



Environment-friendly ester bonded gemini surfactant: Mixed micellization of 14-E2-14 with ionic and nonionic conventional surfactants



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ABSTRACT

This paper deals with a comprehensive study of the biodegradability, cleavability, hemolytic activity, and physicochemical properties of an ester-linked gemini surfactant, ethane-1,2-diyl bis(*N,N*-dimethyl-*N*-tetradecylammoniumacetoxo) dichloride (14-E2-14), along with the gemini-conventional mixed surfactant systems at different mole fractions of 14-E2-14. Some typical conventional surfactants of different polarities were used in the investigation at 303.15 K in aqueous medium by performing conductometric and tensiometric measurements. The data from both the techniques were used to obtain the critical micelle concentration (*cmc*) of mixed surfactant systems at different mole fractions. The decrease in *cmc* values indicates nonideality of the binary systems, and also occurrence of mixed micellization. Interaction parameters (β^m and β^v) along with energetics of mixed micellization were evaluated by using theoretical models suggested by Clint, Rubingh, Rosen, Motomura and Maeda for mixed surfactant systems. Negative values of β indicate an overall attractive force in the mixed state. Also, the excess free energy of mixing has negative values for all the systems. The hydrophilic spacer of the gemini surfactant 14-E2-14 shows strong interaction with the conventional surfactants used as well as with the biological membranes such as human erythrocytes (RBC).

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1. Introduction

Gemini surfactants are made up of two monomeric units connected at the level of head groups by a spacer that can be flexible or rigid, hydrophilic or hydrophobic [1–3]. Owing to their unusual properties (such as high surface activity, much lower *cmc*, higher solubilization capacity, low Krafft temperature, good wetting, detergency and emulsifying properties), the geminis have been considered the next generation surfactants [1–7]. Cationic geminis, in particular, have been shown to possess high antifungal, antibacterial and antimicrobial activities [8–11] and have attracted considerable attention towards their interaction with biologically important ligands [12–16]. Surfactants interact with the membranes causing cell lysis. Cell lysis by the surfactants has fundamental and practical importance mainly in drug targeting or in pharmacology [14–16]. Despite very encouraging results of the above interaction studies, the gemini surfactants invariably been used are of *m-s-m* type (*m* and *s* are the number of carbon atoms in the hydrophobic tail and

the spacer parts, respectively). Cleavable/biodegradable gemini surfactants are the better alternatives. With this view point, a number of surfactants with polar or labile bonds (amide, carbonate, ethoxylated, fluorinated and ester containing) which are highly soluble, easily hydrolysable, less stable and degradable, have, therefore, been synthesized by many workers [17–21]. As the nature of spacer and the constituent groups play a significant role in the micellization process of the gemini surfactants, the abovementioned surfactants show interesting properties. As none of them are available commercially, mixed micellization studies are now gaining more attention because less amount of surfactants are consumed without affecting the physicochemical properties of the pure component surfactants. Several mixed micellization studies have been done for the cationic *m-s-m* type geminis containing basic polymethylene spacer with conventional surfactants [22–25], but studies of mixed micellization on cleavable cationic geminis with conventional surfactants are limited [26,27].

Mixed micelles of gemini (dicationic) and conventional (cationic, anionic, nonionic) surfactants were prepared in terms of mole fraction of the gemini ($\alpha_{14-E2-14}$) in the binary solutions, the total concentrations of all the solutions remained the same for all the mole fractions — for each system *cmc* of the single and binary mixtures were determined. This piece of work is expected to contribute for further development of

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new environmentally acceptable surfactant systems, containing multi-functional groups, in both industrial and academic sectors.

2. Experimental

2.1. Materials

The amphiphile SDS (sodium dodecyl sulfate) (~99%, Sigma) was recrystallized twice before use. The anionic surfactant SDBS (sodium dodecyl benzene sulfonate, TCI), cationic surfactants CPC (cetylpyridinium chloride, Merck) and TTAC (tetradecyltrimethylammonium chloride) (99%, Sigma-Aldrich), nonionic surfactants Brij 58 (polyoxyethylene (20) cetyl ether, Merck) and TX-100 (polyoxyethylene octyl phenyl ether, Fluka) were used as received. *N,N*-dimethyltetradecylamine ($\geq 95\%$, Fluka), ethylene glycol (99%, Sigma-Aldrich) and chloroacetyl chloride (98%, Loba chemie) were also used without further purification. Chemical structures of the conventional surfactants used in this study are shown in scheme S1 (Supplementary materials).

