Mixed Micellization Behavior of Gemini (Cationic Ester-Bonded) Surfactants with Conventional (Cationic, Anionic and Nonionic) Surfactants in Aqueous Medium

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Cleavable Gemini Surfactants / Cmc / Mixed Micelles / Synergistic Interaction

Two cationic ester-bonded cleavable gemini surfactants of different hydrophobic chain length ethane-1,2-diyl bis(N,N-dimethyl-N-alkylammoniumacetoxy)dichloride, $C_nH_{2n+1}(CH_3)_2N^+$ $(CH_2COOCH_2)_2N^+(CH_3)_2C_nH_{2n+1}$. $2Cl^-$ (n-E2-n, n = 12, 16), having ester linkage in the spacer, were synthesized adopting the reported procedure. Physicochemical properties of the single and binary gemini-conventional mixed micelles of different mole fractions were studied by conductivity measurements at 30 °C. The conventional surfactants used were: DTAC (dodecyltrimethylammonium chloride), CTAC (hexadecyltrimethylammonium chloride), CPC (cetylpyridinium chloride), SDS (sodium dodecyl sulfate), SDBS (sodium dodecylbenzene sulfonate), TX-100 (*t*-octylphenoxypolyethoxyethanol) and Brij 58 (polyoxyethylene (20) cetyl ether). Whereas the critical micelle concentration (*cmc*) values for the dicationic geminis (12-E2-12 and 16-E2-16) were found to be very low as compared to the respective monomeric surfactant with the same number of carbon atoms in the hydrophobic chain per hydrophilic head group, those for all the binary systems were found to be less than the ideal *cmc* values studied at different mole fractions of the geminis. This synergistic interaction between the surfactants has been analyzed in the light of various theoretical models such as Clint, Rubingh, Motomura and Maeda.

1. Introduction

Surfactants comprising the hydrophilic head group and hydrophobic hydrocarbon chain [1,2] show self-aggregation with a high degree of cooperativity with the aqueous medium result in micelle formation which occurs at a threshold concentration (*i.e.*, critical micelle concentration, cmc) and depends upon several factors, such as the relative size of the hydrophilic/hydrophobic parts, the presence of charges and the degree of hydration [3]. Being one of the most important representative classes of industrial products, surfactants have manifold applications in every sector of industry such as

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fabric softener [4], emulsifiers, wetting agents, pesticides, agricultural sprays, domestic products, bio-catalysis or bio-processing [5], in pharmaceuticals or drug delivery systems [6,7] and others. Gemini surfactants are made up of two monomeric units connected at the level of head group by a spacer that can be hydrophilic or hydrophobic [1]. It is well known that the traditional amphiphiles (generally cationic) show good stability towards chemicals and microbes that gives chance to accumulate in the soil, water or in environment for a long period of time with slow degradation. Therefore, readily cleavable gemini surfactants are most suitable for use instead of the conventional surfactants. Gemini surfactants with cleavable bond in spacer (like amide or ester) possess superior properties such as lower *cmc*, much greater efficiency in reducing the surface tension of water, reduced interfacial tension, special rheological properties (viscoelasticity, shearthickening) at relatively low concentration than the conventional ones [8–10]. Ester bonded gemini surfactants are found to have good biodegradability as the polar bond contributes to the higher water solubility making them easily degradable [11–16].

Surfactant mixtures, in which one of the components is a biodegradable gemini, are of considerable interest for various applications as they perform better than the solutions containing their monomeric surfactant counterparts. In mixed micelles not only the properties of the individual components are combined, but also synergism is observed in properties like *cmc*, surface tension, *etc.* Although several researchers have chosen the mixed micelles for different kind of studies [17–23], reports regarding the nature of the gemini-conventional mixed micellar solutions are less. Because of the lack of work on the mixed micellization study of biodegradable gemini with ester group functionality in the spacer part as one of the components, we have studied the physicochemical properties of the pure and mixed micellar solutions of different cationic, anionic and non-ionic surfactants with two cationic biodegradable geminis (*n*-E2-*n*, n = 12, 16) of different hydrophobicity. The main inducement for the synthesis of such gemini surfactants is their eco-friendly nature. In this paper, we report the results of investigations carried out by conductivity measurements in aqueous solutions at 30 °C.

2. Materials and methods

2.1 Materials

The cationic surfactants DTAC ($\leq 98\%$, Aldrich), CTAC (99%, Acros) and CPC (Merck), anionic surfactants SDS (99%, Sigma) and SDBS (TCI), nonionic surfactants Brij 58 (Merck) and TX-100 (Fluka) were used as received. *N*,*N*-dimethyldodecylamine (Acros Organic), *N*,*N*-dimethylhexadecylamine ($\geq 95\%$, Aldrich), ethylene glycol (99%, Sigma Aldrich) and chloroacetyl chloride (98%, Loba chemie) were also used as received.

