence of salt also in comparison to aqueous solution representing that easy facilitation of the micellization process as driving force for aggregation was considerably enhanced in attendance of salt. For (CFH + CTAB) mixed systems, the values ΔH_m^0 in aqueous medium

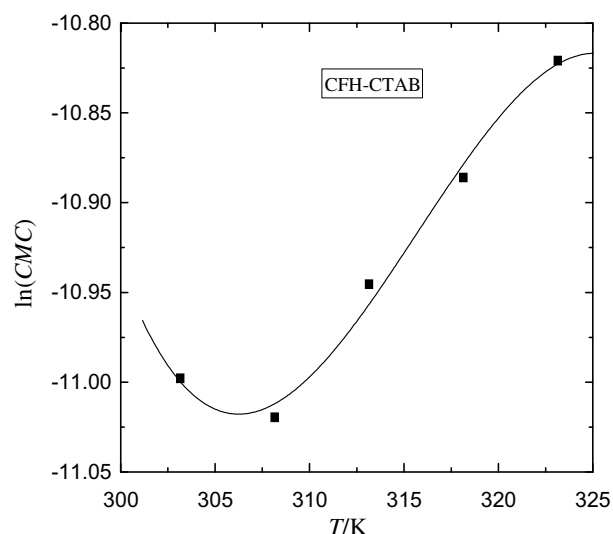


Fig. 3. Plot of $\ln(\text{CMC})$ versus T for (CFH + CTAB) mixed system containing $1.002 \text{ mmol} \cdot \text{L}^{-1}$ CFH in water.

Table 4

Values of thermodynamic parameters for pure CTAB and (CFH + CTAB) mixed system containing $1.002 \text{ mmol} \cdot \text{L}^{-1}$ CFH in water and aqueous solution of NaCl^①

$C_{\text{NaCl}}/\text{mmol} \cdot \text{L}^{-1}$	T/K	$\Delta G_m^0/\text{kJ} \cdot \text{mol}^{-1}$	$\Delta H_m^0/\text{kJ} \cdot \text{mol}^{-1}$	$\Delta S_m^0/\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
CTAB				
0.000	298.15	−46.85	5.08	174.19
	303.15	−47.41	−1.59	151.13
	308.15	−47.65	−8.01	128.63
	313.15	−47.70	−13.10	110.49
	318.15	−48.20	−16.64	99.19
	323.15	−48.31	−22.01	81.39
(CFH + CTAB)				
0.000	298.15	−48.60	3.47	174.64
	303.15	−49.50	−9.14	140.16
	308.15	−49.10	−20.94	115.38
	313.15	−49.79	−20.85	90.40
	318.15	−49.94	−23.24	74.21
	323.15	−48.06	13.44	206.28
0.501	298.15	−48.43	5.26	177.09
	303.15	−48.92	−13.31	115.57
	308.15	−48.33	−21.11	86.92
	313.15	−48.87	−25.22	74.36
	318.15	−48.63	18.12	223.89
	323.15	−49.54	7.33	187.61
1.002	298.15	−49.67	−14.91	112.8
	303.15	−50.04	−24.79	80.61
	308.15	−49.98	−28.77	66.66
	313.15	−49.44	24.40	247.69
	318.15	−49.81	10.51	198.98
	323.15	−50.03	−17.12	106.79
2.032	298.15	−49.80	−24.03	82.29
	303.15	−49.93	−32.24	55.62
	308.15	−49.89	30.56	269.83
	313.15	−50.00	13.23	208.59
	318.15	−49.70	−25.19	79.56
	323.15	−49.00	−28.7	64.83
3.013	298.15	−49.25	−34.04	47.82
	318.15	−49.25	−34.04	47.82

^① Relative standard uncertainties (u_r) are $u_r(\Delta G_m^0) = \pm 3\%$, $u_r(\Delta H_m^0) = \pm 4\%$ and $u_r(\Delta S_m^0) = \pm 4\%$.