2.2. Synthesis of gemini surfactant and structural characterization

The cationic ester-bonded gemini surfactant 14-E2-14 was synthesized in two steps following a reported procedure [19]. The protocol of reaction route for the synthesis of 14-E2-14 is given in scheme 1(a): yield 31.72 g (75%), white solid, $R_f = 0.62$ ($\text{CHCl}_3:\text{CH}_3\text{OH}$, 6:4, v/v). The melting point, visually determined by the microscopic melting point apparatus (Reichert Thermovar Jung, Austria), is 443 ± 0.1 K. The molecular structure of 14-E2-14 is shown in scheme 1(b). Purity

of 14-E2-14 was checked by Silica gel thin layer plate chromatography. Its structural characterization was done by FT-IR, ^1H NMR and ESI-MS (+) spectroscopy (Figs. S1 and S2).

2.2.1. Structural data

FT-IR (KBr, ν/cm^{-1}): 2922.47, 2850.90 (C-H); 1749.52 (C=O); 1471 (C-O); 1188.89 (C-N); 719.71.

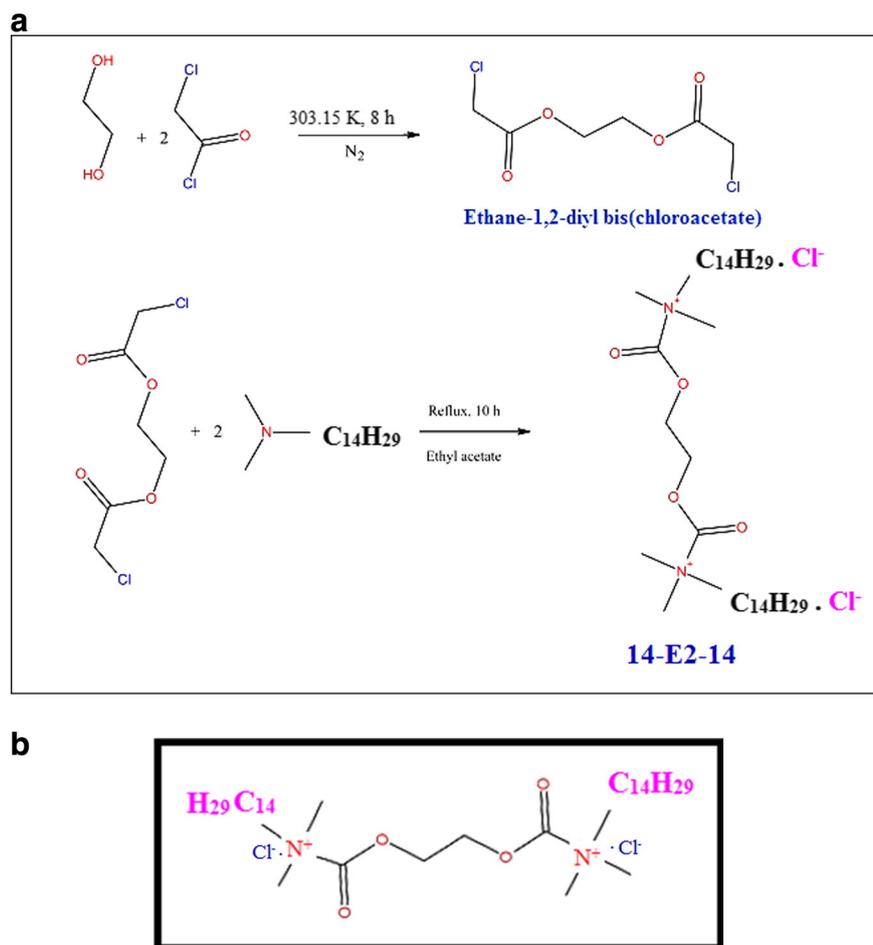
^1H NMR (300 MHz, CDCl_3 , δ/ppm): 0.844–0.867 (t, 6H, $-\text{CH}_3 \times 2$, alkyl chain); 1.237–1.326 (m, 44H, $-(\text{CH}_2)_{11} \times 2$, alkyl chain); 1.759 (m, 4H, $-\text{N}^+\text{CH}_2\text{CH}_2 \times 2$); 3.517 (s, 12H, $-\text{N}^+(\text{CH}_3)_2 \times 2$); 3.768–3.777 (s, 4H, $-\text{CH}_2\text{O} \times 2$); 4.475 (s, 4H, $-\text{N}^+\text{CH}_2 \times 2$); 5.36 (s, 4H, $-\text{N}^+\text{CH}_2\text{COO} \times 2$).