The melting points were visually determined by the microscopic melting point apparatus Reichert Thermovar Jung, Austria. The preliminary characterization of the synthesised gemini surfactants was carried out by IR spectroscopy using Interface 2020 FT-IR Spectrophotometer, U.K. ¹H-NMR spectra were recorded on 300 MHz Bruker Avance NMR Spectrometer, CDRI, Lucknow in CDCl₃ with ¹H chemical shifts relative to internal standard TMS. Electrospray ionization mass spectra (ESI-MS, positive) were obtained on an ESI, LC/MS.



Scheme 1. Synthesis of cationic gemini surfactant ethane-1,2-diyl bis(N,N-dimethyl-N-alkylammonium-acetoxy) dichloride (n = 12, 16).

Chemical structures of the monomeric and dimeric surfactants used in this study are shown in Scheme S1 (Supporting material).

2.2 Synthesis of the biodegradable gemini surfactants

The cationic ester-bonded gemini surfactants (n-E2-n) were synthesized in two steps (Scheme 1) following a reported procedure [12].

(i) In the first step ethane-1,2-diyl bis(chloroacetate) was prepared by heating a mixture of chloroacetyl chloride (0.22 mol) and ethylene glycol (0.1 mol) at 50 °C for 8 h in nitrogen atmosphere. The reaction mixture was washed with saturated brine for complete neutralization and the product was dissolved in ether, dried over magnesium sulfate, and the solvent was then distilled off under reduced pressure. Low melting colourless needle-shaped crystals of the compound were obtained in good yield (15.15 g, 65.36%).

(ii) In the second step, the target compound was obtained by heating ethane-1,2diyl bis(chloroacetate) with *N*,*N*-dimethylalkylamine (dodecyl and hexadecyl, molar ratio, 1 : 2.1) in ethyl acetate for 10 h. When the solvent was removed under reduced pressure, white crystalline solid of the cationic gemini surfactant was obtained. It was further purified by repeated crystallization in ethyl acetate-ethanol mixture (5 : 1, v/v). The purity of the compound was confirmed by thin layer chromatography (TLC) (silica gel, CHCl₃-MeOH, 6 : 4, v/v). The yield of the characterized compounds *n*-E2-*n* were 30.40 g (78.6%) for *n* = 12 and 36.81 g (78.7%) for *n* = 16. The structures were confirmed by FT-IR, ¹H-NMR spectra and mass spectrometry. The ¹H-NMR and MS-ESI (+) spectra of *n*-E2-*n* are shown in Figs. S1 and S2 (Supporting material).

2.3 Characterization

Whereas the characterization of 16-E2-16 has been discussed elsewhere [13], details of 12-E2-12 are given below:

m. p.: 191–194 °C, $R_f = 0.58$

FT-IR (KBr, v cm⁻¹): 2922.75, 2855.42 (C-H); 1746.48 (C=O); 1465 (C-O); 1188.06 (C-N); 724.68.

¹H-NMR (300 MHz, CDCl₃, δ scale): 0.86–0.90 (t, 6H, $-2 \times CH_3$, alkyl chain); 1.25–1.34 (m, 36H, $-2 \times (CH_2)_9$, alkyl chain); 1.77 (m, 4H, $-2 \times N^+CH_2CH_2$); 3.53 (s, 12H, $-2 \times N^+(CH_3)_2$); 3.79 (s, 4H, $-2 \times CH_2O$); 4.49 (s, 4H, $-2 \times N^+CH_2$); 5.36 (s, 4H, $-2 \times N^+CH_2COO$).

MS-ESI (+) m/z: 605.6 (M-Cl⁻), 555.6 (M-Cl⁻-CH₃Cl⁻), 298 (C₁₂H₂₅ CH₃)₂ N⁺CH₂OOCH=CH₂), 130 (CH₃)₂N⁺CH₂OOCH=CH₂).

2.4 Cmc determination by conductometric measurements

The mixed micellization study of *n*-E2-*n* was done with six different monomeric surfactants at different mole fractions. The solutions of gemini (cationic) and conventional (cationic, anionic, nonionic) surfactants were prepared in terms of the mole fractions of gemini (α_1) equaling 0.2, 0.4, 0.6, 0.8 in the mixed systems, with the total concentrations of all the mixed solutions remaining same at each mole fraction. For each surfactant, the *cmc* of the single and binary mixtures with the above mole fractions were determined. Each experiment was repeated to achieve good reproducibility. All the solutions were prepared in double distilled water.