at 298.15 K were found to be positive, and their possible value changes into negative at the temperature 303.15 K and above and also their negative values increase with gradual increase in temperature. The ΔS_m^0 values were obtained to be positive at all temperatures and their values reduce via raise of temperature. Therefore, values of ΔS_m^0 and ΔH_m^0 signify that the micellization phenomenon is entropy directed

at inferior temperatures while at higher temperatures it turns into entropy as well as enthalpy directed. The negative value of ΔH_m^0 and positive value of ΔS_m^0 values for drug–surfactant mixtures indicating that not only hydrophobic interaction, the electrostatic interaction also take part in a vital task in the micellization [42]. The hydrophobic interaction reduces whereas the electrostatic contribution enhances by means of increase of temperature, maintaining the values of ΔG_m^0 almost constant at all temperatures studied. In the single system positive and negative values of enthalpy were also earlier obtained by other researcher [43–47].

In the attendance of salts the ΔH_m^0 values at lower temperatures are obtained to be positive, while at higher temperature their values change into negative and the negative values also increase with increase in temperature. Aggregation of amphiphiles is the phenomena in which monomers transform into micelles; hence, the entropy change is reasonably negative. In contrast, it is positive value that described the breaking of iceberg structures around the hydrophobic parts of the amphiphile monomer in company with the boosted randomness in the micelles core [48]. In occurrence of salts, the magnitude of the positive values of ΔS_m^0 for drug–CTAB mixed systems is a large amount more than their absence at inferior temperature as well as their values also enhance by raise in concentration of salts. Therefore, the aggregation of drug–surfactant mixtures was completely entropically directed phenomena at inferior temperature while that changes mutually entropy as well as enthalpy directed by enhance in temperature. In attendance of salts the ΔS_m^0 values turn out to be much lower as compared to the aqueous solution at higher temperature. Also at inferior temperatures the positive values of ΔH_m^0 enhance via rise in the concentrations of salts. The much higher positive values of both ΔS_m^0 and ΔH_m^0 at inferior temperatures are signifying the improved hydrophobic interactions among the hydrophobic group of surfactant along with interaction between the hydrophobic provinces of drugs and CTAB. The extent of hydrophobic interactions thus reduces by way of increase in temperature. The higher negative values of ΔH_m^0 at higher temperatures in the presence of salts also point out that electrostatic interactions turn out to be more considerable at higher temperature. The larger positive ΔS_m^0 values in NaCl solutions compared to those in KCl & NH_4Cl solutions indicate that hydrophobic interactions become more enhanced in aqueous NaCl solution i.e., disorderness of the solutions increases more owing the presence of NaCl as compared to other salts used in the present study. Besides the temperature, NaCl, KCl & NH_4Cl also causes a partial damage of hydrophobic hydration of amphiphile monomer and consequently, much less energy was needed for micellization. The high entropy value of any systems on the aggregation of amphiphiles has been clarified in two manners: (a) formation of the H_2O molecules close to the hydrocarbon chains in aqueous solution, ensuing the raise in the entropy value as the hydrocarbon chains are taken away from the aqueous solution to the core of the micelle—“hydrophobic bonding” (b) enhanced liberty of the hydrophobic length in the nonpolar interior of the micelle in comparison to monomeric aqueous solution [49,50]. A negative ΔH_m^0 value possibly will arise when hydration of H_2O molecules in the region of the hydrophilic portion turns out to be further significant in comparison to the damage of the H_2O structure in the region of the hydrophobic portion of amphiphile monomers [51–53].

The net value of ΔG_m^0 is the sum of the enthalpic (ΔH_m^0) and entropic ($-T\Delta S_m^0$) contributions [49] and the observations in this case are graphically shown in Fig. S3 (Supplementary material). For (CFH + CTAB) mixed system in aqueous medium the contribution of enthalpy to the negative free energy change decreases and that of entropy increase with increase of temperatures. For (CFH + CTAB) in aqueous solution of salts follow the almost similar trend though some exception is observed in the presence of salts.

