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Physicochemical Characterization of Cationic Gemini Surfactants Micelles and their Effect on Reaction Kinetic in Ethylene Glycol-Water Medium

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ABSTRACT

Micellar and surface properties of two cationic gemini surfactants viz. alkanediyl- α,ω -bis(hydroxyethylmethylhexadecylammonium bromide) (C₁₆-s-C₁₆, MEA 2Br⁺, where s = 4, 6) in aqueous and ethylene glycol-water medium (0-20 % v/v) have been investigated by conductivity and surface tension measurements. The values of critical micellar concentration (CMC) and degree of micellar ionization (α) increase by increasing the concentration of ethylene glycol and the spacer chain length of gemini surfactants. The standard Gibbs free energy changes (ΔG°_m), enthalpies (ΔH°_m) and entropies (ΔS°_m) of micellization of gemini surfactants, determined by studying the variation of critical micelle concentration with temperature, revealed spontaneous and exothermic micellization behavior. The large rate enhancement for the hydrolysis of *p*-nitrophenyl acetate (PNPA) and *p*-nitrophenyldiphenyl phosphate (PNPDPP) by α -nucleophiles such as, benzohydroxamic acid (BHA), acetohydroxamic acid (AHA), salicylhydroxamic acid (SHA) and butane-2,3,-dione monooxime (BDMO) were obtained in the presence of gemini surfactants over the monomeric surfactant i.e. cetyltrimethylammonium bromide (CTAB). Kinetic constants were observed to be dependent on spacer chain length of gemini surfactants as well as on the nature of nucleophiles used. Ethylene glycol retarded the rate of reaction and C₁₆-6-C₁₆, MEA 2Br⁺ showed better catalytic effect for phosphate ester hydrolysis.

Keywords: CMC; Gemini Surfactant; Kinetic Hydrolysis; Ethylene Glycol; Surface Tension; Nucleophiles.

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1. Introduction

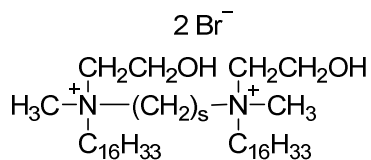
Gemini surfactants have received wide attention not only due to their unique physicochemical properties but also for their better performance in micellar catalysis. Gemini surfactants are made up of two identical/non-identical amphiphilic moieties connected at the level of head groups by a spacer which can be hydrophilic or hydrophobic, rigid or flexible [1-5]. These surfactants are superior to conventional single chain surfactants as they have a much lower critical micelle concentration and low Krafft points, high surface activity, unusual aggregation morphologies and better wetting properties [6-11].

Different solvents have been used to study the role of the solvophobic effect on micellization [12]. The increasing use of novel surfactants in applications which require water-free media [13] make this type of research more interesting and crucial due to novel technology requests. The solvents used in these studies are strongly polar, with water resembling properties, such as ethylene glycol. Rodriguez et al. [14] have studied the effects of ethylene glycol on the micellization process of gemini surfactants ($C_{12-s}-C_{12}$, $2Br^-$, $s = 3, 4, 5$) and the effects of different organic solvent-water mixtures on the micellization of $C_{12-3}-C_{12}$, $2Br^-$ and monomeric surfactants [15]. They have studied the effect of these solvents on the aggregation number and micellar growth of gemini surfactants, showing that the sphere to rod transition occurs at higher surfactant concentration in organic solvent-water mixtures than in pure water.

One of the most interesting characteristics of micelles is their ability to show catalytic behavior towards organic reactions. Bhattacharya et al. [16] have documented esterolytic cleavage of phosphate and carboxylate esters in cationic gemini surfactants of the type $C_{16-s}-C_{16}$ ($s = 2-12$), while Moya et al. [15] and Rodriguez et al. [17] discussed kinetic micellar effects for methyl 4-nitrobenzene sulfonate in the formation of aggregates for gemini surfactants using $C_{12-s}-C_{12}$ ($s = 2-6$). In particular, the hydrolysis of phosphate esters is an important chemical reaction since persistent chemical agents such as the pesticides paraoxon, parathion, and the nerve agents VX or sarin are hydrophobic phosphorus substrates, and their decontamination involves dephosphorylation or hydrolysis [18]. Current interest in studying the reactions of α -nucleophiles has received major importance in many applications of these highly reactive species [19]. Many research groups have investigated the hydrolysis reaction of different toxic and non-toxic esters using hydroxamate [20-21] and oximate [22] ions. These investigations showed that the introduction of surfactant micelles can accelerate the hydrolysis of esters via hydrophobic and electrostatic interactions, etc. [23]. The study on the effects of gemini surfactants on the reaction rates has been the subject of significant interest for the last few decades [24-27]. The kinetic studies help to understand several complex aspects of gemini micelles also for n-s-n ammonium geminis [28-32]. Kinetic evidences of morphological transitions in gemini micelles were obtained by Turco Liveri et al. [33] and by Moya et al. [34]. Our research group has made some significant contribution to the study of nucleophilic hydrolysis in some gemini and conventional surfactants [35-36].

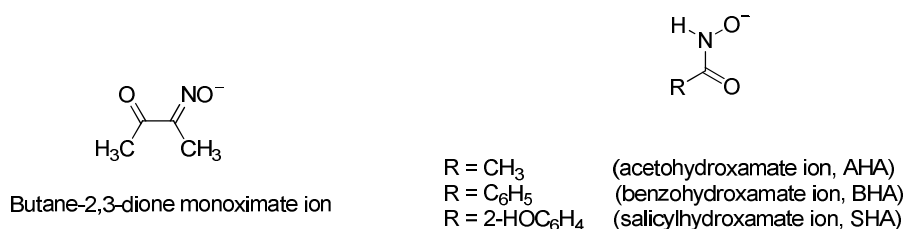
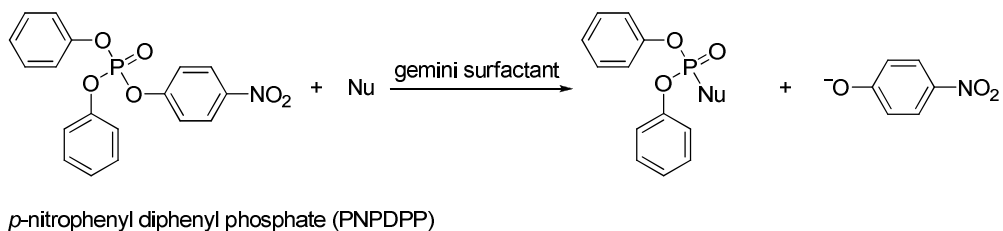
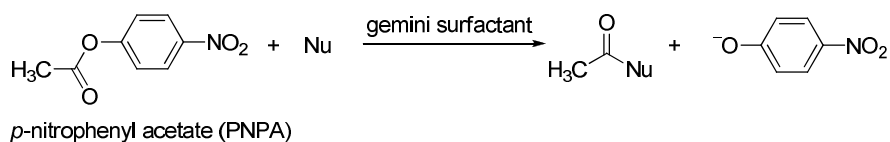
Alkanediyl- α,ω -bis(hydroxyethylmethylhexadecylammonium bromide) cationic gemini surfactants, 16-s-16, MEA $2Br^-$ were prepared and studied by SANS by Sharma et al. [37]. Herein, we investigated the surface and