The conductance [24] as a function of surfactant concentration was measured at $30 \,^{\circ}$ C by using ELICO conductivity bridge Model CM82T and dip cell (cell constant $1.02 \,\mathrm{cm}^{-1}$). The temperature was maintained by a circulating water bath. The conductivity of the single/binary surfactant solutions were found to increase with the aliquot additions of a known concentration of the surfactant. The *cmc* values were obtained at the break points by plotting the specific conductivity *vs*. concentration of surfactant. To compare the *cmc* of various compounds, all the conductivity measurements of the pure/mixed surfactant systems were performed at the same temperature. The specific conductivity *vs*. [surfactant] plots for the pure gemini surfactants are shown in Fig. 1 and for the other systems the plots are shown in Figs. S3, S4A and S4B as "Supporting Material Section". The *cmcs* of the pure monomeric surfactants agree with the literature values [25–31].

2.5 Cleavable properties

The presence of ester linkages in the spacer part of the cationic gemini surfactants suggests that these might be cleavable through chemical means in alkaline condition at pH 7.4 and pH 12. Using phosphate-buffered saline and sodium hydroxide/potassium hydrogen phosphate (Ringer Buffer). 0.05 g gemini surfactant was taken in 10 ml buffer solution [10]. The FT-IR spectra of 12-E2-12 and 16-E2-16 at pH 12 are shown as Fig. S5A and S5B, respectively.

From the FT-IR spectra it is quite evident that the gemini surfactants get cleaved by the buffer in 8 h. The absorption bands for the ester groups (C=O) at $1746.48/1746.36 \text{ cm}^{-1}$ (12-E2-12/16-E2-16) are shifted to $1640.59/1641 \text{ cm}^{-1}$ and new absorption band for the –OH group appears at 3503.49 cm^{-1} . Thus, the formation of easily degradable compounds such as fatty acid salts and respective diol or compounds with hydroxyl group takes place. This indicates the hydrolysis or cleavability of the gemini surfactants.



Fig. 1. Specific conductivity as a function of surfactant concentration for the pure cationic geminis (12-E2-12 and 16-E2-16) at 30 °C.

3. Results and discussion

The cmc values of the gemini-conventional mixed surfactant systems of different compositions were determined by the conductivity measurements. Although it is not possible to perform the conductivity experiments for the pure non-ionic surfactants, for the gemini-conventional surfactant mixtures the conductivity could be measured. The *cmc* values of the pure surfactants decrease in the order DTAC > SDS > SDBS > CTAC >CPC > 12-E2-12 > 16-E2-16. Compared with the corresponding conventional monomeric surfactants, the dimeric surfactants have much lower values of *cmc*. The remarkably low *cmc* values of *n*-E2-*n* are due to greater hydrophobicity of the geminis – the two hydrocarbon chains break more "structured" water (vis-a-vis single head/single chain conventional surfactant) which is an energetically favored process. Therefore, the *cmc* values are always lower for gemini surfactants than their analogous conventional counterparts [7]. The position of functional group also affects the micellization process. Two ester bonds in the spacer make it more hydrophilic that prompts micelle formation at low concentration [13,32]. The *cmc* values, along with other relevant parameters, such as, ideal cmc (cmc_{ideal}), counterion binding (b), standard Gibbs excess free energy (ΔG_{ex}^m), Gibbs free energy of micellization (ΔG_{mic}), mole fraction of surfactant in ideal state (X_1^{ideal}) , interaction parameter (β^m) and activity coefficients (f_1^m, f_2^m) , are recorded in Tables 1-3 for gemini and conventional surfactants in pure and mixed states.

3.1 Counterion binding

The conductivity data of the pure and mixed systems were used for the determination of the fraction of counter ions (b) bound to the micelles. The counterions which are the main contributing parts for the conductivity of the solutions due to their ionic mobility, bind just adjacent to the surface of the micelles, *i.e.*, to the Stern layer. Below