The free energy of transfer ($\Delta G_{\text{m.tr.}}^0$), enthalpy of transfer ($\Delta H_{\text{m.tr.}}^0$) and entropy of transfer ($\Delta S_{\text{m.tr.}}^0$) micelles from pure (CTAB + water)

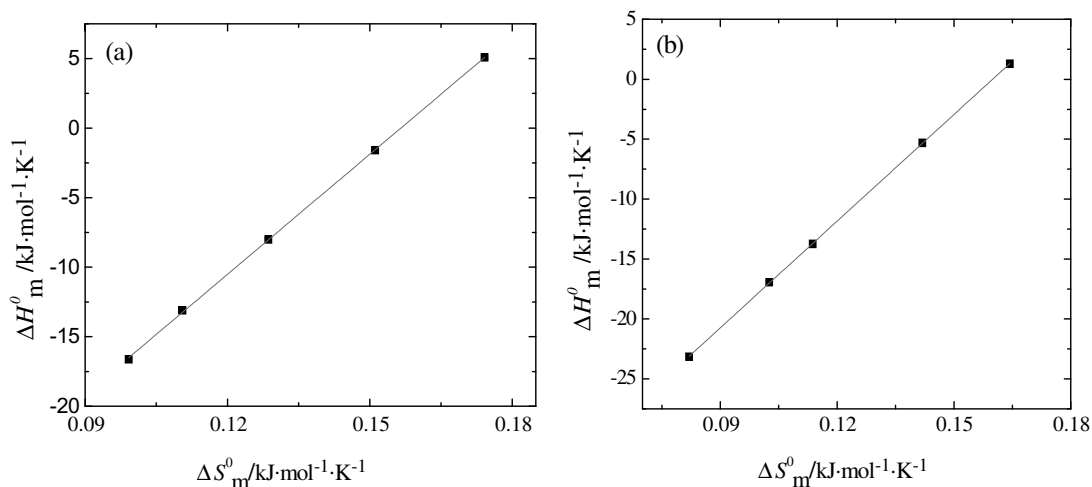


Fig. 4. Enthalpy-entropy compensation plot for (a) CTAB in H₂O and (b) (CFH + CTAB) mixed system containing 1.002 mmol·L⁻¹ CFH in aqueous medium.

to (CTAB + CFH + water) and (CTAB + CFH + salt) are attained by means of the following equation [54]:

$$\begin{aligned}\Delta G_{m.tr.}^0 &= \Delta G_m^0(\text{aqueous additive}) - \Delta G_m^0(\text{aqueous}) \\ \Delta H_{m.tr.}^0 &= \Delta H_m^0(\text{aqueous additive}) - \Delta H_m^0(\text{aqueous}) \text{ and} \\ \Delta S_{p.m.tr.}^0 &= \Delta S_{p.m.}^0(\text{aqueous additive}) - \Delta S_{p.m.}^0(\text{aqueous})\end{aligned}$$

The values of $\Delta G_{m.tr.}^0$, $\Delta H_{m.tr.}^0$ and $\Delta S_{p.m.tr.}^0$ for (CFH + CTAB) mixed system in aqueous solution as well as in occurrence of salts are summarized in Tables TS6–TS8 (Supplementary material). The free energy of transfer ($\Delta G_{m.tr.}^0$) for (CFH + CTAB) mixed system in the absence and presence of salts containing higher salt concentrations studied is found to be negative while the values in aqueous solution of salts containing lower salt concentrations studied are positive. The transfer enthalpies ($\Delta H_{m.tr.}^0$) for the micellization of (CFH + CTAB) mixture in the absence as well as in attendance of salts at higher temperatures are mostly negative while the values in the presence of salts at lower temperatures are found to be positive. Negative values of $\Delta H_{m.tr.}^0$ were also observed for the transfer of enthalpies from aqueous medium of salt as well as amino acids to the urea solution [55,56]. The negative value of transfer enthalpies indicates that the transfer of hydrophilic portion of amphiphiles from H₂O to the solution of CFH drug and (CFH + salts) mixtures means that it is exothermic process while for positive $\Delta H_{m.tr.}^0$ values suggest that transfer of the hydrophobic portion of amphiphiles from H₂O to the solution means that it becomes endothermic.

