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Mixed micellization of novel cationic ester-bonded gemini surfactants: Investigations by conductometric and tensiometric measurements

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ABSTRACT

The micellization and interfacial properties of three homologous dicationic ester-bonded cleavable and biodegradable gemini surfactants, ethane-1,2-diyl bis(*N*,*N*-dimethyl-*N*-alkylammoniumacetoxy) dichlorides, referred as m-E2-m (m = 12, 14, 16), and their binary mixtures were investigated in aqueous solution by performing conductivity and surface tension measurements. The decrease in critical micelle concentration (CMC) indicates nonideality of the mixed systems of different compositions. The unequal hydrophobic chain length might be playing a significant role in the reduction of CMC values. Several theoretical treatments were used to analyze and compare the mutual interaction parameters, counter ion binding, surface parameters, excess free energy of micellization and standard free energies for the mixed surfactant systems as well. The negative values of interaction parameters show an overall attractive force, i.e., synergistic effect in the mixed state. The excess free energy of mixing has negative values for all the systems.

1. Introduction

Chemists are designing unusual-structured surfactants with improved physicochemical properties, lower toxicity, good biodegradability and cost effectiveness [1]. Gemini surfactants can be regarded as green surfactants because lesser amounts of these amphiphiles are consumed during their use [2]. Further, if a gemini surfactant is readily cleavable, it is more desirable mainly because of its environment-friendly nature and that is why the diester-bonded gemini surfactants [3] were chosen for the present study.

Presently, mixed surfactants are being preferred over single surfactant systems as they possess superior surface and colloidal properties than the individual surfactants, such as much higher surface activity, good wetting property, better solubilization capacity and lower critical micelle concentration (CMC). The last parameter (i.e., CMC) of concerned mixed systems is governed by several factors, such as surfactant structure, head group charge, counter ions, and the intermolecular interactions, etc. [4]. There exist limited studies on the mixed micellization of systems containing gemini surfactants as both the components [5,6], but no detailed report is available on systems consisting of biodegradable and cleavable geminis as the components. We have, therefore, examined the physicochemical properties of the solutions containing ester-bonded cationic gemini surfactants with similarly charged head groups and unequal hydrophobic chain lengths as the components of binary mixtures. The diester linkage (E2) makes the spacer hydrophilic whereas the twin-tail part (m) remains hydrophobic. The selection of m-E2-m geminis was made on the basis of our earlier studies that showed their better performance on several counts [7,8].

The objective of the present work is to study the effect of hydrophobic chain lengths on the interfacial and micellization aspects of the gemini-gemini mixed surfactant systems that would help in selection of such surfactants for their use in different applications like phase transfer catalysis, solubilization, foaming, preparation of colloidal nanoparticles, cosmetics, etc. The surfactants contain dodecyl (12-E2-12), tetradecyl (14-E2-14) and hexadecyl (16-E2-16) chains with dicationic head groups. The models proposed by Clint [9], Rubingh [10] and Motomura et al. [11] are employed to interpret the formation of mixed micelles and to find out the mutual interactions among the component surfactants in the mixed binary solutions.

2. Experimental

2.1. Materials

The cationic gemini surfactants (m-E2-m, m = 12, 14, 16) were synthesized as outlined in Scheme 1 which contained two main steps [3]. The first step involves preparation of the spacer part, i.e., ethane-1,2-diyl bis(chloroacetate), by heating a mixture of chloroacetyl chloride (0.22 mol) and ethylene glycol (0.1 mol) in a round bottom flask at 323.15 K for 8 h in nitrogen atmosphere. The product was washed with saturated brine (NaCl) solution till complete neutralization. The product was dissolved in diethyl ether and magnesium sulphate was added to it for drying. After few hours the dissolved compound was

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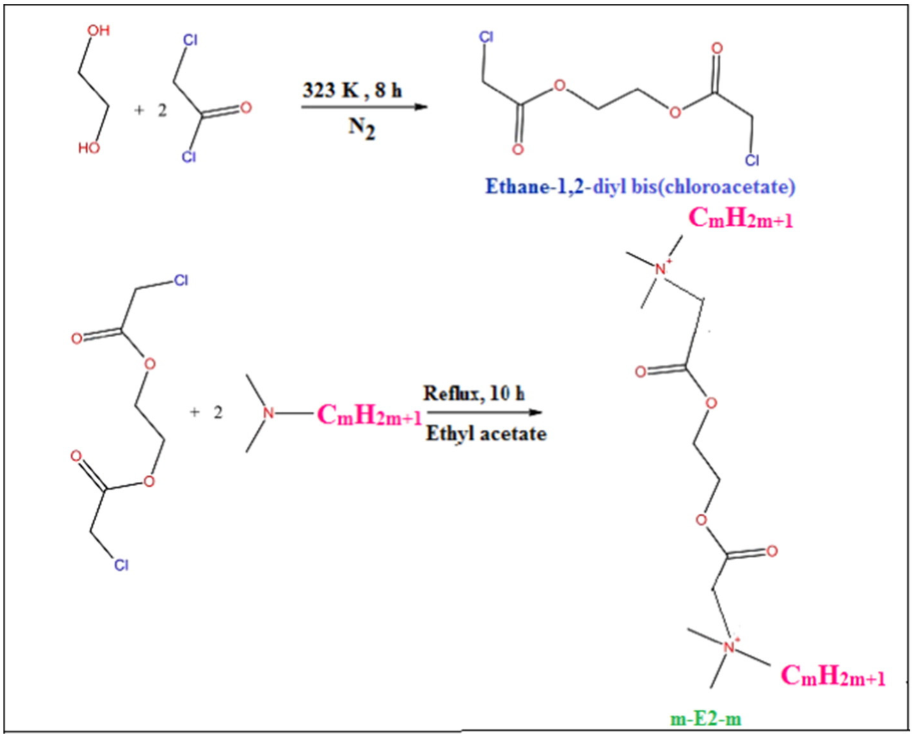