| Table 1. | Various phy | sicochemic | cal parame | ters for <i>n</i> -E | 2- <i>n</i> (<i>n</i> = 1 | 2, 16) + ca | tionic mixed | l systems | at 30°C. | |
|--------------------|-----------------------------------|------------------------|----------------|----------------------|----------------------------|------------------|------------------|-----------------|---------------------------------------------|------------------------------------------------------|
| $lpha_{ m Gemini}$ | <i>cmc/cmc</i> ₁₂ (mM) | $cmc_{\rm ideal}$ (mM) | X_1^m | X_1^M | β^m | f_1^m | f_1^m | p | $\Delta G_{ m mic}$ (kJ mol ⁻¹) | $\Delta G^{m}_{\mathrm{ex}}$ (kJ mol ⁻¹) |
| | | | | 1 | 2-E2-12 + | DTAC | | | | |
| 0 | 21.2 | | | | | | | 0.29 | | |
| 0.2 | 0.0051 | 0.0081 | 0.831 | 0.3513 | -9.81 | 0.7571 | 0.0011 | 0.41 | -74.87 | -3.46 |
| 0.4 | 0.0031 | 0.0040 | 0.882 | 0.6326 | -9.25 | 0.8790 | 0.0007 | 0.90 | -117.93 | -2.42 |
| 0.6 | 0.0023 | 0.0027 | 0.913 | 0.8702 | -9.15 | 0.9330 | 0.0005 | 0.30 | -69.07 | -1.83 |
| 0.8 1.0 | 0.0019 0.0016 | 0.0020 | 0.944 | I | -9.05 | 0.9724 | 0.0003 | $0.37 \\ 0.145$ | -75.71 | -1.19 |
| | | | | | | | | | | |
| | | | | | 12-E2-12 - | ⊢ CPC | | | | |
| 0 | 0.975 | | | | | | | 0.53 | | |
| 0.2 | 0.0045 | 0.0080 | 0.738 | 0.3769 | -6.80 | 0.7133 | 0.0164 | 0.35 | -70.52 | -2.97 |
| 0.4 | 0.0037 | 0.0040 | 0.751 | 0.6328 | -4.11 | 0.9770 | 0.0297 | 0.52 | -85.45 | -0.72 |
| 0.6 | 0.0025 | 0.0027 | 0.803 | 0.8803 | -4.27 | 0.9896 | 0.0210 | 0.72 | -104.00 | -0.51 |
| 0.8 | 0.0013 | 0.0020 | 0.822 | I | -9.47 | 0.7569 | 0.0015 | 0.61 | -98.39 | -3.39 |
| | | | | Ŧ | | | | | | |
| Ċ | 707 | | | - | + 01-77-0 | CIAC | | 69 0 | | |
| | 1.24 | 0,000 | | 0.4900 | 121 | 2002 0 | 1010.0 | co.0 | | , c , c |
| 7.0 | 0.0034 | 0.0003 | 0./82 | 0.4890 | 10.1- | 0.0980 | 0.0101 | 0.03 | -94.77 | -3.43 |
| 0.4 | 0.0021 | 0.0031 | 0.825 | 0.8637 | -7.59 | 0.7925 | 0.0056 | 0.70 | -104.26 | -2.76 |
| 0.6 | 0.0011 | 0.0021 | 0.792 | I | -10.2 | 0.6432 | 0.0016 | 0.82 | -119.08 | -4.23 |
| 0.8 1.0 | 0.0008 0.0013 | 0.0016 | 0.806 | I | -11.2 | 0.6548 | 0.0006 | $0.43 \\ 0.86$ | -85.11 | -4.42 |
| | | | | | | | | | | |
| | | | | | 16-E2-16 - | ⊦ CPC | | 1 | | |
| 0 0.2 | 0.975 0.0022 | 0.0063 | 0.720 | 0.4854 | -9.54 | 0.4859 | 0.0066 | 0.53 0.54 | -89.42 | -4.79 |
| 0.4 | 0.0023 | 0.0031 | 0.844 | 0.7113 | -6.54 | 0.8582 | 0.0091 | 0.66 | -100.14 | -2.13 |
| 0.6 0.8 | 0.0020 0.0010 | 0.0021 0.0016 | 0.966 0.832 | | -4.01 -9.61 | 0.9954 0.7684 | 0.0235 0.0012 | 0.71 0.66 | -104.49 -105.00 | -0.32 -3.34 |
| | | | | | - | | | | | |

cmc the concentration of the counterions increases with the surfactant concentration and thus the conductivity increases whereas above *cmc* the dissociation decreases thereby reducing the concentration of counterions and thus the conductivity of the solution. The degree of counterion dissociation was determined by taking the ratio of post-micellar slope (S_2) and pre-micellar slope (S_1). The ratio of S_2 to S_1 is considered as the fraction of counter ions dissociated from the micelles (g), so that the fraction of counterions bound (b) to the micelle is calculated by subtracting counterion dissociation from unity $b = (1 - S_2/S_1)$ [33,34]. For 16-E2-16 + CTAC/CPC and 12-E2-12 + CPC systems, b increases with increasing α_1 (except at 0.8). However, for 12-E2-12 + DTAC, no trend