micellar properties of these gemini surfactants, C₁₆-s-C₁₆, MEA 2Br⁻ (s = 4, 6) (Scheme I) in water-EG mixtures. From the obtained CMC and α value, we calculated different thermodynamic parameters. The nucleophilic hydrolysis of *p*-nitrophenyl acetate (PNPA) and *p*-nitrophenyl diphenyl phosphate (PNPDPP) by some α -nucleophiles (hydroxamic acids, viz. benzohydroxamic acid (BHA), acetohydroxamic acid (AHA), salicylhydroxamic acid (SHA) and butane-2,3-dione monoxime (BDMO) were also investigated in the presence of these gemini surfactants (Scheme II), and cetyltrimethylammonium bromide micelles (CTAB), used as a standard, in order to relate the significant difference in reactivity and to obtain surfactant structure-property relationships. The study of micellization and interfacial properties of novel gemini surfactants are expected to shed more light on the interpretation and quantification of the phenomena in the field of physical chemistry and thermodynamics. From the viewpoint of usability, stability and spontaneity of micelle formation, this type of investigation is essential. This work will hopefully lead to a more thorough understanding of the micellization and solubilization properties of gemini surfactants. The knowledge of physicochemical properties of amphiphilic aggregates is needed to understand their role in micellar catalytic systems. The actual kinetic behavior of surfactants can be explained only if their micellar, interfacial and thermodynamic aspects are considered.



(s = 4, 6)

Scheme (I)



Scheme (II)

2. Materials and Methods

2.1. Materials

p-Nitrophenyl acetate (PNPA) was purchased from Fluka (Switzerland) and *p*-nitrophenyl diphenyl phosphate (PNPDPP) was prepared in the Vertex laboratory of Defense Research Development Establishment, Gwalior (India). Benzohydroxamic acid, acetohydroxamic acid, salicylhydroxamic acid, butane-2,3-dione monoxime and cetyltrimethylammonium bromide were purchased from Sigma, USA. Ethylene glycol (EG) was obtained from Merck fine chemicals (Mumbai, India). All the solutions were prepared in triple distilled water.

2.1.1. Synthesis of gemini surfactants

2.1.1.1. N-(2-hydroxyethyl)-N-methylhexadecylamine [38]

In a three necked round bottom flask, hexadecyl bromide (110 ml, 109.99 g., 0.360 mol) and N-(2-hydroxyethyl)methylamine (180 ml, 168.30 g., 2.24 mol) were introduced and stirred at 90°C for one hour. At the end, the N-(2-hydroxyethyl)methylamine excess was distilled under vacuum (b.p.=155-157 C°). The upper layer of the resulting biphasic system was separated, diluted with dichloromethane and washed with NaOH 1N (50 ml) and with brine (2 x 50 ml). The solution was dried with Na₂SO₄, filtered and evaporated. The product is a yellow liquid. Yield 104.20 g. (96%).

2.1.1.2. Butanediyl- α,ω -bis(N-(2-hydroxyethyl)-N-methylhexadecylammonium bromide) [37]

The reaction was performed in carefully dried glassware.

N-(2-hydroxyethyl)-N-methylhexadecylamine (24 g., 80 mM) was dissolved in anhydrous acetone and the resulting solution was transferred under Argon in a three necked round bottom flask, and the temperature was raised to 60°C, then 3.86 ml (33 mM) of 1,4-dibromobutane was slowly added dropwise. The reaction was left at 60°C for seventy hours and then cooled in an ice bath and after in a refrigerator overnight, to promote product crystallization. The solvent was evaporated, the residue was washed with petroleum ether /ethyl acetate 1:1, and the solid mass was filtered on a cold buchner funnel. The crude product was crystallized twice from hot methanol and acetone. The solution was left to crystallize for a few hours in a refrigerator and was rapidly filtered on a cold buchner funnel. The product was white powder: 14.25 g. (54 %).

$^1\text{H-NMR}$ (CDCl_3) δ 0,83 (t, 6H, 2 CH_3), 1,1-1,35 (br, m, 52H, 26 CH_2), 1,74-2,0 (br, d, 8H, 4 CH_2), 3,36 (s, 6H, 2 NCH_3), 3,47-3,74 (br, t, 12H, 2 \times N(CH_2) $_3$), 4,08 (br, t, 4H, 2 CH_2O), 5,01 (br, s, 2H, 2OH).

2.1.1.3. Hexanediyl- α,ω -bis(N-(2-hydroxyethyl)-N-methylhexadecylammonium bromide) [37]

The same method as for butanediyl- α,ω -bis(N-(2-hydroxyethyl)-N-methylhexadecylammonium bromide) was used, using N-(2-hydroxyethyl)-N-methylhexadecylamine (24 g., 80 mM) and 1,6-dibromohexane (5.54 ml, 36 mM) in 50 ml of anhydrous acetone. The crude product was isolated as shown above and crystallized from methanol/acetone, obtaining a white crystalline powder: 11.31 g. (37%).

$^1\text{H-NMR}$ (CDCl_3) δ 0,85 (t, 6H, 2 CH_3), 1,24-1,45 (br, m, 56H, 26 CH_2 alkyl chain, 4 CH_2 spacer), 1,40-1,79 (br, m, 12H, 4 $\text{N}^+\text{CH}_2\text{CH}_2$, 2 CH_2 spacer), 3,2-3,6 (br, m, 12H, 6 N^+CH_2 alkyl chain and spacer), 4,11 (br, t, 4H, 2 CH_2O), 5,20 (br, s, 2H, 2OH).

2.2. Methods

2.2.1. Conductivity Method

Conductometric measurements were carried out using Systronics direct reading conductivity meter (Type 306). The conductivity cell was calibrated with KCl solutions in appropriate concentration range. A concentrated surfactant solution [\sim 10-20 times the critical micelle concentration (CMC)] was progressively added, using a micropipette, to 20 mL of water-organic solvent medium in a water jacketed cell whose temperature was carefully controlled by a thermostat (having a temperature accuracy of \pm 0.01°C). After ensuring thorough mixing and temperature equilibration of 300-320 K, the specific conductance (κ) was measured.

To prepare samples for the Krafft point determination by conductivity measurements, a surfactant was dissolved in hot water and the solution was cooled to 0 °C for at least overnight until the surfactant precipitated. During the determination of Krafft temperature, the temperature of the water bath was raised gradually. At each temperature, the conductance reading was checked every 2-5 min until it reached a steady value. Then, the temperature was

raised by 1-2 °C again for another conductance measurement. Every time the reading was checked, the conductivity probe was moved up and down to stir the sample.