Scheme 1. Reaction route for the synthesis of gemini surfactants m-E2-m (m = 12, 14, 16).

separated from magnesium sulphate and needle shaped crystals were obtained on standing. In the second step, the gemini surfactant was obtained by heating the product of step one with the respective amine (*N*,*N*-dimethylalkylamine) (molar ratio = 1:2.1) in ethyl acetate for 10 h. Afterward, the solvent was removed under reduced pressure. The crude products were recrystallized in ethyl acetate-ethanol mixture (5:1). The surfactants were characterized by various analytical methods such as elemental analysis, ^{1}H NMR, FT-IR and ESI-MS (+) spectroscopy (Figs. S1 to S6 and Table S1, Supporting information).

2.2. Methods

2.2.1. Preparation of the binary mixtures

The binary solutions were prepared by mixing the required volumes of stock solutions (of the same concentration prepared in double-distilled water) of both the components to get the exact mole fractions like 0.2, 0.4, 0.6 and 0.8.

2.2.2. Thermal stability by differential scanning calorimetry (DSC)

The thermograms of m-E2-m were recorded by using DTG-60H (Simultaneous DTA-TG Apparatus, Shimadzu, Japan) with scanning rate of 10–20 K/min, from 273.15 K to 473.15 K. The experiments were carried out on an alumina sample pan by using a nitrogen flow rate of 40 ml/min. The DSC (heat flow versus temperature) plots are shown in Figs. S7–S9 (Supporting information).

2.2.3. Specific conductivity measurements

All the solutions were prepared in double-distilled water. The specific conductivity of pure and mixed surfactant solutions were measured at (303.15 ± 0.1) K by using ELICO conductivity bridge Model CM82T and dip-type cell (cell constant: 1.02 cm^{-1}). Each measurement was done in triplicate. The temperature was controlled by flowing thermostated water around a double-walled glass vessel. The instrument was initially calibrated with standard solutions of 0.01×10^{-3} mol kg^{-1} and 0.1×10^{-3} mol kg^{-1} KCl. Conductivity of each of the surfactant solution was measured as a function of its concentration and typical plots for the single/binary gemini-gemini surfactant systems at different mole fractions are shown in Fig. 1. Sufficient time (5 min) was allowed for each successive addition to equilibrate the systems.

2.2.4. Surface tension measurements

The surface tension values were determined by the platinum ring detachment method using Kruss11 Tensiometer (K11MK3, Germany) with an accuracy of ±0.1 $mN \cdot m^{-1}$. All the experiments were carried out at (303.15 ± 0.1) K. Throughout the measurements, temperature was maintained by the thermostat ORBIT RS 10S with circulating water around double-walled container. For equilibration of the surfactant solution, 5 min was taken in between two successive additions. The CMC value was obtained as the break point of the surface tension (γ) versus logarithm of surfactant concentration (C) curve (Fig. 2).

3. Results and discussion

The physicochemical properties of the pure/mixed gemini-gemini surfactant solutions were investigated by conductometric and tensiometric measurements at different mole fractions. The relevant parameters were evaluated using the average CMC values determined by the conductometry and tensiometry methods (Figs. 1, 2 and Tables 1, 2).

3.1. Differential scanning calorimetry (DSC)

The phase-transition temperatures of the gemini surfactants were determined from simultaneous DSC graphs which assure the enantiotropy of liquid-crystalline behavior [12]. It showed melting peaks and decomposing peaks in the heating scan. The heating–cooling cycle was performed to ensure that the homogeneous mixture of water and surfactant was formed. The DSC results in complete phase transformation by simultaneous heating and cooling of samples (Figs. S7–S9, Supporting information). In all the thermograms two remarkable peaks were observed for heat of fusion of the surfactant. The

