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Influence of octanohydroxamic acid on the association behavior of cationic surfactants: Hydrolytic cleavage of phosphate ester



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ABSTRACT

The surface properties and mixed micellization behavior of cetyltrimethylammonium bromide (CTAB), tetradecyltrimethylammonium bromide (TTAB) and dodecyltrimethylammonium bromide (DTAB) with octanohydroxamic acid (OHA) have been investigated by means of conductivity and surface tension measurements in aqueous solution and borate buffer at 300 K. The critical micelle concentration (cmc), surface properties such as maximum surface access (Γ_{max}), surface pressure at the cmc (Π_{cmc}) and minimum surface area per molecule (A_{min}) has been determined. The standard Gibbs free energy of micellization (ΔG_m^0), standard Gibbs free energy of adsorption (ΔG_{ad}^0), and standard Gibbs free energy of micellization per alkyl chain ($\Delta G_{m,lail}^0$) of cationic surfactant with OHA have been evaluated. The fluorescence quenching technique was used to estimate the aggregation number (N_{agg}) and packing parameter (P) for determining the structural feature of cationic surfactants in the presence of octanohydroxamic acid. The hydrolytic reaction of paraoxon with octanohydroxamic acid was studied under a cationic micellar system by using OHA⁻ at 9.2 pH and 300 K. The variations of surface properties from aqueous medium to the reaction condition have also been discussed. Pseudophase model (PPM) has been fitted for the quantitative treatment of the data.

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1. Introduction

The micellization behavior of conventional surfactants has been drawing much attention in the past two decades due to their unique properties and to minimize the unfavorable interaction with aqueous and organic solvent [1,2]. The aggregation behavior of different types of surfactants, i.e. cationic, anionic, non-ionic, zwitterionic and gemini surfactants are affected by properties of solvent such as the fluidity, polarity, hydrogen-bonded structure, hydro- and lipophilicity, which can be varied/controlled in mixed solvents with suitable combinations and compositions [3–5]. In recent years, the application of surfactants has a robust transition in both academic and industrial research [6–7]. These application areas include the use of surfactants as non-viral vectors for gene delivery [8], anti-fungal agents [9], drug delivery agents [10], as well as anti-microbial agents [11]. The physiochemical properties of surfactants viz. critical micelle concentration (cmc), surface pressure and free energy of micellization play a fundamental role to understand the interfacial behavior of monomer [12]. These properties

* Corresponding author. E-mail address: manmohanchem@gmail.com (M.L. Satnami). can be affected by adding the organic solvent and most important of those are between solute and solvent molecule interaction. The study of these interactions opens a new site into recognizing the morphology changes of the structure of surfactant from spherical to non-spherical shape in aqueous solution [13]. A number of literatures have investigated [14.15], to study the physiochemical properties of surfactant in the absence and presence of various additives such as alcohol, acid and organic polar solvents. Rahemat et al. [16] have studied the interaction of various alcohols (EtOH, BuOH) with 1-dodecyl-3-methylimidazolium bromide and DTAB in aqueous media by measuring several characteristic physical properties such as cmc, counter ion dissociation, surface pressure at the cmc etc. The result has been explained assuming behavior of alcohol with surfactants, some alcohol, i.e. MeOH and EtOH act as cosolvent and increases the cmc of surfactants and n-PrOH and n-BuOH performed as cosurfactants and decrease the cmc by their presence. Harutyunyan et al. [17] have investigated the micellization behavior, surface activity, aggregation number and packing parameter in the presence and absence of different types of amino acid, i.e. glycine, alanine, phenylalanine and leucine by surface tension and fluorescence measurement of surfactant solutions. The results have been found that the cmc, aggregation number and packing parameter increases with increasing the concentration of acid and surface area per head group

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decreases. Although the mixed micellization and structural transitions of quaternary alkylammonium surfactants with linear alkylamine [18], alkanol and alkanoic acids [19] have been studied, but, there is no report on the effect of octanohydroxamic acid (OHA) on the micellization and physiochemical properties of conventional surfactant viz. CTAB, TTAB and DTAB. Therefore, studying the behavior of octanohydroxamic acid in aqueous solution is a great importance. Hydroxamic acids have also been widely used as a catalytic agent towards the hydrolysis of phosphate esters which are responsible for inhibiting the activities of an enzyme which plays a crucial role for proper functioning of neurotransmitter in nervous system [20-22]. Hydroxamic acid has shown promising effects towards the catalysis of phosphate ester in the presence of cationic surfactant. The conventional surfactants such as CTAB, TTAB and DTAB enhance the reactivity accompanying with hydroxamic acid [23]. The reactivity of hydroxamic acid with surfactant depends on many physiochemical and thermodynamic factors, and morphology of micelle can alter in the presence of hydroxamic acid and affect the chemical reaction.