ESI-MS (+): m/z 662 ($\text{M}-\text{Cl}^-$), 661 (M^+-Cl^-), 611 ($\text{M}-\text{CH}_3\text{Cl}^-$), 633 ($\text{M}-\text{C}_2\text{H}_5\text{Cl}^-$), 298 ($\text{C}_{12}\text{H}_{25}(\text{CH}_3)_2\text{N}^+\text{CH}_2\text{COOCH}=\text{CH}_2$), 130 ($(\text{CH}_3)_2\text{N}^+\text{CH}_2\text{COOCH}=\text{CH}_2$).

2.3. Biodegradability

Once utilized, surfactants, in general, are discharged into the environment where they remain for a long time – this is because of their lower degradability. Thus, we need to develop biodegradable surfactants for safer environment.

A standard test of biodegradability, the biological oxygen demand (BOD) test by the oxygen consumption method, was used to determine the biodegradation of the synthesized surfactant, 14-E2-14. The experiment needed 5 days to complete [28]. 100 mg of the sample was added to 100 ml of basic culture solution. The change in the BOD (mg) of the



Scheme 1. (a). Synthesis protocol of the cationic gemini surfactant ethane-1,2-diyl bis(*N,N*-dimethyl-*N*-tetradecylammoniumacetoxyl) dichloride (14-E2-14). (b). Molecular structure of the gemini surfactant.

system was monitored for 5 days. The biodegradability was evaluated using the following equation:

$$\text{Biodegradability}(\%) = [(BOD - \text{blank}) / TOD] \times 100$$

(TOD is the theoretical oxygen demand (mg) when the test compound is completely oxidized).

2.4. Cleavable properties

The gemini surfactant, owing to the presence of weak bonds, *i.e.*, ester groups in the spacer, is cleavable in nature. Cationic 14-E2-14 was found to undergo chemical hydrolysis in alkaline condition and thus was cleaved through chemical means by using phosphate-buffered saline and sodium hydroxide/potassium hydrogen phosphate (Ringer Buffer) [21].

The FT-IR spectral results at pHs 7.4 and 12 (Figs. S3(a) and S3(b)) show that 14-E2-14 gets cleaved in presence of the buffer solution in 8 h. Absorption band for the carbonyl functional group of ester [$-\text{OC}=\text{O}$] at 1749.52 cm^{-1} is shifted to 1637.87 cm^{-1} and new absorption band for the $-\text{OH}$ groups appears at 3532.55 cm^{-1} . Thus, formation of the easily degradable compounds such as fatty acid salt, respective diol or the compound with hydroxyl group takes place implying the cleavability of 14-E2-14.

2.5. Hemolytic assessment

Hemolysis of erythrocytes by interaction of surfactants has a great fundamental and practical importance mainly in pharmacology. The hemolytic activity of 14-E2-14 against human erythrocytes can be used as a measure for its cytotoxicity. For the hemolysis of 14-E2-14, we have followed a reported procedure [12,26]. When surfactants are added to erythrocyte suspension in aqueous medium, these distribute between the erythrocyte membrane and surfactant solution by adsorption until equilibrium is attained. Interaction between the surfactant and erythrocytes at sublytic concentration could be governed by affinity of each surfactant for the aqueous medium or the membrane, *i.e.*, closely related to hydrophobicity of the amphiphiles. HC_{50} is the concentration that induces hemolysis of 50% of erythrocyte cells and is quantified from the plots of percentage hemolysis as a function of amphiphile concentration. Our results (Fig. 1) show that 14-E2-14 is less hemolytic than the conventional surfactant TTAC of equivalent chain length. It is reported that hemolytic activity of gemini surfactants increases with aliphatic alkyl chain lengths of the hydrophobic tail [29].