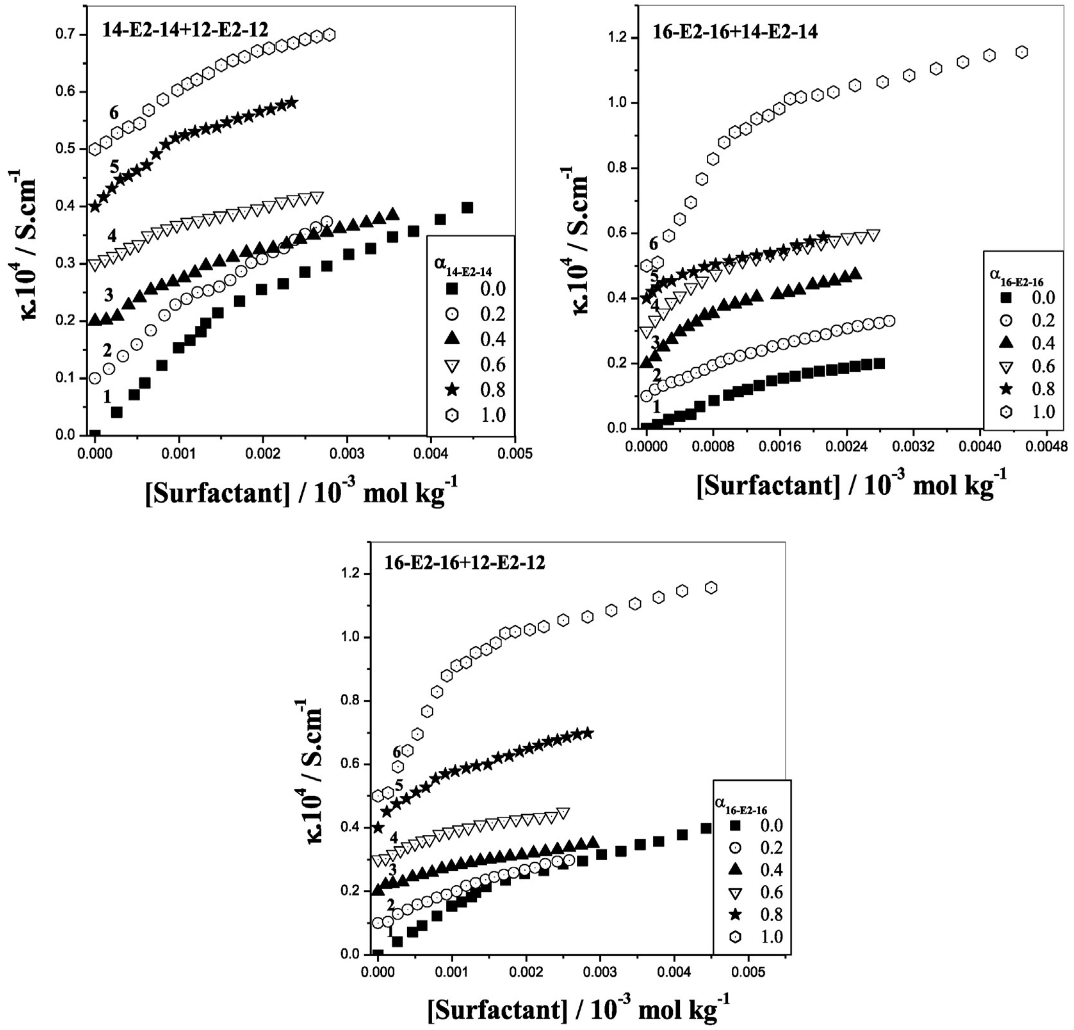

Fig. 1. Conductivity plots for the pure and mixed gemini-gemini surfactant systems at different mole fractions at 303.15 K. The curves 2, 3, 4, 5 and 6 have been shifted vertically by 0.1, 0.2, 0.3, 0.4 and 0.5 scale unit (1×10^4 S·cm^{-1}), respectively.

first sharp peak for the geminis appeared at 329.2 K (12-E2-12), 340.4 K (14-E2-14) and 347.3 K (16-E2-16). The crystals transform to the liquid-crystalline state after heating. Only liquid state of the compound was observed beyond the second broad peak at 458.3 K, 434.4 K and 447.7 K, respectively, for 12-E2-12, 14-E2-14 and 16-E2-16. The cooling process is shown by the line in blue color. The compounds were heated up to the temperature where no more exothermic peaks were observed indicating the complete transformation from metastable to stable phase. For 16-E2-16, at lower temperature, the crystal-to-crystal transition occurred and after heating to higher temperatures, two broad endothermic peaks appeared that can be shown by onset temperature, melting temperature and decomposing or endset temperature whereas the heating traces of 12-E2-12 showed only two peaks at 329.3 K and 458.3 K. On heating, the alkyl chains start to melt (shown by onset temperature) whereas the other parts (spacer) having ester linkage are still stable. At this point, the samples are in intermediate phase (a mesophase) between the liquid and crystalline phases. At the onset temperature, melting and decomposition of the surfactant begins. The alkyl chains of gemini surfactants start to melt at 322.7 K for 12-E2-12, 332.3 K for 14-E2-14 and 341.9 K for 16-E2-16. Similarly, decomposition starts at the temperatures 448.7 K, 425.7 K and 444.6 K for 12-E2-12, 14-E2-14 and 16-E2-16 respectively [13]. If heating is continued, the ester linkage breaks down, and an isotropic liquid may form at the clearing point. Thermal stability of these gemini surfactants decreases with the increase in hydrophobic alkyl chain length; 14-E2-14 showed intermediate result between 12-E2-12 and 16-E2-16, in the same way that melting point decreased with the increase in hydrophobic chain [13, 14]. The smaller hydrophobic chain may be able to fold along with hydrophilic spacer allowing closer packing and, consequently, phase transition occurs at higher temperature.

3.2. Mutual interaction between the gemini surfactants in mixed micelles

3.2.1. Critical micelle concentration

In order to explain the behavior of all the three cationic gemini-gemini mixed surfactant systems, pseudophase separation model was used. According to this approach, the micelles are considered as macroscopic bulk phase in equilibrium with a solution containing the corresponding monomers. Presence of the functional group, i.e., ester linkage [CO(O)], in the spacer makes the surfactants more hydrophilic causing micelle formation at low concentrations. Also, oxygen atoms of the spacer can form hydrogen bond with the water molecules reducing unfavorable contact of the hydrocarbon part with water and hydration in the vicinity of spacer reduces the electrostatic repulsion between the head groups [14]. Experimental CMCs (CMC_{12}) of nearly all the studied binary systems are lower than the CMC values of the individual components (Table 1).