In the present work, the physiochemical properties of cationic surfactants (CTAB, TTAB and DTAB) (Chart S1) such as critical micelle concentration (cmc), surface properties, i.e. maximum surface access (Γ_{max}), surface pressure at the cmc (Π_{cmc}) and minimum surface area per molecule (A_{min}) has been determined by conductometric method and thermodynamic properties have also been investigated by tensiometric technique in the presence of octanohydroxamic acid. The aggregation number (N_{agg}) of surfactants in the absence and presence of OHA has been evaluated by fluorescence method and morphological changes of micelles have determined by Israelachvili model. Hydroxamic acid converts its hydroxamate ion [24] (ROCHN-OH to ROCHN-O⁻) at convinced pH and behave as nucleophile. Therefore, further we have employed OHA as a dephosphorylating agent (Shown in Scheme 1) for the hydrolysis of paraoxon in micellar media. The morphological changes of micelles by increasing the concentration of OHA, and their effect on the rate constant (k_{obs}) is suitably discussed here.

2. Material and methods

2.1. Materials

Cationic surfactant viz. cetyltrimethylammonium bromide (CTAB), tetradecyltrimethyl ammonium bromide (TTAB), dodecyltrimethylammonium bromide (DTAB) and paraoxon were procured from Sigma-Aldrich Chemicals Pvt. Ltd. Bangalore (India). Other chemicals used are of AR/high purity (99.0%) grade. All the solution was prepared in triple-distilled water. Octanohydroxamic acid (OHA) was synthesized by the reaction of ethyl octanoate with hydroxylamine hydrochloride [25] and characterized through ¹H NMR (Fig. S1).

¹H NMR (400 MHz, CD₃OD): δ = 3.29 (t, *J* = 6.4 Hz, 3H), δ = 2.26 (q, j = 7.6 Hz, 2H), δ = 2.0 (t, 7.2 Hz, 6H), δ = 1.92 (t, 2 Hz, 2H), δ = 2.5 (t, 4 Hz, 2H).

2.2. Methods

2.2.1. Conductivity measurement

Conductivity measurements were carried out with a Systronics direct reading conductivity meter (Type 306). The conductivity cell was calibrated with KCl solutions in the appropriate concentration range. Accuracy of measured conductance was within \pm 0.5%. The cmc of single and mixed surfactants were determined by conductivity measurements at 300 K. The pure surfactant solutions were prepared by diluting the concentrated stock solution. The conductivity at each mole fraction was measured by successive addition of concentrated solution of surfactant mixture in pure water (Fig. 1).

2.2.2. Surface tension measurement

The surface tensions of aqueous solutions of cationic surfactants with various concentrations of OHA were determined (Fig. 2) with a surface tensiometer (Jencon, India) using a platinum ring by the ring detachment technique. The tensiometer was calibrated against distilled water. Platinum ring was thoroughly cleaned and dried before each measurement. The measurements were done in such a way that the vertically hung ring was dipped into the liquid to measure its surface tension. It was then pulled out. The maximum force needed to pull the ring through the interface was then expressed as the surface tension. Each experiment was repeated several times until good reproducibility was achieved. The results were accurate within $\pm 0.1 \text{ mNm}^{-1}$.

2.2.3. Determination of average micellar aggregation number

Fluorescence measurements were performed using a Cary Eclipse Fluorescence Spectrophotometer. In order to obtain the average micellar aggregation number (N_{agg}) of cationic surfactants, fluorescence quenching of pyrene by cetylpyridinium chloride (CPC) was studied. Pyrene was excited at 334 nm and its emission was recorded at 373.5 nm (Fig. 3) with the use of excitation and emission slit of 5 and 2.5 nm. Pyrene solution was added to the micellar solution of the solution of surfactants. The probe concentration (1.0×10^{-6} M) was kept low enough to avoid eximer formation [26]. Quencher was added progressively and intensity was recorded.

2.2.4. Kinetic measurements

All reactions were performed at 300 K with a Thermo Fisher Evolution 300 UV–Visible spectrophotometer being equipped for temperature control (Peltier). All the kinetic runs were followed under pseudo-first-order conditions in which the concentration of nucleophile was at least 10 times more than substrates. The additions of nucleophile and substrate were done under thermal control at 300 K. The cuvettes were allowed to equilibrate thermally (300 K) in the cell holder for 30 min. After temperature equilibrium, the stock solutions of substrates were added to each cuvette and kinetic runs were started. The initial concentration of substrates in the cuvettes was 1.0×10^{-4} M. The rates constant (k_{obs}) of nucleophilic reaction with paraoxon were determined by following the increase in absorption of p-nitrophenoxide



Octanohydroxamate Ions

Scheme 1. Nucleophilic attack of octanohydroxamate ions at P=O center of paraoxon in cationic surfactant.



Fig. 1. Specific conductivity (*π*) versus concentration plots for (A) CTAB in (♥) 1.0, (▲) 0.5, (●) 0.1 and (⊙) 0.0 mM OHA (B) TTAB in (●) 1.0, (♥) 0.5, (▲) 0.1 and 0.0 (⊙) mM OHA and (C) DTAB in (▲) 0.0, (♥) 0.1 (⊙) 0.5, and (■) 0.8 mM OHA at 300 K.

anion at 400 nm. All the kinetic experiments were performed at an ionic strength of 0.1 M (with KCl). Borate buffer was employed as reaction medium. For all the kinetic runs, the absorbance/time results fit very well in the first-order rate Eq. (1).

$$\ln(A_{\infty} - A_t) = \ln(A_{\infty} - A_0) - kt \tag{1}$$

3. Results

3.1. Critical micelle concentration (cmc)

The critical micelle concentrations (cmc) of cationic surfactants viz. CTAB, TTAB and DTAB with octanohydroxamic acid have been determined by conductometric and surface tension measurement at 300 K. The resulting data of cmc of cationic surfactant and degree of micellar ionization (α) in the presence of octanohydroxamic acid (OHA) are given in Table S1. The cmc values were computed from the plots of specific conductance vs. surfactant concentration (Fig. 1 (A-C)). The critical micelle concentration of CTAB, TTAB and DTAB are reported [27] 1.0, 3–4 and 14–16 mM in aqueous media respectively.