| | $\Delta G^m_{\mathrm{ex}} \mod^{-1})$ | | -6.26 | -6.58 | -4.94 | -4.81 | | | -3.88 | -3.80 | -2.16 | -3.12 | | | -2.12 | -1.65 | -2.57 | -4.94 | | | -0.44 | -4.43 | -1.11 -3.96 |
|---------------------|---------------------------------------|------------|-----------------|---------|---------|--------------------|-----------|------|---------|---------|---------|---------|------------|------|--------|--------|--------|------------------|------------|------|--------|--------|------------------|
| | ic ^Z | | - 20 | 55 - | - 62 | 35 - | | | | | 53 | | | | | - | | - 52 | | | - 1 | 84 | |
| at 30°C. | $\Delta G_{\rm m}$ (kJ mo | | -105. | -120. | -115. | -103. | | | -78.2 | -81.0 | -74.0 | 97.5 | | | -59.1 | -80.] | -94.7 | -123. | | | -70.4 | -105. | -40.5 -116. |
| systems | p | | 0.66 0.73 | 0.86 | 0.81 | $0.66 \\ 0.15$ | | 0 27 | 0.44 | 0.45 | 0.366 | 0.60 | | 0.66 | 0.22 | 0.44 | 0.58 | 0.86 | | 0.27 | 0.37 | 0.70 | 0.30 0.79 |
| ionic mixed | f_1^m | | 0.0009 | 0.0003 | 0.0003 | 0.0001 | | | 0.0051 | 0.0024 | 0.0024 | 0.0007 | | | 0.0036 | 0.0020 | 0.0006 | 0.0001 | | | 0.0338 | 0.0015 | 0.0004 |
| 2, 16) + an | f_1^m | + SDS | 0.4133 | 0.4207 | 0.6179 | 0.6610 | SDRS | | 0.6367 | 0.6854 | 0.8845 | 0.8093 | + SDS | | 0.8815 | 0.9333 | 0.8676 | 0.6535 | SDBS | | 0.9907 | 0.6182 | 0.7280 0.7280 |
| $2-n \ (n=1)$ | β^m | 12-E2-12 - | -12.80 | -14.00 | -12.41 | -13.04 | 12-F2-12+ | | -8.81 | -9.41 | -7.86 | -9.95 | 16-E2-16 - | | -7.42 | -7.58 | -9.55 | -13.4 | l6-F2-16 + | | -3.74 | -10.4 | -0.00 -11.2 |
| ers for <i>n</i> -E | X_1^M | | 0.4187 | 0.8255 | 0.9368 | I | | • | 0.4534 | 0.8753 | I | I | | | 0.3872 | 0.7688 | I | I | | • | 0.5325 | I | |
| al paramet | X_1^m | | 0.738 | 0.751 | 0.803 | 0.822 | | | 0.774 | 0.800 | 0.875 | 0.854 | | | 0.870 | 0.905 | 0.878 | 0.822 | | | 0.950 | 0.786 | 0.927 |
| sicochemic | $cmc_{\rm ideal}$ (mM) | | 0.0081 | 0.0040 | 0.0027 | 0.0020 | | | 0.0081 | 0.0040 | 0.0027 | 0.0020 | | | 0.0063 | 0.0031 | 0.0021 | 0.0016 | | | 0.0063 | 0.0031 | 0.0016 |
| Various phy: | <i>cmc/cmc</i> ₁₂ (mM) | | 8.14 0.00247 | 0.00128 | 0.00134 | 0.00110 0.00162 | | CL C | 0.00399 | 0.00222 | 0.00209 | 0.00140 | | 8.14 | 0.0048 | 0.0027 | 0.0016 | 0.0008 0.0013 | | 2.72 | 0.0059 | 0.0015 | 0.0010 |
| Table 2. | $lpha_{ m Gemini}$ | | 0 0.2 | 0.4 | 0.6 | 0.8 1.0 | | 0 | 0.2 | 0.4 | 0.6 | 0.8 | | 0 | 0.2 | 0.4 | 0.6 | 0.8 1.0 | | 0 | 0.2 | 0.4 | 0.0 0.8 |

in *b* value was observed. For 16-E2-16 + SDS system, the *b* value increases with the increase of the mole fraction of gemini whereas no trend in *b* value was found for any of the gemini + anionic surfactant systems. Higher *b* values were observed at lower mole fractions of the gemini in the gemini + nonionic systems (Table 3).