2.2.2. Surface Tension Measurement

The surface tension of aqueous solutions of surfactants at various concentrations were determined 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 ring was hung to the balance, dipped into the solution and then pulled out. The maximum force needed to pull the ring through the interface was measured and correlated to 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. Kinetic Measurements

The reactions were studied spectrophotometrically with Varian Cary 50 spectrophotometer and Systronics Type-118 UV-Vis spectrophotometer by monitoring the appearance of the *p*-nitrophenoxide ion at 400 nm at $27 \pm 0.2^\circ \text{C}$. All the kinetic experiments were performed at an ionic strength of 0.1 M KCl. Phosphate buffer (0.1 M) was employed to control the pH of the media. All the pH measurements were obtained using a Systronics pH meter (Type 362). All reactions were conducted under pseudo-first order conditions with the nucleophile in excess (minimum 10 times). For all the kinetic runs, the absorbance/time data were fitted to the first order rate equation. The pseudo-first-order rate constants (k_{obs}) were determined from the plots of $\log (A_0 - A_t / A_\infty - A_t)$ versus time with A_0 , A_t and A_∞ being the absorbance readings at starting point, proper and infinite time respectively. Substrate concentration was kept the same for all the reactions. Fig. 1 shows a representative graph for hydrolysis of PNPDP (0.5 x 10⁻⁴ M) with BHA (0.5 x 10⁻³ M) in the micelles of C₁₆-6-C₁₆, MEA, 2Br (1.0 x 10⁻³ M) at pH 8.0 and temperature 27°C.

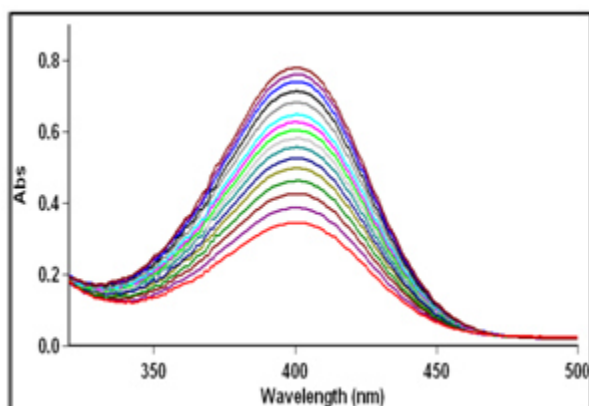


Fig. 1. UV spectra collected at different reaction times, showing the increase in absorbance of *p*-nitrophenoxide ion for the cleavage of PNPDP with BHA in the presence of gemini (C₁₆-6-C₁₆, MEA 2Br⁻). Reaction Conditions: [PNPA] = 0.5 × 10⁻⁴ M, [BHA] = 0.5 × 10⁻³ M, [KCl] = 0.1 M, [Gemini] = 1.0 × 10⁻³ M, pH = 8.0, T = 27°C.

3. Results and Discussion

Physicochemical properties of gemini surfactants (C₁₆-s-C₁₆, MEA 2 Br⁻) and their efficiencies as micellar catalysts for esterolytic reactions were studied due to their fundamental and practical interest as previously shown. The catalytic activity of C₁₆-s-C₁₆, MEA 2Br⁻ (s = 4, 6) for the hydrolysis of PNPA and PNPDP was studied in the presence of hydroxamic acids (AHA, BHA and SHA) and BDMO as α-nucleophiles. Micellar catalytic activity of gemini surfactants were compared with that of a most commonly used conventional surfactant i.e. CTAB. The nucleophilic concentration-dependent first-order rate constants were determined for the reaction of PNPDP and PNPA with nucleophiles in excess.

3.1 Physicochemical Properties

3.1.1. Krafft Point

The Krafft temperature or Krafft point, *K_p*, is an important physical property of ionic surfactants closely related to their molecular structure. Below *K_p* the solubility of ionic surfactants depends on their crystal lattice energy and the heat of hydration. Above *K_p*, a hydrated surfactant crystalline solid melts and forms micelles in solution, thus enhancing solubility drastically. Several aspects of the influence of ionic surfactant molecular structure on the Krafft point are known. The Krafft point can be changed by increasing the degree of unsaturation or branching in the hydrocarbon chains or by varying the nature of head groups or counterions [39]. The Krafft points of gemini surfactants were found to be 40°C and 37 °C for C₁₆-4-C₁₆, MEA and C₁₆-6-C₁₆, MEA respectively. While normally cmc measurement should not be performed below the Krafft point, those compounds [37] and their C₁₆-6-C₁₆, DMA parent compounds [4a, 39] were shown to aggregate even below their Krafft point and thus were normally studied also in this temperature range. In our study we performed measurements in the temperature range similar (or higher) to that studied by the investigators who prepared those compounds for the first time.

3.1.2. CMC Determination and Effect of Ethylene Glycol on Critical Micelle Concentration

The CMC values for C₁₆-s-C₁₆, MEA were determined by surface tension and conductance measurements. The critical micelle concentration (CMC) of various surfactant solutions were usually determined by the discontinuity in specific conductance versus total concentration plots. The classical method to obtain the CMC requires the determination of two lines in the pre- and post-micellar regimes (Fig. 2a), respectively [40]. Since the determination of the CMC for gemini surfactant is sometimes difficult due to smoothness of the κ vs concentration plot, in the last years the use of a non linear fitting method was proposed as a general method [41] and successfully applied to gemini surfactants [42]. In the case shown by Carpena et al. [41] the problem of smooth conductivity vs C plots is arising when the solvent is a mixture of organic solvents and water even for monomeric surfactants.

In the case of gemini surfactants the aggregation is promoted by the transfer of two alkyl chains to the micellar phase but also made difficult by the steric requirements connected to put the two chains in the restricted micellar core environment [43]. The data were fitted to a non linear equation and the resulting CMC of surfactants in pure water and aqueous binary mixtures are given in Table 1:

$$F(x) = F(0) + A_1 x + \Delta x (A_2 - A_1) \ln \left(\frac{1 + e^{(x-x_0)/\Delta x}}{1 + e^{-x_0/\Delta x}} \right) \quad (1)$$

where $F(0)$ is the initial conductivity of water, A_1 and A_2 are the limiting slopes for low and high concentration respectively, x_0 is the central point of the transition, i.e. the CMC and Δx is the width of the transition. The α value, representing the degree of micellar ionization can be deduced from the ratio A_2/A_1 . This equation can carefully represent the conductivity vs C data set, since it is the integral of the Boltzmann sigmoid.

We thus obtained the results by applying both the classical and the non linear fitting method. The results are very similar for both methods and are shown in Table 1 and Fig. 2. The surface tension versus log molar concentration plots for gemini surfactants are shown in Fig. 3. The breakpoint in the surface tension vs $\log C$ plot was taken as the concentration corresponding to the micelle formation, allowing the identification of the CMC. The discussion of surface tension measurements is performed in the next paragraph.