3.2. Interfacial properties

The interfacial properties of the surfactants in solution can provide information about solute-solute, solvent-solute interactions and the effectiveness of the surface active molecules. The surface excess is an effective measure of the absorption at the air/water interface which can be calculated using the Gibbs adsorption Eqs. (2)-(4).

$$\Gamma_{\rm max} = -\frac{1}{2.303 \rm nRT} \left[\frac{\rm dy}{\rm dlogC} \right] \rm T.P$$
(2)

where R is the gas constant (8.314 J mol⁻¹ K⁻¹) T is absolute temperature, C is the surfactant concentration, (dy/dlogC) is the slope of the premicellar plot between 'y' and log C (Fig. 2 (A–C)). For single surfactant, the constant (prefactor) n takes the value 2 and 3 for ionic and Gemini respectively and for binary surfactant systems n = 5²⁸.

The minimum surface area per molecule at the air/water interface (A_{\min}) can be obtained from surface tension measurements and were determined from surface tension data using Eq. (3).

$$A_{\min} = \frac{1}{N\Gamma_{\max}} \tag{3}$$

N is Avogadro's number. The value of the surface excess concentration of surfactant (r_{max}) and minimum area per molecule at the airwater interface (A_{min}) are given in Table 1.

Surface pressure at the cmc (Π_{cmc}) and surface tension reduction at cmc was calculated using Eq. (4).

$$\Pi_{\rm cmc} = y_{\rm o} - y_{\rm cmc} \tag{4}$$

where y_0 is the surface tension of pure water and y_{cmc} is the surface tension at the cmc. The values of Γ_{max} and Π_{cmc} decreases with increasing the concentration of OHA and A_{min} follows the reverse trend (Table 1). A_{min} of DTAB in water is 1.21 nm² and 1.15 nm² increases for TTAB compare than CTAB per molecules which increase to 2.13 nm², 2.07 nm² and 1.74 nm² for CTAB, TTAB and DTAB respectively in the presence of 1.0 mM OHA. In water, higher Γ_{max} values obtained for CTAB than the TTAB and DTAB.



Fig. 2. Surface tension (γ) vs log C plots for (A) CTAB (B) TTAB (C) DTAB in the presence and absence of OHA at 300 K. Only four plots are given for the clarity.

3.3. Thermodynamics of micellization and interfacial adsorption

The effects of addition of OHA on the micellization process of cationic surfactant i.e. CTAB, TTAB and DTAB have been quantitatively estimated from the standard Gibbs free energy of micellization (ΔG_m^0) and Standard free energy of adsorption (ΔG_{ad}^0). For evidently understanding the energetic of micellization process can be interpreted by two extensively used method, phase separation and mass action. The mass action method usually preferred for ionic surfactants [29]. The micellization process can be described by the equilibrium between surfactant monomer; counter ions and monodispersed micelle.

The standard free energy of adsorption (ΔG_{ad}^0) of the cationic surfactants at the air-water interface has been evaluated by the Eq. (5).

$$\Delta G_{ad}^{\ 0} = \Delta G_m^{\ 0} - (\Pi_{cmc} / \Gamma_{max}) \tag{5}$$

where ΔG_m^0 is the free energy of micellization (discussed below), Π_{cmc} is



Fig. 3. Schematic representation of penetration of OHA on an interfacial region and mixed-micelle formation.

Table 1

The Maximum Surface Excess (Γ_{max}), the Minimum Surface Area Per Molecule (A_{min}) and Surface Pressure at cmc (Π_{cmc}) Values of Cationic Surfactant with OHA in Aqueous Media at 300 K.

	$\Gamma_{\rm max}$ (10 ⁶ mol m ⁻²)			A _{min} (10 ²² 1	nm²)		$\Pi_{\rm cmc}$ (mN m ⁻¹)			
[OHA]mM	СТАВ	TTAB	DTAB	СТАВ	TTAB	DTAB	CTAB	TTAB	DTAB	
0.0	2.43	2.12	2.02	6.8	7.83	8.23	29.0	34.0	45.0	
0.1	1.45	1.79	1.43	11.4	9.27	11.61	31.0	27.0	42.0	
0.5	1.32	1.52	1.37	12.5	10.92	12.11	30.5	32.0	37.0	
0.8	1.17	1.40	1.30	14.1	11.85	12.74	25.0	31.0	34.0	
1.0	1.14	1.17	1.15	14.5	14.10	14.37	22.5	18.0	33.0	
2.0	0.86	0.98	1.06	19.1	16.89	15.55	21.0	16.0	31.0	

the surface pressure at cmc and $\Gamma_{\rm max}$ is the maximum surface excess of the amphiphile.