Table 5

Values of $\Delta H_{m.tr.}^0$ and T_c for pure CTAB in water and (CFH + CTAB) mixed system containing 1.002 mmol·L⁻¹ CFH in water as well as aqueous solution of salts^①

System	Medium	$c_{\text{salts}}/\text{mmol}\cdot\text{L}^{-1}$	$\Delta H_{m.tr.}^0/\text{kJ}\cdot\text{mol}^{-1}$	T_c/K
CTAB	H ₂ O	0.0	-45.00	287.90
(CFH + CTAB)	H ₂ O	0.0	-47.40	296.50
(CFH + CTAB)	(H ₂ O + NaCl)	0.501	-46.07	282.76
		1.002	-48.35	295.66
		2.032	-50.85	298.15
		3.013	-51.71	300.81
(CFH + CTAB)	(H ₂ O + KCl)	0.505	-43.50	290.36
		1.067	-44.68	292.72
		2.035	-48.15	294.44
		3.013	-50.58	299.22
(CFH + CTAB)	(H ₂ O + NH ₄ Cl)	0.506	-46.02	289.42
		1.078	-47.50	291.28
		2.038	-48.17	293.68
		3.087	-49.59	295.03

^① Relative standard uncertainty (u_r) is $u_r(\Delta H_{m.tr.}^0) = \pm 4\%$.

The plots of ΔH_m^0 versus ΔS_m^0 were found to be linear with R^2 values in the range 0.990–0.999 in all the cases and such observable fact is recognized as entropy–enthalpy compensation that was obtained (Fig. 4) using Eq. (4) [57]:

$$\Delta H_m^0 = \Delta H_m^{0,*} + T_c \Delta S_m^0 \quad (4)$$

In general, the micellization phenomenon is believed to hold a chemical part and solvation part. In Eq. (4), T_c is the slope and called as compensation temperature that describes the interaction between solute and solvent (solvation part). The intercept $\Delta H_m^{0,*}$ is the intrinsic

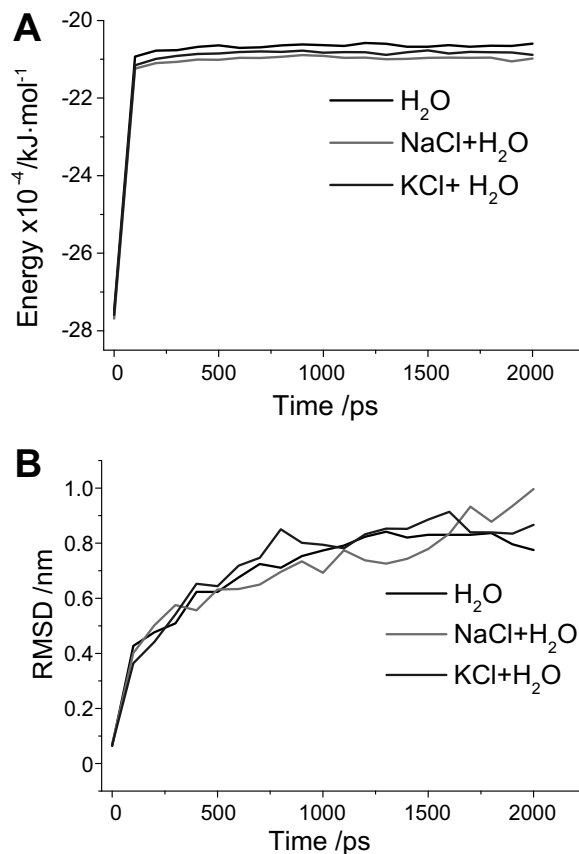


Fig. 5. A) Energy (kJ·mol⁻¹), B) RMSD (nm) of CFH–CATB complex in H₂O, NaCl + H₂O and KCl + H₂O over time (ps).

enthalpy gain that provides idea regarding solute–solute interaction (chemical part). Akin behavior regarding compensation phenomenon was also obtained by other researchers containing different surfactants and solutes [11–14]. The negative intercept is the intrinsic enthalpy gain, $\Delta H_m^{0,*}$ and the slope of the compensation plots is the T_c . The values of $\Delta H_m^{0,*}$ and T_c for pure CTAB and (CFH + CTAB) mixtures in aqueous as well as in the presence of salts are shown in Table 5. The T_c values for (CFH + CTAB) system are almost the same both in the absence and attendance of salts. The T_c values are found to be in the range of 282–300 K in this study. The T_c values lying in the range of 270–300 K have been employed as an investigative assessment for the contribution of H_2O in the protein solution [58]. Such compensation phenomenon was also detected earlier for the aggregation of charged surfactants in

aqueous solution [59]. The higher negative $\Delta H_m^{0,*}$ values indicate that the aggregation of CTAB was facilitated even at $\Delta S_m^0 = 0$. The raise of the negative $\Delta H_m^{0,*}$ values reveals the enhancement of the stability of the micelle formation.