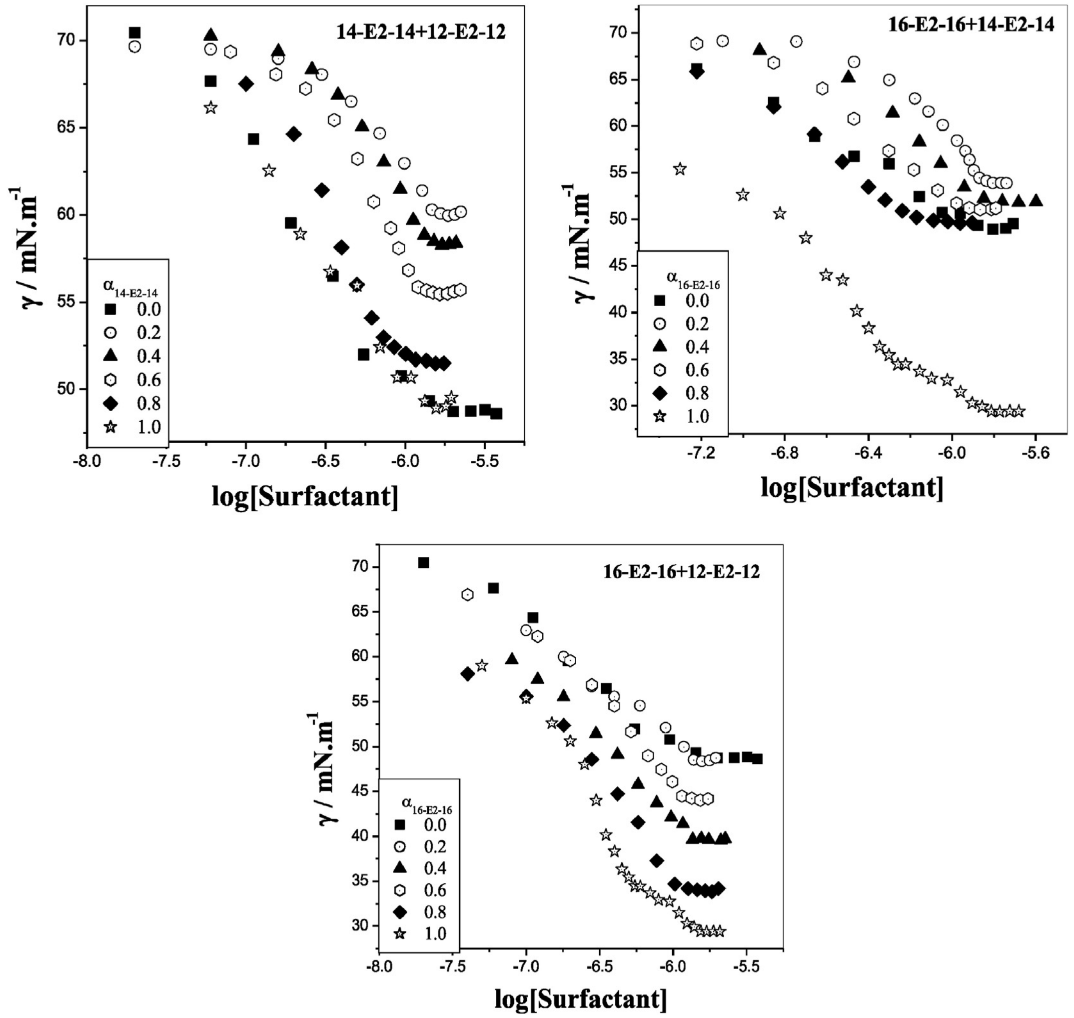

Fig. 2. Plots of surface tension vs. logarithm of surfactant concentration for various single and binary surfactant solutions at 303.15 K.

Table 1
Experimental CMC (CMC and CMC_{12}), ideal CMC (CMC_{ideal}), micellar mole fraction (X_i), interaction parameter (β^m), activity coefficients (f_i^m), counter ion binding (g_1) of gemini-gemini binary surfactant mixtures at 303.15 K.

Mole fraction of m-E2-m	CMC[a] or CMC_{12} 10^{-3} mol kg^{-1}	CMC_{ideal} 10^{-3} mol kg^{-1}	X_1^m	X_1^{ideal}	X_1^M	β^m	f_1^m	f_2^m	g_1[b]
$\alpha_{14\text{-}E2\text{-}14}$	14-E2-14 + 12-E212								
0.0	0.0016								
0.2	0.0014	0.0016	0.2890	0.3278	0.2299	−0.77	0.6769	0.9376	0.35
0.4	0.0013	0.0015	0.4544	0.4987	0.4055	−0.68	0.8165	0.8688	0.44
0.6	0.0010	0.0015	0.5783	0.6147	0.5757	−1.60	0.7518	0.5848	0.60
0.8	0.0009	0.0014	0.6642	0.6845	0.7228	−2.64	0.7427	0.3124	0.59
1.0	0.0014								
$\alpha_{16\text{-}E2\text{-}16}$	16-E2-16 + 14-E2-14								
0.0	0.0014								
0.2	0.0012	0.0014	0.2634	0.2449	0.2598	−0.94	0.5984	0.9364	0.48
0.4	0.0009	0.0014	0.4378	0.4143	0.4668	−1.97	0.5361	0.6852	0.68
0.6	0.0009	0.0015	0.5396	0.5200	0.6274	−1.98	0.6568	0.5614	0.76
0.8	0.0006	0.0015	0.6029	0.5917	0.8323	−4.27	0.5096	0.2115	0.58
1.0	0.0014								
$\alpha_{16\text{-}E2\text{-}16}$	16-E2-16 + 12-E2-12								
0.0	0.0016								
0.2	0.0012	0.0016	0.3115	0.3294	0.2110	−1.38	0.5187	0.8743	0.58
0.4	0.0011	0.0016	0.4549	0.4742	0.3840	−1.56	0.6289	0.7240	0.46
0.6	0.0010	0.0016	0.5623	0.5780	0.5378	−1.81	0.7066	0.5638	0.75
0.8	0.0009	0.0015	0.6497	0.6586	0.6762	−2.80	0.7086	0.3059	0.53
1.0	0.0014								

[a] Average of the values obtained by conductivity and surface tension measurements.