The ΔG_{ad}^0 values are given in column 4–6 of Table 2. It shows that, except all cationic surfactant CTAB, TTAB and DTAB and Mixed CTAB + OHA, TTAB + OHA and DTAB + OHA systems have exhibited comparable spontaneity of adsorption. It seems that the standard free energy of adsorption for DTAB is more favorable as compared to CTAB and TTAB in both pure and mixed systems.

The standard Gibbs free energy of micellization per mole of monomer unit (ΔG_0^{o}) of ionic surfactant was calculated by using Eq. (6).

$$\Delta G_{\rm m}^{\ 0} = (2 - \alpha) \, RT \, \ln X_{\rm cmc} \tag{6}$$

 X_{cmc} is the cmc of the surfactant in mole fraction unit and α is the micellar ionization evaluated conductometrically from the ratio of the postmicellar and premicellar slopes of the plot of specific conductance vs. concentration of the surfactant solution, as shown previously [30–31]. The value of α (Presented in Table S1) is higher at a higher mole fraction of the monomeric surfactant. The ΔG_{ad}^0 are both negative. The hydrophobicity of the amphiphiles primarily leads towards the air-water interface and the formation of micelle occurs above a critical micelle concentration.

The standard Gibbs free energy of micellization per alkyl chain $(\Delta G_{m,tail}^{0})$ was calculated from the following relations

$$\Delta G_{m,tail}^{0} = \frac{\Delta G_{m}^{0}}{2} \tag{7}$$

Table 2 summarizes the Gibbs free energy ($\Delta G_m^0, \Delta G_{m,tail}^0$) values obtained using Eqs. (6) and (7) for surfactant in different concentration of OHA. The values of ΔG_m^0 and $\Delta G_{m,tail}^0$ become negative in all cases to raise the concentration of OHA.

3.4. Aggregation number (N_{agg})

The fluorescence quenching of pyrene by cetylpyridinium chloride was used for determining the aggregation number (N_{agg}) of conventional cationic surfactants. Pyrene and cetylpyridinium chloride acted as the probe and a quencher, respectively. This technique was used to evaluate

Table 2

The standard Gibbs free energy of micellization (ΔG^0_m), standard Gibbs free energy of adsorption (ΔG^0_{ad}) and standard Gibbs free energy of micellization per alkyl chain ($\Delta G^0_{m,tail}$) for Cationic Surfactant in the Presence of OHA in Aqueous Medium at 300 K.

$-\Delta G_m^0 kj/mol$			$-\Delta G_{ad}^0$	kj/mol		$-\Delta G_{m,}$	$-\Delta G_{m,tail}^{\ 0} kj/mol$			
CTAB	TTAB	DTAB	СТАВ	TTAB	DTAB	CTAB	TTAB	DTAB		
31.65	23.56	18.79	11.96	16.06	22.51	13.82	11.78	9.39		
29.83	22.96	17.88	22.17	15.10	29.38	14.91	11.48	8.94		
30.24	21.16	17.15	23.13	21.07	27.02	15.12	10.58	8.57		
29.15	21.13	17.12	21.39	22.16	26.17	14.57	10.56	8.56		
29.14	20.97	16.97	19.76	15.40	28.71	14.58	10.48	8.48		
28.58	20.82	16.94	24.44	16.34	29.26	14.29	10.41	8.47		

the effect of OHA on the aggregation number of cationic surfactants viz. CTAB, TTAB and DTAB. N_{agg} can be calculated by the following expression (8)

$$\ln\left(\frac{I_0}{I}\right) = \frac{N_{\text{agg}}[Q]}{[S] - \text{cmc}}$$
(8)

where I_0 and I are the fluorescence intensities at 373.5 nm of pyrene in the absence and presence of quencher (CPB), respectively. [Q] and [S] is the concentration of quencher and surfactant, respectively. N_{agg} can be determined from the slope of $In(\frac{I_0}{T})vs$. [Q] (Fig. 3) and values of aggregation number are presented in Table 3. All plots were fitted straight lines and slope was obtained. In our experiment the study of the aggregation properties of the cationic surfactants with octanohydroxamic acid i.e. CTA-OHA-water systems it can be assumed that, N_{agg} decreased with increasing the concentration of acid.

3.5. Packing parameter (P)

The packing parameter of CTAB, TTAB and DTAB in aqueous solution with OHA were calculated by Israelachvili model [32] in which the packing parameter (P) has been defined by the Eq. (9)

$$P = \frac{v}{Al} \tag{9}$$

where A is the head group cross-sectional area of the surfactant monomer, l is the critical length per surfactant in the micelle and v is the volume of the hydrocarbon chain of the monomer.

The values of *l* and *v* were calculated using Tanford's expression,

$$l = (0.154 + 0.1265 C_{\rm n}) \tag{10}$$

$$\nu = (0.0274 + 0.0269 C_n) \tag{11}$$

 C_n is the number of carbon atoms in the surfactants tail and was taken as 16, 14, and 12 for the CTAB, TTAB and DTAB surfactant respectively. In the calculation of *P*, the cross-sectional area per head group of the cationic surfactants was calculated from the relation, $A = \frac{4\pi l^2}{2N_{\text{agg}}}$. The values of *A* and *P* are listed in Table 3. The radius of the aggregate *R* was evaluated from $R = 3\nu/A$ nm.