The CMC values as obtained from both the techniques are in agreement with the literature [37] and are given in Table 1. CMC data of the C_{16} -s- C_{16} , MEA gemini surfactants are 10-100 times lower than the conventional surfactants [44-45] and nearly 10 times lower than C_{16} -s- C_{16} , DMA ammonium surfactants. For C_{16} -s- C_{16} , MEA, hydrogen bonding can take place with water and among the head groups through oxygen atom of $-C_2H_4OH$ groups. This is likely to provide additional hydration at the head group level resulting in screening of repulsion Coulombic forces between charged heads and also enforcing a connection among head groups, helping C_{16} -s- C_{16} , MEA

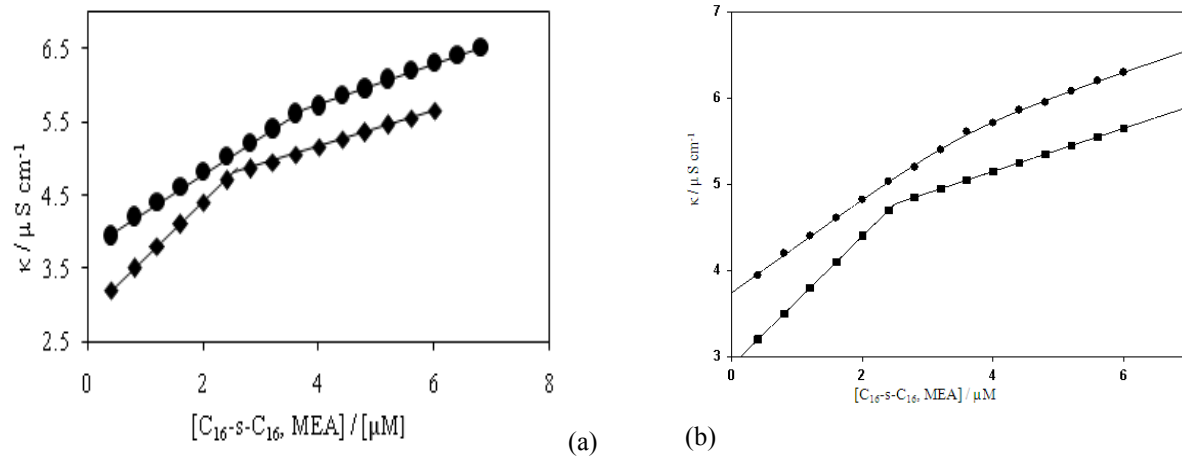


Fig. 2. Specific conductivity (κ) versus concentration plots for gemini surfactants C_{16} -s- C_{16} , MEA, $2Br^-$ in aqueous solution at 300 K (a) Classical method (b) Non linear fitting method, (\blacksquare) C_{16} -4- C_{16} , MEA, $2Br^-$ (\bullet) C_{16} -6- C_{16} MEA,

2Br⁻.

surfactants to form aggregates at a lower concentration than those of conventional surfactants. Table 1 summarizes the variation of CMC and α with temperature and solvent composition. The data clearly indicate that the increase in both temperature and organic solvent leads to higher CMC and α value. In fact, Table 1 shows that the CMC increases by increasing the amount of EG present in the surfactant solutions.

From a thermodynamic point of view, the dependence of the CMC on the EG content in the mixed solvent is due to the EG solvent ability towards the surfactant alkyl chains that makes the transfer of the surfactant tail from the bulk phase into the micellar core less favorable when the amount of ethylene glycol in the mixture increases [46]. The same applies towards the hydrophobic spacer. In practice, water-EG mixtures are interesting solvents for the surfactant molecules than pure water [47].

This is confirmed by the observation that an increase in the weight percentage of EG in the solvent mixture results in a less abrupt change in conductivity, going from the premicellar to the postmicellar surfactant concentration range as compared to that in pure water, as given in Table 1. At a given solvent concentration the CMC and the degree of micellar ionization increase with temperature (Table 1). The temperature effect is weaker in pure water than that in water/cosolvent mixtures. The effect of temperature on the micellization is usually discussed in terms of two opposite factors. The increase in temperature results in (i) a reduction of degree of hydration of the head groups favoring micellization and (ii) breaking the water structure surrounding the hydrophobic groups inhibiting micellization. It seems clear that the second effect is dominant in the temperature range studied. Moreover, the degree of micellar ionization (α) of gemini surfactants becomes larger with an increase in EG concentration and temperatures.

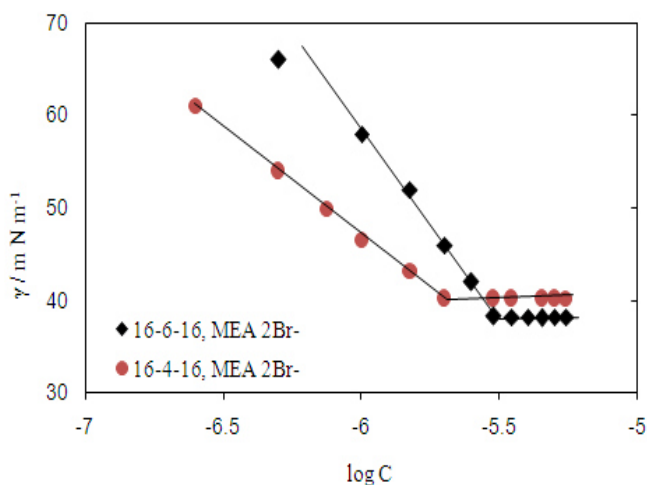


Fig. 3. Plots of surface tension versus log C of C₁₆-4-C₁₆, MEA 2Br⁻ and C₁₆-6-C₁₆, MEA 2Br⁻ in aqueous solution at 300 K.

Table 1. CMC (μM) and degree of micellar ionization (α) values of gemini surfactants (C₁₆-s-C₁₆, MEA 2Br⁻) in aquo-organic solution.

Cond. = Conductivity method, ST = Surface Tensiometer, N-L = Non linear fitting method,
Cl. = Classical method.

At higher temperatures, the surfactant becomes more soluble in the solvent medium and thus less prone to aggregate. This results in a more gradual transition from the monomeric to the micellar state, requiring less counterions to stabilize the micelle (higher α). This is in general agreement with the general effect of alcohols as solvents on the micellization process. Looking for structure-properties relationships, the increase in the spacer length makes C₁₆-6-C₁₆, MEA, 2Br⁻ less prone to aggregate than C₁₆-4-C₁₆, MEA, 2Br⁻ in pure water and in EG-water mixtures, and its micellar ionization accounts for a slightly less compact micellar surface and structure.

Solvent	% (v/v)	Temp. K	C ₁₆ -4-C ₁₆ , MEA 2Br ⁻					C ₁₆ -6-C ₁₆ , MEA 2Br ⁻				
			Krafft Point Kp	CMC (μM)			α	Krafft Point Kp	CMC (μM)			α
				Cond.		ST			Cond.		ST	
				N-L	Cl.				N-L	Cl.		
Aqueous	0.0	300	40° C	2.50	2.50	2.00	0.54	37°C	3.51	3.75	3.00	0.56
		310		3.02	3.25		0.56		3.95	4.50		0.57
		320		3.90	4.00		0.59		4.97	5.20		0.61
EG	10.0	300		3.42	3.50	3.00	0.55		4.36	4.75	4.00	0.59
		310		4.49	4.50		0.58		5.11	5.50		0.62
		320		5.57	5.40		0.62		6.39	6.50		0.65
	20.0	300		4.20	4.20	4.20	0.56		4.82	5.60	5.40	0.59
		310		5.24	4.80		0.57		6.48	6.50		0.61
		320		6.11	5.80		0.60		7.42	7.80		0.66

3.1.3. Surface Properties of Gemini Surfactants

From surface tension measurements, several parameters can be obtained the surface excess concentration of surfactant (Γ_{\max}) and minimum area per molecule at the air-water interface (A_{\min}) were determined from surface tension data using Eqs. (2) and (3) [48-49]

$$\Gamma_{\max} = - \frac{1}{2.303nRT} \left[\frac{d\gamma}{d \log C} \right]_{T, p} \quad (2)$$

$$A_{\min} = 1/N \Gamma_{\max}. \quad (3)$$

where R is the gas constant ($8.314 \text{ Jmol}^{-1} \text{ K}^{-1}$), T is the absolute temperature, C is the surfactant concentration, $(d\gamma / d\log C)$ is the slope of the γ vs $\log C$ plot taken at the CMC, and N is Avogadro's number. The constant (prefactor) n takes the values 2 for an ionic surfactant where the surfactant ion and the counterion are univalent and $n = 3$ for a gemini surfactant made up of a divalent surfactant ion and two univalent counterions, [48]. As will be explained just below the use of $n = 2$ or 3 do not affect the general trend. Hence a value of $n = 3$ was used in Eq. (2) for the present ionic gemini surfactant system.