[b] g_1 values are obtained from conductometric plots.

Table 2
Various surface and thermodynamic parameters of the gemini-gemini mixed surfactant systems at 303.15 K.

Mole fraction of m-E2-m	π_{cmc}/mN·m^{-1}	$\Gamma_{max} \times 10^7$/mol·m^{-2}	A_{min}/nm^2	−GEm/kJ·mol^{-1}	−ΔG^{o}_{m}/kJ·mol^{-1}	−Δads$G$/kJ·mol^{-1}	G_{min}/kJ·mol^{-1}
$\alpha_{14\text{-E2-14}}$	14-E2-14 + 12-E2-12						
0.0	22.4	8.4	1.97		43.7	46.4	58.1
0.2	40.1	4.9	3.35	0.4	44.0	52.1	60.0
0.4	42.5	7.6	2.18	0.4	44.3	49.8	35.9
0.6	33.5	7.0	2.39	1.0	44.7	49.5	52.3
0.8	26.2	6.9	2.40	1.5	45.5	49.2	63.3
1.0	20.4	8.8	1.88		44.1	46.4	55.6
$\alpha_{16\text{-E2-16}}$	16-E2-16 + 14-E2-14						
0.0	20.4	8.8	1.88		44.1	46.4	55.6
0.2	13.8	8.1	2.04	0.5	44.2	45.8	69.3
0.4	14.7	7.5	2.22	1.2	44.3	46.2	73.5
0.6	15.7	5.8	2.88	1.2	44.9	47.1	67.8
0.8	16.6	8.7	1.91	2.6	46.1	48.0	61.2
1.0	29.7	11.8	1.41		43.9	46.4	33.3
$\alpha_{16\text{-E2-16}}$	16-E2-16 + 12-E2-12						
0.0	22.4	8.4	1.97		43.7	46.4	58.1
0.2	20.6	4.9	3.35	0.8	44.3	48.5	98.9
0.4	28.4	7.1	2.34	0.9	44.4	48.4	56.5
0.6	24.3	7.6	2.18	1.1	44.7	48.0	58.8
0.8	30.9	9.2	1.81	1.6	45.0	48.4	38.4
1.0	29.7	11.8	1.41		43.9	46.4	33.3

3.2.2. Counter ion binding

The layer just adjacent to the surface of the ionic micelles is known as the Stern layer to which the counter ions are bound strongly and migrate with the micelles in an electrical field (as the influence of thermal agitation on it is negligible). Counter ions are the main contributing parts affecting conductivity of solutions due to their ionic mobility. Total concentration of counter ions increases with the increase of surfactant concentration and thus the conductivity increases. The counter ion association (g_1) of the pure and mixed micelles was evaluated from the degree of dissociation, g_2, obtained from the ratio of the post- to pre-micellar slopes of the specific conductance (κ) versus [surfactant] plots [15]. Higher counter ion binding was observed for the 16-E2-16 + 14-E2-14 system (Table 1) than the other two surfactant mixtures. Stronger counter ion association reduces CMCs of the surfactant mixtures.

3.2.3. Mixed micelle formation

The ideal CMC ($\text{CMC}_{\text{ideal}}$) values were obtained by using the Clint model [9]

$$\frac{1}{\text{CMC}_{\text{ideal}}} = \frac{\alpha_1}{\text{CMC}_1} + \frac{\alpha_2}{\text{CMC}_2}. \tag{1}$$

Here, α_1 and α_2 are the stoichiometric mole fractions of the individual surfactants in the mixed systems. For mixed surfactant systems the values of CMC_{12} (Table 1) were found to deviate from the CMCs of individual surfactants and the $\text{CMC}_{\text{ideal}}$ values. Lower values of CMC_{12} than $\text{CMC}_{\text{ideal}}$ imply that the micelles are formed at a concentration lower than that expected in case of ideal mixing, and is attributable to the attractive interactions between the two components of the binary surfactant mixtures.

The CMC_{12} and $\text{CMC}_{\text{ideal}}$ values of the mixed micelles, for various mole fractions (α), are shown in Fig. 3. It is clear from the plots that the CMC_{12} values deviate negatively from $\text{CMC}_{\text{ideal}}$, at all the studied mole fractions of the gemini surfactants, indicating favorable mixing of the surfactants. The transfer of hydrophobic tails from the monomeric phase to the micellar phase increases the hydrophobic interactions among the micelles, and hence the CMC_{12} values are found to be lower than the $\text{CMC}_{\text{ideal}}$. In a surfactant mixture, mixing of hydrophobic chains can be considered as an ideal process and free energy of the system decreases when the surfactant chain moves from monomeric phase to the micellar phase. However, interaction between the head groups can be considered as a nonideal process. The order of CMC_{12} is 14-E2-14 + 12-E2-12 > 16-E2-16 + 12-E2-12 > 16-E2-16 + 14-E2-14.

Mutual interactions between the surfactants can be analyzed by the Regular Solution Theory (RST) [10] which is used to evaluate the micellar mole fraction (X_1^{m}) and the interaction parameter (β^{m}) in the mixed surfactant micelles. Although several thermodynamic models have been developed, Rubingh's model [10] can be used more conveniently for the study of nonideal mixing in the mixed surfactant systems. It is mostly used, due to its simplicity, even after the development of more complex models. It is clear from Table 1 that, in all the cases, X_1^{m} increases with the increase of α.