3.6. Micellization behavior of surfactants under reaction condition

The physiochemical properties viz. critical micelle concentrations (cmc), fraction ionization (α), the Standard Gibbs free energy of micellization (ΔG^0_m), adsorption (ΔG^0_{ad}) and micellization per alkyl chain ($\Delta G^0_{m,tail}$) of ionic surfactants play a significant role for incorporation of anionic nucleophile in micelle catalyzed reaction. With this viewpoint, the cmc of CTAB, TTAB and DTAB have been determined under reaction condition and data were obtained from a plot of surface tension (ST) vs log value of the concentration of surfactants (Table S2).

3.7. Hydrolysis of paraoxon by OHA⁻ in cationic micellar media

The nucleophilic dependent pseudo-first-order rate constant was measured spectrophotometrically for the reaction of paraoxon with OHA⁻ in excess in the presence of cationic surfactant and aqueous media at 9.2 pH. The data summarizes in Table S4 for the reaction of paraoxon with different concentration of OHA⁻ at 9.2 pH. The obtained kinetic data completely support that hydroxamate ions acting as a nucleophilic catalyst for the hydrolysis of paraoxon.

Table 3

Aggregations number (*N*_{agg}), the surface area per head group (*A*), packing parameter (*P*) and radius (*R*) of cationic surfactants viz. CTAB, TTAB and DTAB in the presence of octanohydroxamic acid (OHA).

	(CTAB)				(TTAB)				(DTAB)			
[OHA], (mM)	$N_{ m agg}\pm 0.1$	A nm ²	Р	<i>R</i> (nm)	$N_{\rm agg} \pm 0.1$	A nm ²	Р	<i>R</i> (nm)	$N_{ m agg}\pm 0.1$	A nm ²	Р	<i>R</i> (nm)
0.0	63 (62) ⁴³	0.382	0.538	3.589	59 (58) ⁴⁴	0.391	0.522	3.099	51 (50) ⁴⁵	0.344	0.407	3.051
0.1	60.85	0.486	0.434	2.820	53.85	0.429	0.477	2.825	48.31	0.566	0.372	1.855
0.5	54.91	0.539	0.391	2.543	31.53	0.733	0.279	1.653	30.54	0.773	0.260	1.358
0.8	46.37	0.638	0.330	2.148	26.64	0.865	0.236	1.401	24.65	0.890	0.236	1.179
1.0	38.23	0.774	0.272	1.770	21.74	1.063	0.192	1.140	20.98	1.108	0.212	0.947
2.0	33.35	0.887	0.237	1.371	18.54	1.246	0.164	0.972	17.32	1.263	0.120	0.831

4. Discussion

4.1. Micellization of cationic surfactants with OHA

Fig. 1 indicates that the critical micelle concentration of surfactant decreases with increasing the concentration of OHA. Generally, the degree of ionization (α) , taken through the ratio of the slopes of pre-micellar and post-micellar by conductivity is linearly correlated with the surfactant concentrations [33]. The degree of ionization (α) values of CTAB, TTAB and DTAB increases with increasing the concentration of OHA (Table S1). It is suggested that an increase in the degree of ionization (α) with respect to concentration of OHA is expected due to the destruction of water molecule and also decrease in the polarity of the bulk phase caused by the addition of cosolvents. That is, in order to diminish the attraction between the ionic head groups, thus prefer a large surface area to stay the counterions. Essentially, the hydrophobic and solvophobic interactions are considered to be the main driving force for micellization. The micellization of surfactants in water is driven by the low solubility of the alkyl chains. Predominantly, an addition of organic solvent improves the solubility of the alkyl chain, and the micellization process becomes less favorable as compared to water [34]. Moya et al. have documented that the cmc values sharply increases with increasing EG (Ethylene Glycol) concentration because EG is highly associative [35] and behave as cosolvent [36]. It also forms hydrogen-bonded chains having mainly two-dimensional cooperative domains and has an analogous nature to that of water [37]. The micellization behavior can be modifying or affected by solvent properties. Significant contributions in this field are made by Ghosh and their coworkers [38] as they studied the effects of short chain alcohols upon the micellization of cationic surfactant and observed that the cmc values increases with increasing length of alcohol from methanol to ethanol and decreases slowly with 1-propanol. The decrease in cmc on addition of methanol and ethanol is due to the increase in solvation power of the surfactant-alcohol mixture. In our case, the cmc values sharply decreased with increasing concentration of OHA (Table S1). At 1.0 mM OHA, cmc of CTAB and TTAB are 1.45, 1.34 times lower than the cmc in the absence of OHA, respectively. Consequently, 1.60 times lower cmc of DTAB than their aqueous medium have been observed. The diminishing of cmc of surfactants by increasing the concentration of OHA is because of the penetration of OHA in stern layer of micelle and thus destroying the water structure [39]. There is possibility OHA-surfactant interaction resultant mixed micelle formation (Fig. 3). This effect can be rationalized by considering the addition of acid to the bulk solvent sphere that surrounds the hydrocarbon chain of the surfactant. In fact, the carboxylic acid and alcohol can be considered as cosolvent, which can replace water in the sphere and thus bind to the surfactant molecules (co-solvent effect). On the other hand, when increased chain length of acid or alcohol from (C₅-C₈) molecules, and they intercalate between the surfactant head group. The number of water molecules can be decreased by penetration of acid molecules to stern layer and electrostatic repulsion between head groups. In addition, acid molecules penetrate into the micellar core and intercalate between the hydrophobic parts of the surfactant (co-surfactant effect). Penetration of acid to the stern layer and micellar core leads to an increase of area per head group, and in this way, decreases the charge density at the micellar surface. Thus, they are expected to increase the interfacial tension between the micelle, hydrophobic core and bulk solvent. All these effects could be responsible for the decrease in the cmc of cationic surfactant in the presence of octanohydroxamic acid (OHA).