3.2 Interaction of dimeric surfactants with monomeric surfactants in mixed micelles

All the theories suggested by Clint, Rubingh, Motomura and Maeda are summarized (see "Supporting Material Section" for the definition of terms and the equations used

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| ble 3. | Various phy | sicochemi | cal parame | eters for n- | E2-n (n = | 12, 16) + 1 | non-ionic n | nixed syst | tems at 30 °C | - : | |
|--------------|-----------------------------------|------------------------------|-----------------------|--------------|----------------|------------------|-------------|--------------|---------------------------------------------|----------------------------------------------------|-------------------------------------------------|
| jemini | <i>cmc/cmc</i> ₁₂ (mM) | cmc _{ideal} (mM) | X_1^m | X_1^M | β^m | f_1^m | f_1^m | p | $\Delta G_{ m mic}$ (kJ mol ⁻¹) | ΔG^m_{ex} (kJ mol ⁻¹) | $\Delta G^\circ_{ m Maeda}_{ m (kJ mol^{-1})}$ |
| | | | | | 12-E2 | -12+Brij | 58 | | | | |
| | 0.0046 | 10000 | 1 1 1 1 1 | 001.0 | 10 7 | | 1107.0 | | 02 01 1 | | |
| 74 | 0.0021 0.0012 | 0.0036 0.0027 | 0.562 0.562 | 0.667 | -1.85 -3.15 | c//c.0 0.5451 | 0.3695 | 0.72 | -110.59 -108.40 | -1.16 -1.96 | -15.85 |
| 90 | 0.0011 | 0.0022 | 0.630 | 0.818 | -3.52 | 0.6172 | 0.2469 | 0.55 | 94.04 73 88 | -2.07 | -16.25 |
| 0 0 | 0.0016 | 0100.0 | 160.0 | C76.0 | | 1160.0 | 0.41.0 | 0.14 | 00.01 | +1.2 | 11.01 |
| | | | | | 12-E2 | -12 + TX- | 00 | | | | |
| | 0.180 | | | | | | | | | | |
| <i>с</i> і . | 0.0016 | 0.0078 | 0.689 | 0.429 | -6.71 | 0.5217 | 0.0415 | 0.68 | -99.68 | -3.62 | -15.63 |
| 4 | 0.0022 | 0.0040 | 0.771 | 0.667 | -5.71 | 0.7401 | 0.0335 | 0.85 | -100.84 | -2.54 | -15.77 |
| 9 | 0.0010 | 0.0027 | 0.811 | 0.818 | -5.90 | 0.8088 | 0.0206 | 0.62 | -97.45 | -2.28 | -15.90 |
| × | 0.0010 | 0.0020 | 0.750 | 0.923 | -10.0 | 0.5336 | 0.0035 | 0.56 | -120.29 | -4.73 | -16.16 |
| | | | | | 16-E2 | -16+Brii | 58 | | | | |
| | 0.0046 | | | | | | | | | | |
| 0 | 0.0016 | 0.0036 | 0.489 | 0.429 | -2.60 | 0.5086 | 0.5360 | 0.87 | -120.53 | -1.63 | -16.69 |
| 4 | 0.0019 | 0.0025 | 0.657 | 0.667 | -0.74 | 0.9168 | 0.7252 | 0.85 | -117.69 | -0.42 | -16.23 |
| 9 | 0.0014 | 0.0019 | 0.745 | 0.818 | -1.27 | 0.9202 | 0.4917 | 0.47 | -85.49 | -0.61 | -16.69 |
| 8 O | 0.0013 0.0013 | 0.0015 | 0.859 | 0.923 | -1.22 | 0.9758 | 0.4054 | 0.75 | -110.78 | -0.37 | -17.78 |
| | | | | | 16-E2 | -16 + TX- | 001 | | | | |
| | 0.180 | | | | | | | | | | |
| 6 | 0.0016 | 0.0061 | 0.666 | 0.431 | -8.72 | 0.3767 | 0.0209 | 0.68 | -103.48 | -4.89 | -15.75 |
| 4 4 | 0.0022 | 0.0031 | 0.817 | 0.669 | -4.83 0 1 1 | 0.8507 | 0.0395 | 0.85 | -116.45 | -1.82 2.72 | -16.27 |
| 0 ∞ | 0.0010 | 0.0016 | 0.824 | 0.924 | -0.11 -7.43 | 0.7938 | 0.0064 | 0.02 0.56 | -100.90 -95.60 | -2.72 | -10.75 |
| | | | | | | | | | | | |

to evaluate the parameters) to explain the physicochemical parameters such as X_1^m (micellar mole fraction), β^m (micellar interaction parameter), f_1^m and f_2^m (activity coefficients), $\Delta G_{\rm ex}^m$ (excess free energy of mixing), $\Delta G_{\rm mic}$ (Gibbs free energy of micellization), X_1^M and $X_1^{\rm ideal}$ (mole fraction in micellar as well as in ideal state), $\Delta G_{\rm Maeda}^\circ$ (Standard free energy). The following results emerge:

Lower values of cmc_{12} (the experimental cmc, Fig. 2, Tables 1–3) than cmc_{ideal} obtained by Clint's Eq. (S1) [35] indicate the nonideal behavior of the binary systems;

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this is a required condition for the synergism between the constituents in the mixed micelles. Several types of intermolecular forces acting between the surfactant molecules are responsible for the formation of the mixed micelles.