The micelle mole fraction in the ideal state (X_1^{ideal}) was computed using Motomura Eq. (11): $X_1^{\text{ideal}} = (\alpha_1\text{CMC}_2) / [(\alpha_1\text{CMC}_2 + (1 - \alpha_1)\ \text{CMC}_1]$. The difference between the values of X_1^{m} and X_1^{ideal} is very less.

Extent of interaction between the surfactants in mixed micelles is due to the difference in structures of the two components, e.g., length and type of the hydrophobic chains and electrostatic or steric interactions among the hydrophilic parts. Here, the head groups, i.e., the hydrophilic parts, are similar for all the three amphiphiles. The only difference is the variation in their hydrophobic chain lengths. The β^{m} values were evaluated by using Eq. (2)

$$\beta^{\text{m}} = \frac{\ln\left(\text{CMC}_{12}\alpha_1/\text{CMC}_1 X_1^{\text{m}}\right)}{\left(1 - X_1^{\text{m}}\right)^2}. \tag{2}$$

A negative value of β^{m} indicates attractive interaction between the two components in a mixed micelle which is higher than the self-attraction of both the geminis before mixing. Zero β^{m}value indicates ideal mixing while positive values show lesser attraction after mixing than before mixing (antagonism).

The interaction parameters for all the mixtures, at different mole fractions, are listed in Table 1. Negative β^{m} values were obtained throughout the study for all the mixed systems with the average values (β^{m}_{av}) of −2.29, −1.89 and −1.42, respectively, for 16-E2-16 + 14-E2-14, 16-E2-16 + 12-E2-12, 14-E2-14 + 12-E2-12 suggesting synergism in the mixed micelle formation. Higher absolute values of β^{m}_{av} for 16-E2-16 + 14-E2-14 system (i.e., higher synergism) is due to the greater hydrophobicity of both the geminis — both the hydrocarbon chains break more "structured" water which is an energetically favored

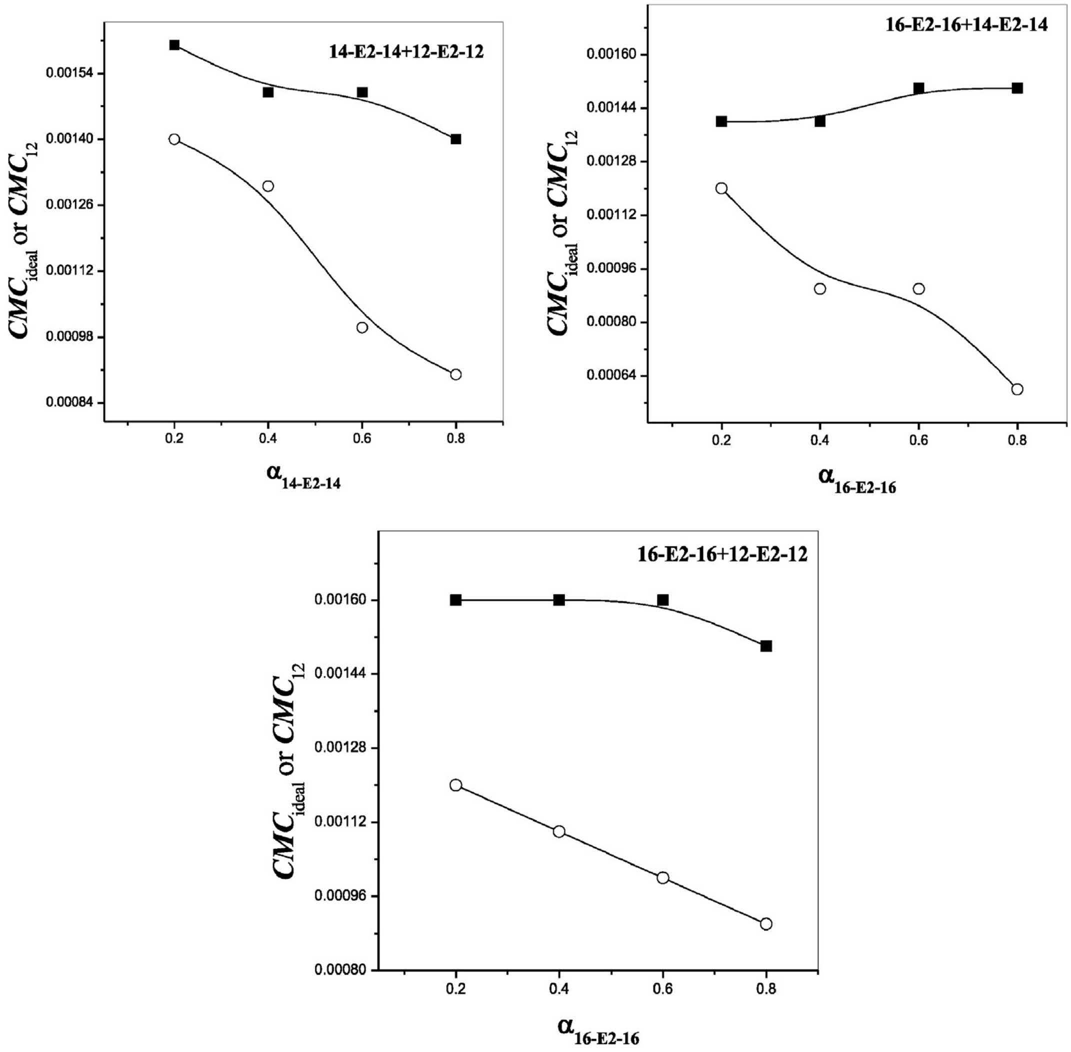

Fig. 3. Plots of the CMC variation with mole fraction of the geminis for the binary surfactant mixtures. Filled symbols represent $\text{CMC}_{\text{ideal}}$ and open symbols represent CMC_{12}.