The addition of OHA from 0.1–2.0 mM to the conventional surfactants, the order of Γ_{max} values decreases (Table 1). The variation of maximum surface excess (Γ_{max}) is caused by intermolecular head group distance and promotes the increase in the adsorption of surfactants. The minimum surface area per molecule (A_{\min}) shows elevated value with 1.0 mM OHA due to bulky hydrophobic part that makes it difficult to adjust at the air/water interface. The lower A_{\min} of TTAB + OHA (1.0 mM) system is because of the attraction between the oppositely charged head groups resulting in the molecule to be more tightly packed.

Table 2 shows thermodynamic parameter of surfactants. It is found that at 1.0 mM OHA, micelle formation with CTAB 1.39 and 1.71 kJ/ mol more favorable than TTAB and DTAB respectively. On the other hand, the micelle formation of DTAB with same concentration of OHA is less favorable than CTAB and TTAB due to the reduction of hydrophobic interaction and increase of electrostatic interaction. The solubility of hydrocarbon tail increases $(C_{12}-C_{16})$ [40,41] and bulk phase becomes better solvent for the surfactant with increasing concentration of the OHA. According to Nagarajan et al. [42] the involvement of Gibbs energy to ΔG^0 m depends on the following circumstances: (a) Surfactant tail transferred Gibbs free energy ΔG_{trans}^0 , which is due to the transfer of surfactant tail from the bulk phase into the micellar phase (b) The formation of a micelle creates an interface, resulting in contact between the hydrophobic core and the bulk phase stand by the aggregate-core solvent interfacial Gibbs free energy, $\Delta G_{intf}^{0}(c)$ The electrostatic repulsion between the surfactant head groups at the micellar surface which is represent by the head group interaction Gibbs free energy, ΔG_{elect}^0 .

4.2. Aggregation number (N_{agg})

The aggregation number of the conventional surfactants has been determined in the presence of octanohydroxamic acid by fluorescence quenching method. Fig. 4 shows the effects of octanohydroxamic acid on the aggregation number of surfactants. An increase in the content of the polar organic solvent results in decrease in N_{agg} for cationic, anionic, non-ionic and zwitterionic surfactants [43]. The decrease of N_{agg} was considered by the variations of thermodynamic properties viz. Gibbs micellization free energy and the interfacial Gibb's energy $(\Delta Ginterf^0)$. The contribution of interfacial Gibb's energy $(\Delta Ginterf^0)$ to the Gibb's energy of micellization (ΔGm^0) is reduced with the increase in the concentration of octanohydroxamic acid in the medium as it (i.e. Δ Ginterf⁰) is proportional to bulk phase/micelle core interfacial tension [44]. This result points out that the addition of octanohydroxamic acid, the surface tension of solution decreases. As the digression of surface tension, mixed medium-hydrocarbon interfacial tension becomes smaller than pure water. However, it must be noted that as the content of octanohydroxamic acid in the media



Fig. 4. (A) Representative fluorescence (emission) spectra of pyrene in micellar solution of CTAB at different quencher concentrations and the successive curve are for [Q] = (0.0083, 0.016, 0.025, 0.029, 0.033 and 0.041 mM). (B) Inset: Plot of In (I₀/I) vs [CPC] for the CTAB at 300 K. (C) Fluorescence spectra of pyrene at different concentration quencher.

increases, a chance for transfer of some pyrene molecules from the micellar phase to the bulk phase, especially in the mixed medium containing a higher concentration of octanohydroxamic acid. The N_{agg} value for aqueous CTAB, TTAB and DTAB is in good agreement with that reported in the literature [45]. A decrease in the aggregation number would bring about an increase in the polarity of the micellar interfacial region [46]. The smaller N_{agg} values indicate a more loosely packed micellar structure than that in pure water, which may be the relieve of incorporation of octanohydroxamic acid in the interfacial region of micelles, which also confirms the domination of electrostatic repulsion over the hydrophobic interactions. A less-packed micelle makes the penetration of solvent molecules (water and organic solvent) in the palisade layer easier. As a consequence, the decrease in the polarity of the bulk phase on adding octanohydroxamic acid.

4.3. Packing parameter (P)

According to Israelachvili's model, the packing properties helps to determine the transition of geometry i.e. shape and size from spherical to non spherical of the micellar assemblies, which is based on the many parameters (i) the area of surface (*A*) of the micelle, (ii) the volume (*v*) of the micelle and (iii) the maximum effective length (*l*), a semi empirical parameter, relevant only for a smaller extension of the hydrophobic chain. These parameters used to estimate the geometry of the micellar aggregate by the value of the packing parameter (*P*) which can be expressed in Eq. (9). The micellar aggregate will be mentioned as spherical (P < 1/3), non spherical (1/3 < P < 1/2), bilayers (1/2 < P < 1), or inverted structures (P > 1), depending on the value of the packing parameter. The radius of the aggregate, R, was evaluated from R = 3v/A nm.