The value of the surface pressure at the CMC (π_{CMC}) was obtained from equation (4),

$$\pi_{cmc} = \gamma_o - \gamma_{CMC} \quad (4)$$

where γ_o being the surface tension of pure solvent and γ_{CMC} being the surface tension at the CMC. This parameter indicates that the maximum reduction of surface tension is caused by the adsorption of surfactant molecules and this is attained when surfactant start to micellize and do not adsorb anymore at the surfaces. Hence, it becomes a measure of effectiveness of the surface tension reduction, and the greater the π_{CMC} values, the higher the effectiveness of the surfactants. π_{CMC} values are listed in Table 2.

Before analyzing the results a brief discussion on the typical issue coming out when performing surface tension measurements is opportune, since the presence of impurities can heavily affect the results and should correctly addressed.

The absence of a minimum near the CMC is normally taken as a confirmation of substantial surfactant purity [50]. When using mixed solvents, the impurities can come from different sources and the utmost care should be taken to avoid their presence working at the best conditions one can attain. The problem of assessing the surfactant purity and how the impurities could affect the surface tension vs $\log C$ plots was thoroughly addressed in the last decades [51]. Exceptionally pure surfactant solutions gave insight on particular behavior of surfactants that in general are hardly to be detected [52]. This kind of purity of surfactant solutions is normally not attained, but at least the absence of a minimum in the γ vs $\log C$ plot is highly advisable and this is a requisite in order to be sure to rely on a reasonable purity of the surfactant solutions and to give the opportunity to perform careful studies and to obtain repeatable results. Even when the minimum is not present, very small quantities of impurities can affect the portion of the plot in which the surface tension is steeply decreasing, giving a too linear decrease. If the decrease was really linear, the slope and thus the excess concentration (Γ_{\max}) would be constant with the change of concentration, in a large range. On the basis of the Gibbs adsorption theory this would be impossible, since the minimum area would be constant over that concentration range and the surfactants would not be adsorbed anymore. A question would be raised at this point: if the surfactant adsorption does not occur in this concentration range, why is the surface tension decreasing? This is normally known as the Gibbs paradox. Even if modifications of the original Gibbs interpretation

where proposed in the last years [53] it was already shown that a careful purification can evidence that the γ vs LogC plot is not completely linear but shows a small but perceptible curvature towards the LogC axis [54]. This accounts for the Γ_{\max} always increasing, and A_{\min} always decreasing, with enhancing the surfactant concentration, in agreement with the Gibbs theory. Quite recently we could demonstrate that even almost cheap and easily applied methods (already proposed by Rosen) [50, 51b] for the surfactant purification could be enough to obtain a sufficient surfactant solution purity that can enable to detect that the surface tension decrease is not really linear but that it shows a small curvature towards the logC axis [50]. In the present case the experimental constraint would make the framework almost problematic, since also the organic solvent could contain small quantities of highly hydrophobic impurities that would affect the final result. Luckily, the surfactants were pure enough and also a substantial pure organic solvent and water were used, making the surface tension measurements possible and reliable. In general, the surface tension decrease is linear enough to permit to accurately extrapolate the CMC, but a careful inspection (Fig. 3) reveals that a small curvature is present. The complete exclusion of an extremely low content of hydrophobic impurities cannot be ensured at the level reached by Lunkeheimer et al. [52], but it was sufficient to have reasonable confidence on the reliability and accuracy of those surface tension measurements, working at our best.

Another issue that should be considered with care is the use of the prefactor in the Gibbs equation. The prefactor should depend only on the structure of the surfactant and on the number of species (ions for ionic surfactants) that are produced upon surfactant solubilization, e.g. 2 for CTAB, generating an organic surface active cation and a bromide anion, and 3 for our gemini surfactants. While the use of $n = 2$ or 3 on geminis does not change the trend of surface excess, Γ_{\max} , and minimum area, A_{\min} , the use of techniques that can give direct measurement of the excess concentration at the surface was proposed in the last decade. Unfortunately, those techniques are based on high level and very expensive instrumentations, like Second Harmonic Generation (SHG) and Neutron Reflectivity (NR) [54]. The comparison of the results obtained with direct (SHG and NR) and indirect (surface tension) techniques, however, was very instructive, revealing that main discrepancies can be attributed to impurities, mainly inorganic for anionic surfactants and organic (hydrophobic) for cationic surfactants. It was evidenced, as an example, that for gemini of the C_{12} -2- C_{12} 2Br, the prefactor should be near 2 for spacer length from 2 to 12. This fact should make researchers aware to take every phenomenon with the outmost care, and that a careful inspection of surface tension behavior, in particular, is essential to give consistency to the obtained results.

The CMC and A_{\min} values were observed to increase for a spacer chain length going from 4 to 6 methylene units. The variations of micellar parameters with spacer length can be attributed to conformational changes of spacer at the micelle-water interface. Zana [49] and De et al. [55] also observed a similar trend in the dependence of micellar parameters on spacer chain length for C_{12} -s- C_{12} , DMA and C_{16} -s- C_{16} , DMA gemini surfactants, respectively. As the percentage of ethylene glycol increases, values of maximum surface excess also increases and consequently, A_{\min} decreases. Also, for C_{16} -6- C_{16} , MEA 2Br⁻, the surface excess is higher than for C_{16} -4- C_{16} , MEA, 2Br⁻ in presence of glycol while the opposite happens in water. The C_{16} -6- C_{16} , MEA, 2 Br⁻ seems to form a more compact film at the air-water boundary. The presence of EG in the solvent system could make it to replace in part water at the surface thus modifying the repulsion among the headgroups (see above, for the effect on CMC and α)

and show better solvation for the alkyl spacer. Since the spacer is too short to fold towards the interior of the adsorbed layer or micelles, it should be located, more or less, at the surface. The modification of the solvent composition at the surface is then crucial and can affect the adsorption. While the CMC is increased, the ability to accommodate surfactant molecules at the surface is enhanced, thus increasing the surface excess concentration. Moya et al. [14] studying C_{12} -s- C_{12} , DMA, $2Br^-$ surfactants in EG-water mixtures observed the opposite behavior, i.e. the surface excess diminishes with the increase for the EG content in the solvent. The observed behavior should be related to the presence of the ethanol moiety in the C_{16} -s- C_{16} MEA, $2Br^-$ head group. Its ability to form hydrogen bonding can be enforced by the presence of EG in the solvent mixture. Since EG is known to disrupt the hydrogen bonding network of water, it is possible that the hydrogen bonding would establish among ethanol moieties on the head groups that can be dehydrated leaving more opportunities to keep the head groups closer and counteracting the electrostatic repulsion.