process. The lower magnitude of β^m_{av} for 14-E2-14+ 12-E2-12 is because of the smaller hydrophobic tail length in addition to lesser variation in hydrophobic chains of the two components as compared to 16-E2-16+ 12-E2-12. The absolute β^{m} values increase with the increase in mole fraction of the higher homologue in all the binary systems with only one exception, i.e., for $\alpha_{14\text{-E2-14}} = 0.4$ in the 14-E2-14 + 12-E2-12 system (Table 1). The results agree with the findings reported for conventional (or gemini) cationic-cationic mixed systems [16–19].

The activity coefficients,f_{i}^{m}, of the individual surfactants in the mixed micelles are related to interaction parameter through the Eqs. (3) and (4)

$$f_1^{\text{m}} = \exp\left\{\beta^{\text{m}}\left(1-X_1^{\text{m}}\right)^2\right\} \tag{3}$$

$$f_2^{\text{m}} = \exp\left\{\beta^{\text{m}}\left(X_1^{\text{m}}\right)^2\right\}. \tag{4}$$

The mole fractions in micellar (X_1^{m}) as well as in ideal state (X_1^{ideal}) were computed by applying Motomura's approximation also. The RST, which treats mixed micelles as a regular solution, was used for the evaluation of interaction parameters; it takes into account the micellar compositions and is silent for unlike chain lengths, counter ions and ionic strength. The Motomura's model, which is independent of the nature of the surfactants and their counterions, and considers the mixed micelles as a macroscopic bulk phase, can be applied for the more detailed study. The related energetic parameters of such systems can be evaluated in terms of excess thermodynamic quantities [20,21]. The fundamental equation for the micellar mole fraction of a surfactant in the surfactant mixture, presuming the miscibility of surfactants in the mixed micelles, was determined by the equations

$$X_1^{\text{M}} = \overline{\alpha}_1 - \frac{\left(\overline{\alpha}_1\overline{\alpha}_2/\overline{\text{CMC}}\right)\left(\partial\overline{\text{CMC}}/\partial\overline{\alpha}_1\right)_{\text{T,P}}}{1-\dfrac{\delta v_{1,\text{c}}v_{2,\text{d}}}{v_{1,\text{c}}v_2.\overline{\alpha}_1 + v_{2,\text{d}}.v_1\overline{\alpha}_2}} \tag{5}$$

where

$$\overline{\text{CMC}} = (v_1\alpha_1 + v_2\alpha_2)\text{CMC} \tag{6}$$

and

$$\overline{\alpha}_i = \frac{v_{\text{i}}\alpha_{\text{i}}}{v_1\alpha_1 + v_2\alpha_2} \quad (i = 1, 2). \tag{7}$$

In the above equations, X_1^{M} = micellar mole fraction of m-E2-m, $\overline{\alpha_{\text{i}}}$ = bulk mole fraction, ν_{i} = number of ions dissociated by the ith component and δ = Kronecker delta (which is 1 for identical counter ions and 0 for different counter ions). In the present case, for the cationic gemini-

gemini surfactant mixtures (with the same counter ion), Eq. (5) can be modified as

$$X_1^M = \left(\frac{3\alpha_1}{\alpha_1+3}\right) - \frac{\frac{1}{(\alpha_1+3)cmc}\left(\frac{3\alpha_1}{\alpha_1+3}\right)\left(\frac{3-2\alpha_1}{\alpha_1+3}\right)\left(\frac{\partial \overline{\mathrm{CMC}}}{\partial \overline{\alpha}_1}\right)}{1-\frac{1}{3\overline{\alpha}_1+3\overline{\alpha}_2}}. \qquad (8)$$

$$(v_1 = v_{1a} + v_{1c} = (2+1) = 3,\ \ v_2 = v_{2b} + v_{2d} = (2+1) = 3)$$

The X_1^{M} values are found to increase with the increase in stoichiometric mole fraction of the higher homologue for all the mixed systems (Table 1) and are in line with the micellar mole fraction (X_1^{m}, evaluated by Rubingh's model).

3.3. Adsorption at the air/solution interface

The surface excess ($\Gamma_{\max}$) and molecular area ($A_{\min}$) are two important interfacial properties. The former is a measure of the extent of adsorption of various components at the interface whereas the latter provides the idea about close or loose packing of surfactant molecules at the gas-liquid interface. The two can be calculated using the following set of equations [22,23]

$$\Gamma_{\max} = -\frac{1}{2.303\mathrm{nRT}}\left(\frac{\partial\gamma}{\partial \log \mathrm{C}}\right)_{\mathrm{C}\rightarrow\mathrm{CMC}} \qquad (9)$$

$$A_{\min} = \frac{10^{20}}{N_{\mathrm{A}}\,\Gamma_{\max}} \quad (N_A\,\mathrm{is the Avogadro's number})\cdot \qquad (10)$$

The calculated values of $\Gamma_{\max}$ and $A_{\min}$ for the single and binary solutions are summarized in Table 2. It is obvious from the above equation that $A_{\min}$ increases when $\Gamma_{\max}$ decreases. The value of n for the gemini surfactant is taken as 3 and for the gemini-gemini surfactant mixtures, $n = 4$. $A_{\min}$ values of the pure surfactants were smaller than the mixtures because of the electrostatic repulsion which requires larger area per molecule. For 16-E2-16 + 14-E2-14, the lower value of $A_{\min}$ is caused by the hydrophobic interactions between the alkyl chains of comparable chain length resulting in dense packing.