The values of *l*, *A*, *R*, and *P* have been calculated and listed in Table 3. In the case of non-spherical micelle, R is greater than l. For cationic surfactants at room temperature as R exceeds *l*, it should be non spherical arising due to an attraction between the cationic head group in cationic/nonionic mixed micelle.

4.4. Micelle formation under reaction condition

The formations of micelle in the presence of many additives (under reaction condition) such as paraoxon, hydroxamate ions and disodium tetra borate (buffer) have been studied. A break in the plots (Fig. S2 (A–C)) gives cmc values that change largely with increasing the concentration of additives. The cmc of CTAB, TTAB and DTAB in aqueous medium are 1 mM, 3.5 mM and 14–16 mM [28], respectively, but under the reaction conditions cmc values decrease to 0.03 mM, 2.4 mM and 1.8 mM for DTAB correspondingly (Table S2). The decrease of the cmc of CTAB is because of hydroxamic acid–induced micellization and, also decrease in the aggregation number and micellar surface potential. It is generally observed that cmc values decrease with the addition of

additives. The significant increase of fractional micellar ionization (α) from 0.29 to 0.45 for CTAB, 0.37 to 0.64 for TTAB and 0.24 to 0.58 for DTAB in the presence of OHA is because of the electrostatic attraction of the octanohydroxamate ion at the stern layer of the cationic micelles. The fractional ionization constants in reaction conditions are comparable, indicating the competitive efficiency to bind the cationic micellar surface. All the Standard Gibbs free energy of the micelle formation indicating a negative value (Table 2) which is helpful to determine the spontaneity of reaction.

4.5. Hydrolysis of paraoxon in micellar media

We have studied the reactivity of OHA with paraoxon in the presence of cationic surfactant with different chain length i.e. CTAB, TTAB, and DTAB (C_{12} - C_{16}). It is found that the hydroxamate ion (OHA⁻) which exhibits a considerable catalytic activity for the cleavage of paraoxon in cationic micellar media. The rate of reaction increases (Fig. S3) with increasing the concentration of OHA⁻ ion in the presence of cationic micelle. We observed that the reactivity performance of OHA⁻ with CTAB shows better than TTAB and DTAB towards the hydrolysis of paraoxon. The increased rate constant (k_{obs}) values with increasing alkyl chain length $(C_{12}-C_{16})$ of the surfactants, that is, the aggregation number of monomer for the construction of micelles are larger for CTAB than DTAB (C₁₂). Thus electrostatic interaction between OHA⁻ and cationic head group of surfactant easily takes place at stern layer, which enhance the reactivity of hydroxamate ions. The increased k_{obs} values are also because of increased electrical surface potential of the micelle, and partially due to an increase in hydrophobicity of the palisade layer of the micelle [47].

The enhancements of k_{obs} values with octanohydroxamate ions were interpreted and fully supported by interfacial properties of surfactant i.e. Γ_{max} , A_{min} and Π_{cmc} . The high value of surface excess (Γ_{max}) and low value of A_{\min} (Table S3) indicate that the cationic surfactant pack tightly at air/water interface and bromide ions are fully dissociated [48]. It is clearly manifested that the population of monomer protected as a soldier around the stern layer of micelle and paraoxon completely defend so counteract hydroxamate ions to coming for an encounter the paraoxon at the battlefield where the war take place between paraoxon and hydroxamate ions, hence rate of reaction is very slow. On the other hand, increasing the concentration of hydroxamate ions, the surface excess concentration ($\Gamma_{\rm max}$) value decreases (Fig. 5) and the area occupied per surfactant molecule (A_{\min}) is elevated. The rate of reaction is increased 27.60 folds than aqueous medium is due to the crowd of monomer (packing parameter) of a surfactant molecules. The formation of micelles are deficient, therefore, the packing parameter is loose and there is large space available for attacking the hydroxamate ion towards the paraoxon at the battlefield (stern layer). Thus, enhance the ability for killing the paraoxon and hence the rate of reaction increases. One reason might be possible that the morphological changes of micelles



Fig. 5. Plots of maximum surface excess (Γ_{max}) and minimum surface area (A_{min}) vs. rate constant (k_{obs}) (A) CTAB, (B) TTAB and (C) DTAB.

by increasing the concentration of hydroxamic acid affect the rate constant. The morphology and packing parameter of micelles depend on many factors, i.e. aggregation number, volume and length of a hydrocarbon chain of the surfactant molecule as well as additives [17] With the addition of additives such as octanohydroxaimc acid, the aggregation number of monomer decreases for the formation of micelle (Table 3). It means the packing parameter is also decreased. A decrease of packing parameter favors the formation of spherical micelles. The length and volume of the tail chain of the surfactants are independent of the presence of ocatnohydroxamic acid. According to Israelachvili [32] the morphology of micelle aggregate can be predicted from the packing parameter P = v/Al. This parameter was used in order to explain the behavior of the micellar morphology from rod to sphere transition. The structure of micelle will be spherical when P < 1/3, nonspherical P > 1/2 or inverted structure when P > 1. According to Israelachvili model, the morphology of micelle is changed from spherical to nonspherical structure (Table 3).