Table 2

Surface properties and thermodynamic parameters of gemini surfactants (C_{16} -s- C_{16} , MEA $2Br^-$) in aquo-organic solution.

Surfactants	% (v/v)	Π_{CMC} mNm^{-1}	Γ_{max} 10^6 $mol.m^{-2}$	A_{min} $10^{20} m^2$	ΔG_m° $kJ.mol^{-1}$	ΔG_{ads}° $kJ.mol^{-1}$	$\Delta G_{m,tail}^\circ$ $kJ.mol^{-1}$	ΔG_{trans}° $kJ.mol^{-1}$
C_{16} -4- C_{16} , MEA $2Br^-$	0.0	32.0	1.39	119.4	-81.1	-104.1	-40.5	
	10.0	25.5	1.51	109.9	-78.5	-95.4	-39.3	2.6
	20.0	21.2	1.82	91.3	-76.8	-88.4	-38.4	4.3
C_{16} -6- C_{16} , MEA $2Br^-$	0.0	34.0	1.27	130.7	-79.9	-106.6	-39.9	
	10.0	26.5	1.72	96.5	-73.8	-89.2	-36.9	6.1
	20.0	22.1	2.10	79.1	-73.2	-83.7	-36.2	6.7

3.1.4. Effect of Temperature on Micellization

The Gibbs energy of micelle formation was calculated from the pseudo-phase separation model for ionic surfactants according to equation (5)

$$\Delta G_m^\circ = 2(1.5 - \alpha) RT \ln X_{CMC} \quad (5)$$

where R is the gas constant, T is temperature, and X_{cmc} is the CMC value on the mole fraction scale, α is the degree of micellar ionization and the other symbols have their usual meaning. The above expression, proposed by Zana, [56] accounts for the presence of two alkyl chains (and two polar head groups) in the surfactant. The data given in Tables 2 and 3 shows that the free energy of micellization (ΔG_m°) is negative in all considered cases and becomes less negative as the cosolvent content in the solution increases. However, at a fixed cosolvent

concentration, the free energy of micellization shows small variations in the investigated temperature range. The influence of the organic solvent on the CMC, α and on the size of the aggregates, can be explained by considering the following solvent-dependent contributions to the free energy of micellization [57]: (i) the surfactant tail transfer free energy, (ii) the aggregate-core solvent interfacial free energy, and (iii) the head group interaction free energy. Besides these factors, the head groups steric interactions and the deformation of the surfactant tails inside the micelles also have an influence on the Gibbs energy of micellization.

$$\text{The Gibbs free energy of micellization per alkyl tail is defined as } \Delta G_{m,\text{tail}}^{\circ} = \Delta G_m^{\circ} / 2. \quad (6)$$

In order to investigate this point, the effect of EG on the micellization process was estimated through the Gibbs energy of transfer, $\Delta G_{\text{trans}}^{\circ}$, which can be written as [58].

$$\Delta G_{\text{trans}}^{\circ} = \Delta G_m^{\circ} (\text{water-organic solvent mixed media}) - \Delta G_m^{\circ} (\text{pure water}) \quad (7)$$

The positive values of $\Delta G_{\text{trans}}^{\circ}$ can be understood on the basis of a reduction in the solvophobic interactions caused by the improved solvation, which leads to an increase in the solubility of the hydrocarbon tails in the presence of ethylene glycol and consequently in an increase in the critical micelle concentration (Table 2). The $\Delta G_{\text{trans}}^{\circ}$ value gradually increases with increasing mass fraction of co-solvent in the mixture. This results from the preferential interactions of the hydrocarbon part of a surfactant with the hydrophobic part of a co-solvent and cationic head with water that decrease the ability of a surfactant to associate.

The standard free energy of adsorption ($\Delta G_{\text{ads}}^{\circ}$) at the air/water interface was calculated by using the expression.

$$\Delta G_{\text{ads}}^{\circ} = \Delta G_m^{\circ} - \pi_{\text{CMC}} / \Gamma_{\text{max}} \quad (8)$$

From Table 2 it can be observed that the ΔG_m° and $\Delta G_{\text{ads}}^{\circ}$ values were all found to be negative in both the aqueous and EG-water system for gemini surfactants, indicating a spontaneous micellization process. The $\Delta G_{\text{ad}}^{\circ}$ is greater than that of ΔG_m° for all the systems. Their difference is a measure of the spontaneity difference of the two

Table 3. Thermodynamic parameters of micellization of gemini surfactants in water and binary mixtures.

Solvent	Temp. K	C ₁₆ -4-C ₁₆ , MEA 2Br ⁻			C ₁₆ -6-C ₁₆ , MEA 2Br ⁻		
		ΔG_m° kJ.mol ⁻¹	ΔH_m° kJ.mol ⁻¹	ΔS_m° JK ⁻¹ mol ⁻¹	ΔG_m° kJ.mol ⁻¹	ΔH_m° kJ.mol ⁻¹	ΔS_m° JK ⁻¹ mol ⁻¹
Water	300	-81.1	-35.9	150	-79.9	-23.2	189
	310	-80.4	-37.5	138	-78.2	-24.5	173
	320	-79.4	-38.7	127	-76.6	-25.0	161
10 % v/v EG	300	-78.6	-31.3	157	-73.8	-21.1	175
	310	-77.4	-32.3	145	-73.1	-21.8	165
	320	-75.6	-32.9	133	-72.2	-22.4	155
20 % v/v EG	300	-76.9	-23.2	179	-73.2	-27.3	153
	310	-77.9	-24.5	172	-73.2	-28.4	144

processes; the adsorption process is fairly stronger than the bulk process of micellization. Thus, the head group architecture of the surfactants plays a decisive role in the surface chemical behaviors of the surfactants.

The standard enthalpy change for the micellization process, ΔH_m° , can be determined using the Gibbs-Helmholtz equation (8):

$$\Delta H_m^\circ = \{\partial (\Delta G_m^\circ)/T\} / \{\partial (1/T)\} \quad (9)$$

$$\Delta H_m^\circ = -2(1.5 - \alpha) RT^2 [\partial \ln X_{CMC} / \partial T] \quad (10)$$

Therefore, if the dependence of the CMC values on temperature is known, a plot of $\ln X_{CMC}$ versus temperature can be constructed, giving a linear trend (Fig S1). The slope can be found at each temperature. The value of enthalpy of micellization has been calculated from the Eq. (9) and it is evident that micellization is always exothermic and ΔH_m° decreases with the increase in co-solvent concentration (Table 3). This may be interpreted because of decrease in the energy required to break up the iceberg structure surrounding the hydrocarbon chains of the gemini surfactants.

Then the standard entropy of micelle formation, ΔS_m° , is obtained by the use of the following relation:

$$\Delta S_m^\circ = (\Delta H_m^\circ - \Delta G_m^\circ) / T \quad (11)$$

The entropy change is positive in all the cases. However, it decreases with increasing temperature. Ethylene glycol is acting as a co-solvent and as a structure-breaking solute. In micellar solutions, structure-breaking solutes lower the hydrophobic effect, which is considered as the driving force for micellization. The presence of structure breakers in the aqueous phase may disrupt the organization of water produced by the dissolved hydrophobic group, thereby decreasing entropy increase in micellization. The magnitude and sign of the ΔH_m° and ΔS_m° values are in agreement with the destruction of hydrophobic hydration in the process of micellization [59].