2.6. Conductometric measurements

Conductivity method is a very useful technique for determination of the *cmc* of ionic surfactants [22–25,27]. Specific conductance of pure/mixed surfactant solutions were measured with an ELICO conductivity bridge (model CM82T) equipped with dip-type platinized electrodes of cell constant = 1.02 cm^{-1} . The alternating current method was used for electrical conductivity experiments. The conductivity runs were carried out by adding concentrated surfactant stock solution gradually to water (a Hamilton microsyringe was used for the addition). Temperature of the system was maintained at $303.15 \pm 0.1 \text{ K}$ by circulating water through jacketed container holding the solution under study. The *cmc* values were obtained from the intersection of the two straight lines drawn before and after the break in the specific conductance vs. total surfactant concentration plots (Fig. 2(a) and S4). Accuracy of the measurements was within $\pm 0.0001 \text{ mS} \cdot \text{cm}^{-1}$. Slopes of the specific conductance plots before and after the *cmc*, as reported in Table 1, yield the apparent degree of counterion binding, g_1 .

2.7. Tensiometric measurements

Surface tension (γ) is probably the most common physical parameter for the determination of *cmc* of surfactant systems. The *cmc* measurements of single/binary surfactant solutions were performed by surface tension measurements with a Kruss11 Tensiometer (K11MK3, Germany) using platinum ring detachment method at a constant temperature of 303.15 K. The temperature was maintained by circulating water from a ORBIT RS 10S thermostat around the sample holder. The ring was cleaned by heating it in alcohol flame. Typical decrease and constancy regions were found in each of the single and binary surfactant solutions of different mole fractions with addition of concentrated surfactant solution in pure water (Fig. 2(b) and S5). The *cmc* values, obtained from such γ ~ logarithm of total surfactant concentration isotherms, are given in Table 2. Each experiment was repeated thrice to achieve good reproducibility. Surface tension values were accurate within $\pm 0.1 \text{ mN} \cdot \text{m}^{-1}$. Various other parameters, *e.g.*, maximum surface excess concentration at the air/solution interface (Γ_{max}), minimum area per head group at the air/solution interface (A_{min}), excess molar Gibbs energy of mixing (G_{em}), standard Gibbs energy of micellization (ΔG_m), standard Gibbs energy of adsorption at the interface ($\Delta \text{ads}G$), minimum energy of surface (G_{min}), were calculated using the surface tension data.

3. Results and discussion

As the gemini surfactant, 14-E2-14, showed good biodegradability (39% of the amphiphile biodegraded after five days), it was considered for the mixed micellization study with the conventional surfactants of different polarities.

The average *cmc* values, obtained by the tensiometry and conductometry methods, were used to calculate the *cmc*-derived parameters. The *cmc* values of the pure surfactants decrease in the order: SDS > TTAC > SDBS > CPC > TX-100 > Brij 58 > 14-E2-14. The gemini surfactant, 14-E2-14, has noticeably very low *cmc* than the corresponding conventional monomeric surfactant TTAC due to its greater hydrophobicity owing to the double-tailed structure. The hydrophilicity of the spacer also might be a reason for the micelle formation at