4.6. Effect of surfactant on k_{obs} : quantitatively treatment by pseudophase model [PPM]

Effects of self-aggregation and association colloids upon bimolecular reactions are conveniently analyzed by terms of pseudophase model [49]. It is regarded as distinct from the reaction region in aggregate



Fig. 6. Rate-surfactant profile for the reaction of paraoxon with OHA⁻ in (A) CTAB (\bullet), TTAB (Δ) and (B) DTAB. Reaction Condition: [Paraoxon] = 1.0×10^{-4} M, [OHA⁻] = 1.0×10^{-3} M, [KCI] = 0.1 M, pH 9.2 borate buffer. Temp. 300 K.

and bulk solvent. Overall reaction rate is the sum of the rate in each pseudophase and depends on the rate constants and reactant concentrations [48]. Fig. 6 shows the dependence of the observed rate constant (k_{obs}) for the reaction of paraoxon with OHA⁻ in the cationic micellar media. The rate constant (k_{obs}) of reaction increases upon increase of the surfactant concentration. The effect of rate can be explained by considering that both the paraoxon and OHA⁻ reagent is distributed between the aqueous and micellar pseudophases. The reaction take place simultaneously in the two pseudophase, therefore, rate is the sum of two contributions. An increase in surfactant concentration brings about a further incorporation of the organic substrate molecule into the micelles. The distribution of the nucleophiles, OHA⁻ between both aqueous and pseudophases are considered through the distribution constant K_m^{OHA} . The different reactivities in the aqueous and micellar pseudophases have been taken into account through the corresponding second-order rate constants: k_2^w and k_2^m . The values of k_2^w have been obtained by studying the reaction in the absence of the surfactant. The binding constants, $K_m^{paraoxon}$ and the second-order rate constants, k_{2m} for the reaction of paraoxon are presented in Table S5. The secondorder rate constant (k_2^{W}) for the reaction with the nucleophile in the absence of micelles and the k_2^m/k_2^w ratio is also given in Table S5.

The OHA⁻ concentration in the micellar pseudophase have been defined as the local, molar concentration within the micelle pseudophase: $[OHA^-]_T = [OHA^-]_m/D\overline{V}$, where \overline{V} is the molar volume in dm³ mol⁻¹ of the reaction region and $[D] \overline{V}$ denotes the micellar fractional volume in which the reaction occurs. We assume \overline{V} equal to the partial molar volume of the interfacial reaction region in the micellar pseudo phase, determined by Bunton' [50] as 0.14 dm³ mol⁻¹. The observed rate constant (k_{obs}) were fitted using by the following equation.

$$k_{\text{obs}} = \frac{k_2^{\text{w}} + \frac{k_2^{\text{HII}}}{\overline{\nu}} K_m^{\text{Paraoxon}} K_m^{\text{OHA}^-} D_n}{\left(1 + K_m^{\text{Paraoxon}} D_n\right) \left(1 + K_m^{\text{OHA}^-} D_n\right)} [\text{OHA}^-]_{\text{T}}$$
(17)

The micellar interaction of OHA⁻ with CTAB, TTAB and DTAB showed greater in an aqueous medium for the hydrolysis of paraoxon. The micellar catalysis (k_2^m/k_2^w) observed of the factor \approx 1709, 1285 and 603 in CTAB, TTAB and DTAB micelle respectively (Table S5). However, significant acceleration of k_{obs} values have been observed for the reaction of OHA⁻ in CTAB,TTAB and DTAB micelles, which may be due to the cooperative intrinsic nucleophilicity of OHA⁻ and micellar rate enhancements. The OHA considerably ionized as OHA⁻ at operational pH therefore, it also binds to the quaternary ammonium head group through electrostatic attractions.

5. Conclusion

A Physiochemical property of conventional surfactant has received much attention since two decades. The micelle formation, interfacial properties and thermodynamic interaction of cationic surfactant in the presence of octanohydroxamic acid showed better interaction in both aqueous and under reaction condition. The cmc values of cationic surfactant decreased with increasing the concentration of OHA. Kinetic rate data for reactivity of OHA⁻ on the hydrolysis of paraoxon in the presence of cationic surfactant and aqueous media have been determined. We have correlated the reactivity with an ionization degree of micellization (α), standard free energy of micellization (ΔG_m^0), adsorption (ΔG_{ad}^0) and micellization per alkyl chain ($\Delta G_{m,tail}^0$). It is clearly manifested that the minimum surface area of per molecule (A_{\min}) increases with increasing the concentration of OHA and the reactivity towards phosphate ester also increase. The thermodynamic parameter supported for enhancing the nucleophilicity, value of standard free energy of micellization and micellization per alkyl chain both negative, that means energy releasing for the formation of micelle is guite agreed at an interface of micelle of surfactant. Standard free energy of micellization of per alky chain decreases with decreasing the chain length of surfactant from C_{16} – C_{12} . The morphology of surfactants change from non-spherical to spherical, the change of structure of micelle rationalized by aggregation number (N_{agg}) and packing parameter (P).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.molliq.2016.06.052.

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