3.2 Kinetic Investigation

3.2.1. Nucleophile Aided Esterolysis in Cationic Gemini and CTAB

The observed rate constant values for PNPA and PNPDPH hydrolysis in gemini surfactants and CTAB are summarized in Table 4. Ester hydrolysis was quite slow in the absence of surfactants while gemini surfactants micelles enhanced the reaction rate more than CTAB surfactants micelles, thus indicating that micellar media assisted the rate of reaction. Introduction of gemini surfactants provided rate acceleration up to 1.88 fold for C_{16} -6- C_{16} , MEA 2Br⁻ and 1.80 fold for C_{16} -4- C_{16} , MEA 2Br⁻ with SHA for cleavage of PNPA with respect to CTAB. Similarly 3.46 fold rate enhancements in C_{16} -6- C_{16} , MEA 2Br⁻ and 2.19 fold with C_{16} -6- C_{16} , MEA 2Br⁻ was observed for PNPDPH hydrolysis with SHA with respect to CTAB micelles (Table 4). Hydroxamate ions are α -

effect nucleophiles, that is, their reactivity is greater than that predicted by the relationship between nucleophilicity and basicity. These are effective deacylating and dephosphorylating agents. Numerous reactions suggest that hydroxamate ions (—N—O^-) act as reactive species in the hydrolysis of esters hence, hydroxamic acids like AHA, BHA and SHA were used as nucleophiles for ester cleavage in the present investigation and their nucleophilic efficacy was compared with that of BDMO. Ester hydrolysis was monitored quite efficiently as all the nucleophiles used were the source of powerful α -nucleophiles and the reactivity of these nucleophiles in gemini and CTAB micelles is clearly manifested in Table 4. Nucleophilic reaction of anionic nucleophiles in the cationic micelles is governed by the basicity and strength of incorporation of nucleophiles into the micellar media. Kinetic data (Table 4) evidence that SHA ($\text{p}K_a$ 7.20) shows larger reactivity than BHA ($\text{p}K_a$ 8.60), AHA ($\text{p}K_a$ 9.32) and BDMO ($\text{p}K_a$ 9.20). Hydroxamic acids, if ionized at a proper pH, can interact with cationic headgroups, and SHA and BHA are slightly higher hydrophobic than AHA and are expected to have large micellar incorporation, leading to the effective rate acceleration. The higher reactivity of SHA is due to bifunctional nucleophilicity of hydroxamate (—N—O^-) and phenolate functions of the salicylhydroxamate ion [19a]. The N—OH groups are considerably ionized as N—O^- at pH 8.0 and therefore bind to gemini head group through electrostatic attractions.

Table 4. Hydrolysis of PNPA and PNPDP with different α -nucleophiles in the presence of gemini surfactants at temperature 27°C and pH 8.0

Surfactant	PNPA				PNPDPP		
	$10^3 k_{\text{obs}} (\text{s}^{-1})$				$10^3 k_{\text{obs}} (\text{s}^{-1})$		
	BDMO	BHA	SHA	AHA	BDMO	SHA	AHA
Nil	1.31	1.86	1.81	0.48	0.50	1.80	0.16
$\text{C}_{16}\text{-4- C}_{16}$ MEA 2Br^-	5.98	8.25	8.82	0.86	0.75	3.03	0.36
$\text{C}_{16}\text{-6- C}_{16}$ MEA 2Br^-	6.96	8.71	9.26	0.60	0.85	4.78	0.65
CTAB	1.53	4.78	4.90	0.08	1.30	1.38	0.55

Reaction Conditions: $[\text{PNPA}]$ & $[\text{PNPDPP}] = 0.5 \times 10^{-4} \text{ M}$, $[\text{Nu}^-] = 0.5 \times 10^{-3} \text{ M}$, $[\text{KCl}] = 0.1 \text{ M}$, $\text{pH} = 8.0$, $\text{Temp.} = 27^\circ\text{C}$ and $[\text{Surfactant}] = 0.5 \times 10^{-3} \text{ M}$.

3.2.2. Reaction of PNPA in Gemini Surfactants

To study the effects of spacer chain length on the rates of PNPA hydrolysis, we followed the hydrolysis of PNPA induced by BHA in gemini surfactants ($\text{C}_{16}\text{-6- C}_{16}$, MEA 2Br^- and $\text{C}_{16}\text{-4- C}_{16}$, MEA 2Br^-) and compared with that of monomeric surfactants (CTAB). The results are summarized in Table S1 and plots of k_{obs} as a function of surfactant concentration are shown in Fig. 4. The kinetic rate data revealed that the rate of reaction increases by increasing surfactant concentration up to a certain concentration of gemini surfactant and then decreases (Fig. 4). The effect of the spacer on the properties of gemini surfactants have been explored recently [60-61]. For gemini surfactants as host micelles, it was observed that the reactivity of nucleophiles also depends on the spacer length variation. The micellar rate of reaction increases with increasing length of spacer between the two cationic headgroups of the gemini surfactants. $\text{C}_{16}\text{-6- C}_{16}$, MEA 2Br^- showed maximum k_{obs} at different surfactant

concentration and the catalytic activity of the surfactants may be presented as $C_{16-6-C_{16}}$, MEA $2Br^- > C_{16-4-C_{16}}$, MEA $2Br^- > CTAB$. Although variation of spacer chain length alters the shape, CMC etc. of gemini micellar aggregates, these changes do not affect very significantly the observed rate constants for the ester cleavage reactions. It is well known that the aggregation numbers and dimensions of micelles decrease when spacer chain length increases from 4 to 6 [35]. This can be explained on the account of conformational changes of spacer at the micelle-water interface.

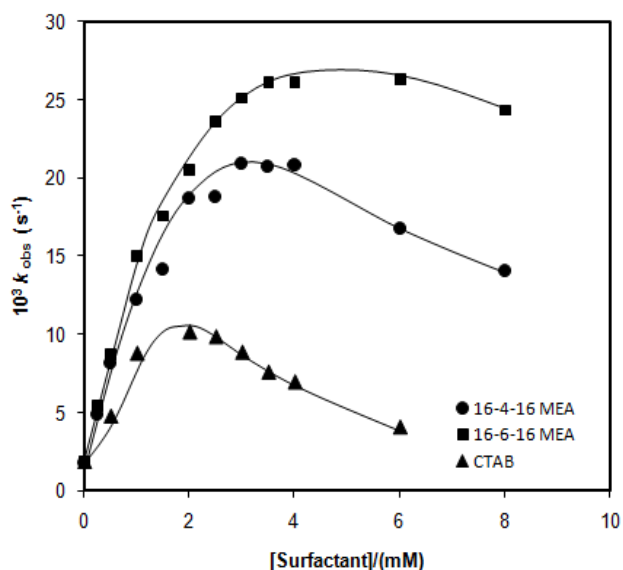


Fig. 4. Influence of surfactant concentration on k_{obs} , for the reaction of PNPA with BHA in the presence of gemini and CTAB. Reaction Conditions: $[PNPA] = 0.5 \times 10^{-4}$ M, $[BHA] = 0.5 \times 10^{-3}$ M, $[KCl] = 0.1$ M, pH = 8.0, Temp. = 27°C.