3.3. Dynamics and interaction of CFH–CATB complex in H_2O , $H_2O + NaCl$ and $H_2O + KCl$

The energy and root-mean-square deviation (RMSD) value of the heavy atom in CFH + CTAB complex with three different environments including H_2O , $H_2O + NaCl$ and $H_2O + KCl$ at 298 K are presented in Fig. 5. In $H_2O + NaCl$ environment, the energy of the CFH–CTAB complex is more negative in comparison with H_2O and $H_2O + KCl$ environment.

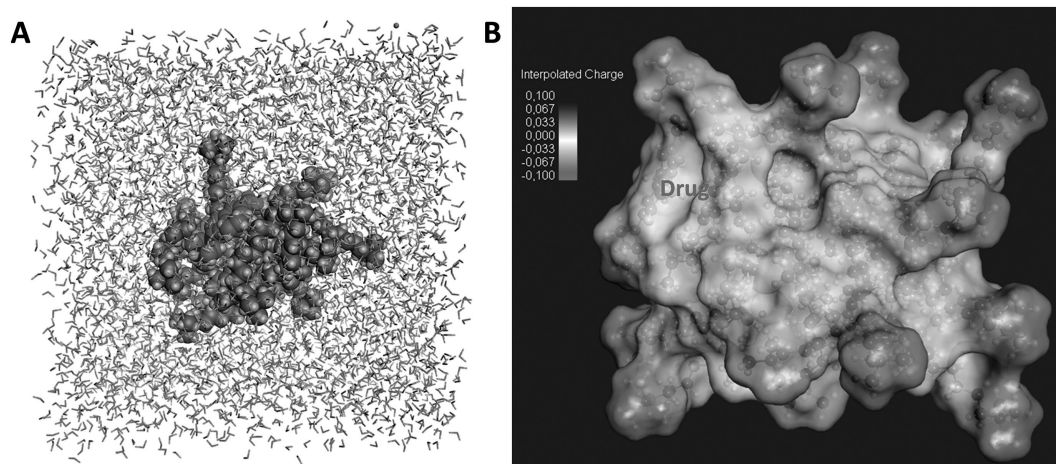


Fig. 6. CFH–CATB complex in A) $H_2O + NaCl$ in which CATB in gray and CFH in pink. B) Charged surface (blue represents the positive and red represents negative charge).