3.2.1 Regular solution theory

The experimental results can be interpreted quantitatively by considering Rubingh's equation [36], which is based on the Regular Solution Theory (RST), and allows for the calculation of the micellar mole fractions as well as the interaction parameters. The nature and strength of interactions between the surfactant molecules in the mixed micelles have been interpreted in terms of β^m by Rubingh's approach. For the gemini-conventional mixed micelles X_1^m and β^m were calculated with the use of Eqs. (S2) and (S3), and are compiled in Tables 1–3. The β^m values give an idea about the type of interaction between the two components in the mixed micelles which leads to the deviation from ideality. As the $\beta^{\bar{m}}$ values vary with the composition of the systems, frequently β_{av}^m values are used [37,38]. The higher absolute value of β^m implies reduction in free energy of micellization, which makes the system thermodynamically more stable indicating higher synergism or more interactive interaction. When β^m is positive, there is repulsion between the constituents of the binary surfactant system and the interaction is antagonistic in nature. But, in all the systems studied, we have obtained negative β^m , indicating the presence of synergistic interaction between both the components in the mixed surfactant systems which again favor the micellization process. The order of β_{av}^m values for the mixed systems is geminianionic > gemini-cationic > gemini-nonionic. β_{av}^m is maximum for 12-E2-12 + SDS (-13.06) suggesting strong synergism due to electrostatic interaction between the oppositely charged head groups of anionic SDS and cationic gemini surfactant, whereas for 12-E2-12 + SDBS, the lower value of β^m implies less surfactant- surfactant interaction due to the molecular structure of SDBS, as it may not be accommodated properly in the mixed micelles. The mutual interactions among the surfactants in micelles depend on their nature, hydrophilic and hydrophobic parts. 16-E2-16 + CTAC (-9.12) shows higher synergism as compared to 12-E2-12 + DTAC (-8.95) due to the longer hydrocarbon chain in the former system which may facilitate more micellization. Low hydrophobicity and high cmc also affect the surfactants interaction. n-E2-n+CPC shows less synergism than straight chain cationic surfactants because of the bulky pyridinium head group which decreases the surface charge density by forming loose mixed micelle aggregates. Least synergism is observed for 16-E2-16 + Brij 58 system (-1.45) (Table 3). Gemini monomers in aqueous solution may exist in cis conformation to allow the intermolecular interaction between two alkyl chains of the molecules. 12-E2-12 is more efficient than 16-E2-16 for the formation of mixed micelles because of least conformational strain in arrangement of alkyl chains exhibiting higher interaction. The presence of ester linkage in one of the components in mixed micelles may facilitate the association between the surfactant molecules through dipole-induced dipole and hydrogen bonding interactions with interfacial water [39]. In mixed micelles, X_2^m values are lower than X_1^m , showing more propensity of the gemini surfactants towards micellization (Tables 1-3, Fig. 3). Positive deviation of X_1^m from X_1^{ideal} was observed for all the binary systems as shown in Fig. 3. In



Fig. 2. Variation of cmc_{ideal} and cmc_{12} vs. mole fraction of gemini (α_1) in surfactant mixtures: 12-E2-12 (\Box , \blacksquare); 16-E2-16 (\triangle , \blacktriangle). Filled symbols are for cmc_{12} and open symbols are for cmc_{ideal} . Lines are drawn as a guide to the eye.

12-E2-12 + SDS/SDBS and 12-E2-12 + DTAC systems, the X_1^m value increases with $\alpha_{12-E2-12}$, whereas for 16-E2-16 + Brij 58, the contribution of Brij 58 is more in the mixed micelles.

The activity coefficient f_i^m of individual surfactants, obtained by using the Eqs. (S4) and (S5), are less than unity indicating the formation of the mixed micelles. The activity coefficients of the gemini (f_1^m) are reasonably higher than the f_2^m (conventional surfac-



Fig. 2. Continued.

tant) supporting the non-ideality of the mixed micelles and the presence of synergistic interaction between the surfactants in it.

The higher absolute values of ΔG_{ex}^m indicates more stable mixed micellar system. The ΔG_{ex}^m values listed in Tables 1–3 are negative indicating the higher stability of the mixed micelles than the single surfactant micelles [23]. The absolute values of ΔG_{ex}^m vary from 0.75 to 5.64 (kJ mol⁻¹), being highest for gemini + anionic systems and lowest for gemini + nonionic systems.

For pure gemini surfactants, Eq. (S7) can be used to evaluate ΔG_{mic} [40].