3.4. Energetics of micellization and adsorption phenomena

The major contributions of the gemini surfactants to the thermodynamic properties of micellization are: the van der Waals interactions between the alkyl chains, head group repulsion, hydrophobic effect, and the energetics associated with the changes in configuration of the spacer and hydrophobic chains. The influences of such forces on the thermodynamic behavior of the studied systems are discussed below.

3.4.1. Gibbs excess free energy

The excess free energy of micellization (GEm) was calculated using Eq. (11)

$$GEm = RT\left[\left(X_1^{\mathrm{m}}\right)\ln f_1^{\mathrm{m}} + \left(X_{2^{\mathrm{m}}}\right)_{\ln} f_2^{\mathrm{m}}\right]. \qquad (11)$$

The negative values of GEm could be due to the synergistic interactions among the two components in the mixed micelles which suggest that the mixed micelles are more stable than the pure surfactant micelles. The absolute GEm values follow the order: 16-E2-16 + 14-E2-14 > 16-E2-16 + 12-E2-12 > 14-E2-14 + 12-E2-12.

3.4.2. Free energy of micellization

The standard free energy of micellization ($\Delta G_{\mathrm{m}}^{\mathrm{o}}$), which measures the tendency to form micelles, was evaluated with the help of Eq. (12)

$$\Delta G_{\mathrm{m}}^{\mathrm{o}} = RT\,\ln X_{\mathrm{cmc}} \qquad (12)$$

Negative $\Delta G_{\mathrm{m}}^{\mathrm{o}}$ values were obtained for all the gemini-gemini surfactant mixtures. The $\Delta G_{\mathrm{m}}^{\mathrm{o}}$ values increase slowly with the increase of mole fraction of the gemini of higher hydrophobicity. The negative $\Delta G_{\mathrm{m}}^{\mathrm{o}}$ suggests that the gemini surfactants have greater ability to form mixed micelles in solution (Table 2) than to form the single surfactant micelles. The $\Delta G_{\mathrm{m}}^{\mathrm{o}}$ values of the binary mixtures of 16-E2-16 + 14-E2-14 are slightly higher than the pure geminis. Thus, the mixed surfactant systems show more propensity towards micellization. The order of absolute $\Delta G_{\mathrm{m}}^{\mathrm{o}}$ values is: 16-E2-16 + 14-E2-14 > 14-E2-14 + 12-E2-12 > 16-E2-16 + 12-E2-12.

3.4.3. Standard free energy of adsorption

Thermodynamic stability of the adsorbed monolayer can be discussed in terms of the standard free energy of adsorption ($\Delta\mathrm{ads}G$) [22]

$$\Delta\mathrm{ads}G = \Delta G_{\mathrm{m}}^{\mathrm{o}} - \frac{\pi_{\mathrm{cmc}}}{\Gamma_{\max}}. \qquad (13)$$

The $\Delta\mathrm{ads}G$ values of the surfactant mixtures, thus obtained, are presented in Table 2. The values show that the cationic gemini surfactants have greater ability to adsorb at the air-water interface of the mixed systems. Lower $\Delta G_{\mathrm{m}}^{\mathrm{o}}$ than $\Delta\mathrm{ads}G$ indicates that the adsorption is preferred more than micellization.

Another thermodynamic quantity used to explain the synergism in mixed monolayer is the free energy of a given surface at equilibrium ($G_{\min}$), defined by Eq. (14)

$$G_{\min} = \gamma_{\mathrm{CMC}} A_{\min} N_{\mathrm{A}}. \qquad (14)$$

$G_{\min}$ is the free energy accompanied by the transition of surfactant from bulk phase to the surface of the solution. Lower the $G_{\min}$ value, more thermodynamically stable surface is formed, and higher is the surface activity. The $G_{\min}$ values show the ease of formation of the mixed monolayers. $G_{\min}$ increases with the increase of hydrophobicity in the binary systems as 14-E2-14 + 12-E2-12 < 16-E2-16 + 12-E2-12 < 16-E2-16 + 14-E2-14.

4. Conclusions

- Physicochemical properties of binary mixtures of dicationic biodegradable gemini surfactants of varied chain length, consisting diester bonded spacer, ethane-1,2-diyl bis(*N*,*N*-dimethyl-*N*-alkylammoniumacetoxy) dichlorides (m-E2-m, m = 12, 14, 16), were studied by conductivity and surface tension measurements.
- Differential scanning calorimetry reveals phase transition as well as thermal stability of pure gemini surfactants.
- Various surface and micellar properties were evaluated in the light of several theoretical models suggested by Clint, Rubingh and Motomura. All the mixed surfactant solutions showed nonideality as indicated by the X_1^{m}, β^{m}, X_1^{ideal}, GEm and $\Delta G_{\mathrm{m}}^{\mathrm{o}}$ values.
- Order of synergism of the mixed surfactant systems is 16-E2-16 + 14-E2-14 > 16-E2-16 + 12-E2-12 > 14-E2-14 + 12-E2-12.
- The results of this work show that a careful design of mixed surfactant systems containing cleavable surfactants can allow for more sophisticated changes in the properties of a surfactant solution.

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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.2016.04.038.

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