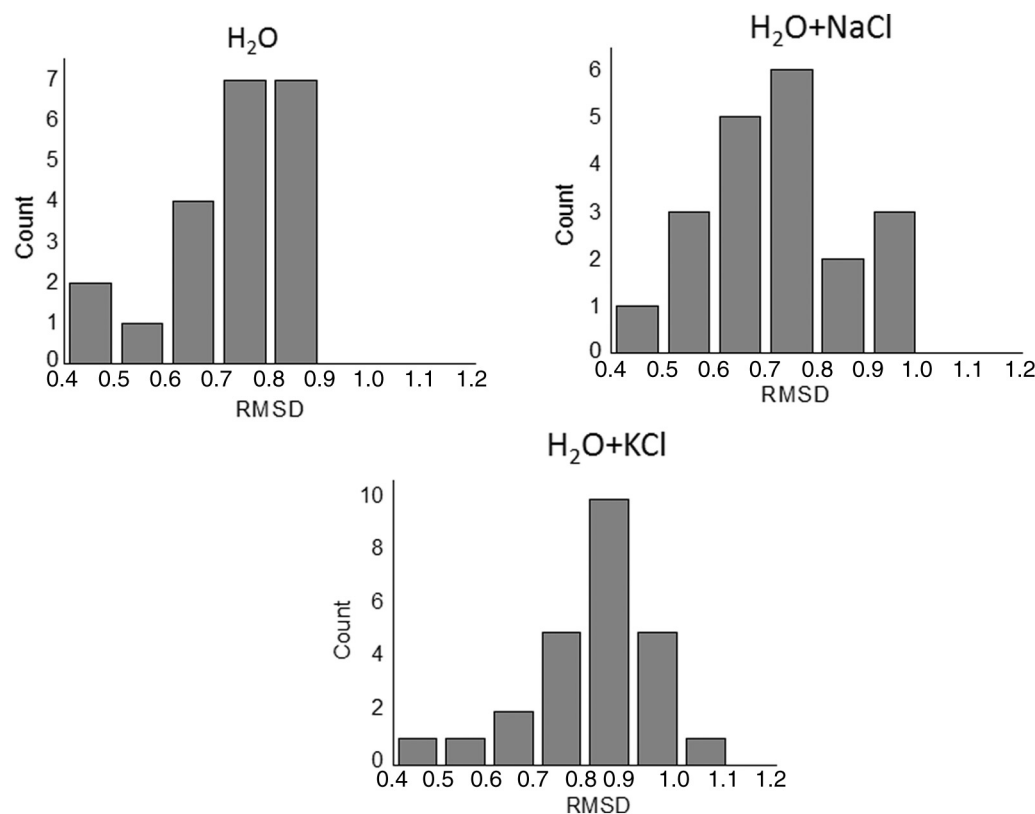


Fig. 7. RMSD (nm) distribution of heavy atoms related to CFH–CATB complex in H_2O , $NaCl + H_2O$ and $KCl + H_2O$. The RMSD distribution is histogrammed using a given bin-size (0.1 nm).

This indicates that micelle formation in $\text{H}_2\text{O} + \text{NaCl}$ environment is more favorable. In all cases, the hydrophilic head of CTAB is interacted with the surrounding water molecules and hydrophobic tails are directed inside (Fig. 6A). The charged surface also confirms that most of the positive charges are located at the micelle surface whereas the core of the micelle remained neutral (Fig. 6B). The shape of the micelle is nearly spherical. The drug molecule CFH remains at the surface of the micelle. Na^+ , K^+ and Cl^- ions are dissolved in waters. The average root-mean-square deviation (RMSD) value of the heavy atom in the surfactant–drug system in $\text{H}_2\text{O} + \text{NaCl}$ is lower (0.75 nm) compared to the deviation (0.8 nm) of that in pure water (Fig. 7). Moreover, RMSD value of the heavy atoms in $\text{H}_2\text{O} + \text{KCl}$ is also as large as 0.85 nm. These results also show that micelle of CTAB–CFH in $\text{H}_2\text{O} + \text{NaCl}$ environment is relatively more compacted or squeezed in comparison with other systems.

4. Conclusions

This study discloses the effect of temperature as well as concentration of drug (ciprofloxacin hydrochloride) on the micellar behavior of cationic surfactant cetyltrimethylammonium bromide (CTAB) both in the absence and presence of salts. Addition of drug decreases CMC value of pure surfactant at different temperature. Salts reduce the CMC of pure CTAB as well as their mixture with drug of different concentration. The calculated values of thermodynamic parameters reveal that the binding forces among CTAB molecules and between CFH and CTAB are mainly hydrophobic and exothermic interactions in nature. The negative ΔG_m^0 values demonstrate that the micellization phenomenon is the spontaneous process. The more positive ΔS_m^0 values in NaCl solutions in comparison to KCl and NH_4Cl solutions point out that hydrophobic interactions become more boosted in aqueous NaCl solution as compared to other salt. The higher negative ΔH_m^0 values point out the formation of stable micelles and the T_c values are almost similar to the biological fluid such as protein solution. The molecular dynamics simulation revealed that CTAB molecules formed spherical micelle in all environments while the micelle formation is favorable in $\text{NaCl} + \text{H}_2\text{O}$ environment in comparison with water and other salt environments.

Supplementary Material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cjche.2017.06.016>.

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