Bhattacharya et al. [18] have discussed that the observation of better rate of hydrolysis reactions in gemini surfactants compared to that of monovalent surfactants could be due to the presence of the hydrophobic polymethylene spacer chains between two head groups in geminis, which in turn decreases the extent of water penetration at such micellar interfaces and this facilitates dephosphorylation and deacylation reactions. Gemini surfactants possessing lower CMC than CTAB exhibit obvious advantage in concentrating hydrophobic substrates like PNPA/PNPDPP and catalysts into the micelles. Hence, highest concentration of hydrophobic substrates and complexes in gemini micelles is reached compared to traditional micelles of CTAB.

3.2.3. Cleavage of PNPDP in Water-Ethylene Glycol Micellar Media

Pseudo-first-order rate constants (k_{obs}) for the nucleophilic cleavage of PNPDP in the presence of cationic gemini surfactants in different water-EG solutions (0-20% v/v) are summarized in Table S2. The presence of EG

retarded the rate of ester cleavage for the reactions in the micellar medium. This can be accounted for the transfer of substrate from water to micelles and the interfacial properties. $C_{16-6-C_{16}}$, MEA showed better catalytic effect for the attack of benzohydroxamate ions on P=O centre than $C_{16-4-C_{16}}$, MEA. In order to investigate the hydrolytic cleavage of PNPDP as a function of concentration of gemini surfactant $C_{16-8-C_{16}}$, MEA in water-EG mixtures, k_{obs} was plotted against surfactant concentration as shown in Figs. 5 and S2. The rate-surfactant concentration profiles obtained are characteristic of the micelle catalyzed reaction. The observed rate constants increased by increasing surfactant concentration and then gradually level off. This can be explained by considering that, by increasing gemini micelles in the solution a stage appears where all the substrates are almost entrapped in the micellar phase. Further, the reactants are micro compartmentalized in the micelles by electrostatic and hydrophobic interactions; the catalytic enhancement results from both the localized concentration of the reactants and the physicochemical properties of the micellar environment, which is quite different from those of the bulk solvent. At a given concentration of gemini surfactant, rate retardation was observed with increase in the concentration of EG in the medium. This can be attributed to the structural changes in gemini micelles due to solvent effect as the presence of organic solvent in the medium decreases the water content and finally polarity of the medium is reduced. The higher polarity of the solvent (or better, of the solvent/micellar surface and/or solvent/micellar palisade sites that are believed to be the typical sites where the reaction should occur) stabilizes the charged intermediate and therefore, increases the reaction rate by its solvation. Thus, the addition of organic solvent lowers the polarity and causes in decrease in stability of the transition state and therefore, the rate of reaction is decreased on increasing the proportion of organic solvents. On the other side, since the introduction of EG, the lower medium polarity better solvates the hydroxamic acids and substrates, thus reducing their incorporation into the micelles and this reduces also the catalytic activity of the system.

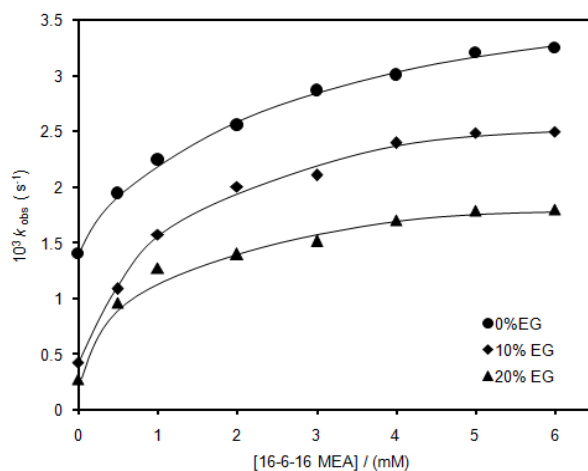


Fig. 5. Influence of surfactant concentration on k_{obs} , for nucleophilic substitution reaction of *p*-nitrophenyldiphenyl phosphate and benzohydroxamate ion in water + EG micellar solutions of $C_{16-6-C_{16}}$, MEA, $2Br^-$. Reaction Conditions: $[PNPDPP] = 0.5 \times 10^{-4} M$, $[BHA] = 0.5 \times 10^{-3} M$, $pH = 8.0$, $[KCl] = 0.1 M$, $Temp. = 27^\circ C$.

4. Conclusions

Two gemini surfactants C₁₆-s- C₁₆, MEA with an ethanol moiety per headgroup and a polymethylene spacer of 4 or 6 methylenes were prepared, characterized and used in micellar catalysis. The CMC values increased with increasing spacer length of gemini surfactants. The degree of micellar ionization of gemini surfactants, α , became larger with an increase in EG concentration and temperature. The Γ_{\max} values rose with increasing percentage of EG and decreased with increasing spacer length of gemini surfactants, in contrast with the general finding assessed in the literature. The hydrogen bonding ability of the ethanol moiety at the surfaces could explain this unusual behavior, helping the molecules to stay adsorbed at the surface. Furthermore, the presence of the ethanol moiety that can help in the modulation of properties of surfactants can, in the near future, be exploited to prepare more versatile structures, to be conceived as “tailor made” surfactants to fit proper applications and the major challenge is now to establish these structure-property relationships on a theoretical and thermodynamic basis. Also the thermodynamic data were in agreement with general findings in the field of gemini surfactants, since ΔG°_m and $\Delta G^{\circ}_{\text{ads}}$ indicated a spontaneous micellization process, exothermic and entropy driven. The kinetic rate retardation effect and increase of CMC values with increasing EG concentrations are supportive to the polarity driven alteration of micellization. Kinetic constants were observed to be dependent on spacer chain length of gemini surfactants as well as on the nature of nucleophile. Among the CTAB and C₁₆-s-C₁₆, MEA 2Br⁻ gemini micellar systems, C₁₆-6-C₁₆, MEA 2Br⁻ was the most efficient micellar catalyst for the hydrolysis of PNPA/PNPDPP. Salicylhydroxamic acid proved to be the best nucleophilic reagent for esterolytic cleavage in micellar media owing to its lower pK_a value.

Supporting Materials

Table S1 Hydrolysis of PNPA with BHA in the presence of gemini and CTAB.

Table S2 Kinetic rate data for nucleophilic substitution reaction of *p*-nitrophenyl diphenyl phosphate and benzohydroxamate ion in water + EG micellar solutions of cationic gemini surfactants.

Fig. S1. $\ln X_{\text{cmc}}$ versus temperature plots of gemini surfactant C₁₆-6-C₁₆ MEA, 2Br⁻ in aqueous and EG-water medium at different temperatures.

Fig. S2. Rate-surfactant profile for nucleophilic substitution reaction of *p*-nitrophenyldiphenyl phosphate and benzohydroxamate ion in water + EG micellar solutions of cationic gemini surfactants. Reaction Conditions: [PNPDPP] = 0.5 x 10⁻⁴ M, [BHA] = 0.5 x 10⁻³ M, pH = 8.0, [KCl] = 0.1 M Temp. = 27°C.

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