The ΔG_{mic} values are negative for all the mole fractions of geminis in the mixed systems as listed in Tables 1–3, which again supports the mixed micellization. The higher values of absolute ΔG_{mic} are due to more favorable micellization in case of 12-E2-12 + SDS/SDBS.

3.2.2 Motomura's model

The mole fractions in the micellar (X_1^M) as well as in ideal state (X_1^{ideal}) have been computed by applying Motomura's approximation too. The RST, which treats mixed



Fig. 3. Variation of X_1^{ideal} and $X_1^m vs$. mole fraction of gemini (α_1) in surfactant mixtures: 12-E2-12 (\Box, \blacksquare); 16-E2-16 (Δ, \blacktriangle). Filled symbols are for Rubingh's and open symbols are for Motomura's model. Lines are drawn as a guide to the eye.

micelles as a regular solution, is used for the evaluation of interaction parameters. It depends on the micellar compositions and is silent for unlike chain lengths, counterions and ionic strength. The Motomura's model, which is independent of the nature of the surfactants and their counterion and considers mixed micelles as a macroscopic bulk phase, can be applied for the study. The related energetic parameters of such systems can be evaluated in terms of excess thermodynamic quantities [41,42]. The fundamental equation for the micellar mole fraction of a surfactant in the surfactant in the surfactant.





factant mixture, presuming the miscibility of the surfactants in the mixed micelles, was determined by the relationship (shown in supporting information: Eq. (S8) to Eq. (S13)). The micellar mole fractions of surfactants in ideal state were calculated using Eq. (S14).

The X_1^M values for mixed systems increase with increase in mole fraction of *n*-E2-*n* (Tables 1–3). In case of gemini + anionic systems at lower mole fraction of SDS/SDBS, the Motomura's model becomes non-convergent. Similar results have also been observed for 16-E2-16 + CTAC/CPC. It is clear from Fig. 3 that even at lower mole fraction of the gemini surfactant, its contribution in mixed micellization is higher





than that of single chain surfactants. This is because of the presence of two hydrophobic chains which enhance its hydrophobicity and try to accommodate in mixed micelles at the same time.

3.2.3 Maeda model

In addition to the electrostatic interactions between the head groups, steric repulsions due to different hydrophobic chain lengths of the surfactants can also be taken into account to justify our explanations. According to Maeda [43] and Aguiar and Ruiz [44], the hydrophobic chain–chain and hydrophilic head group-head group interactions of

the surfactant components are found in the mixed micelles. Maeda has proposed hydrocarbon chain-chain interaction in mixed systems of two amphiphiles including one ionic and one nonionic surfactant. This model assumes that in the micellar phase the decrease in head group repulsion for the ionic surfactants in an ionic + nonionic mixed surfactant system is due to the presence of nonionic surfactant molecules. It is a new approach for the determination of the standard free energy change during micellization ($\Delta G_{\text{Maeda}}^{\circ}$) as a function of ionic mole fraction (X_1^m) in the mixed micelles (Eqs. (S15) to (S17)). A higher value of B_1 (a parameter related to $\Delta G_{\text{Maeda}}^{\circ}$) indicates more chain-chain interaction and higher stability of the mixed micelles. The values of B_1 for 12-E2-12 + Brij58, -2.58, -2.23, -2.66, -3.56; 12-E2-12 + TX-100, -10.30, -9.69, -9.34, -9.98; 16-E2-16 + Brij 58, -3.84, -2.44, -2.89, -4.97 and 16-E2-16 + TX-100, -8.54, -9.30, -10.72, -15.4. The $\Delta G_{\text{Maeda}}^{\circ}$ values, calculated from Eq. S(15), are recorded in Table 3. The values are negative and vary between 15.63-17.78 kJ mol⁻¹, the highest value was obtained for the 16-E2-16 + nonionic systems.

4. Conclusion

Two dicationic biodegradable gemini surfactants of different hydrophobicity consisting ester bonded spacer have been synthesized and the physicochemical properties of their binary mixtures with cationic, anionic and nonionic conventional surfactants have been studied by conductometric method. Various micellar parameters were determined by using theoretical models suggested by Clint, Rubingh, Motomura and Maeda. All the mixed surfactant solutions show nonideality in the mixed micelles indicated by their *cmc* values depending on the micellar compositions and their X_1^m , X_1^{ideal} , ΔG_{ex}^m , ΔG_{mic} , ΔG_{Maeda}° values. The gemini + SDS/SDBS mixed system has the highest synergism supported by β^m values. 16-E2-16 + CTAC shows higher synergism than 12-E2-12 + DTAC which may be due to the difference in their hydrocarbon chain lengths that favors micellization. The *cmc* values of the geminis are significantly less than their corresponding monomeric counterparts and are the key factors which favor the lower consumption of cationic gemini surfactants.

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