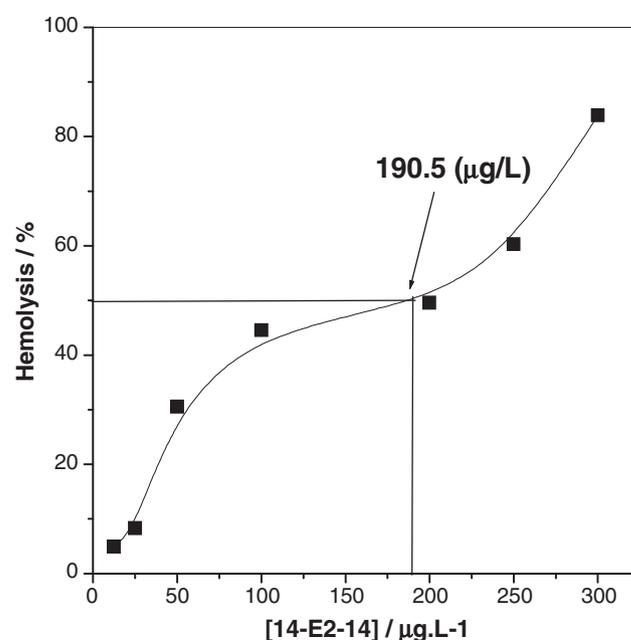


Fig. 1. Hemolytic activity as a function of 14-E2-14 concentration.

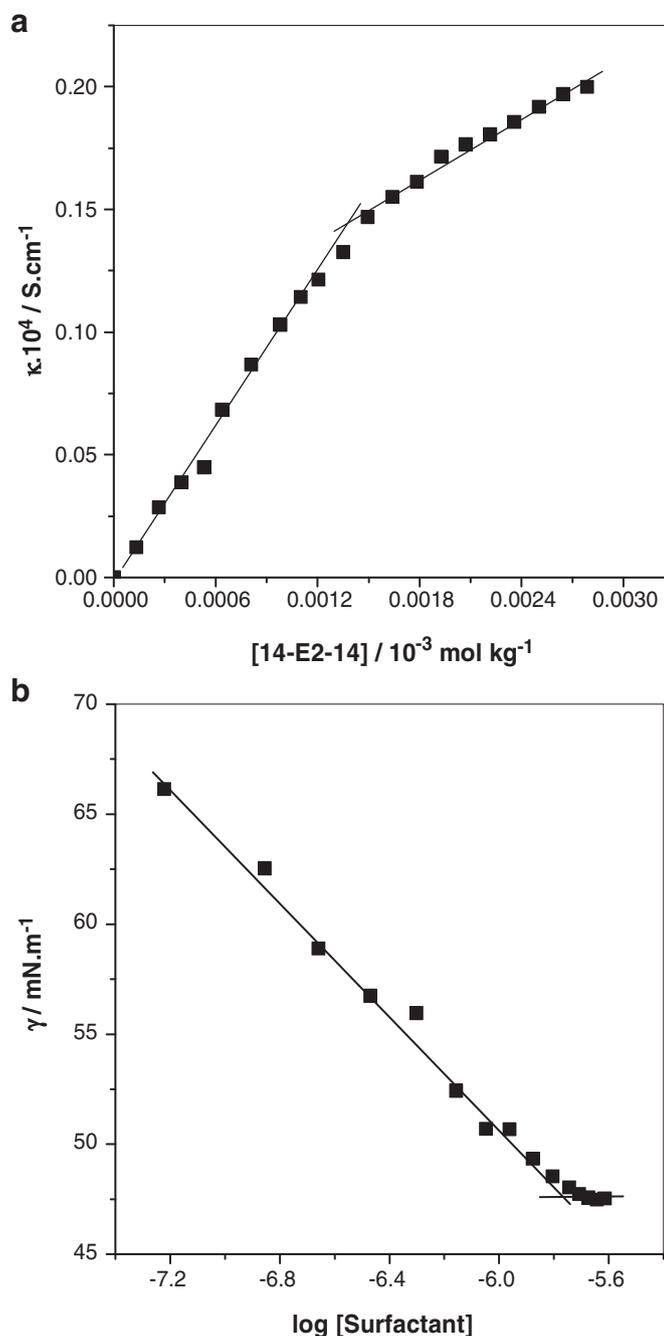


Fig. 2. (a). Variation of specific conductivity as a function of surfactant concentration for pure 14-E2-14 at 303.15 K. (b). Plot of surface tension vs. log [surfactant] for pure 14-E2-14 at 303.15 K.

a much lower concentration. As expected, the nonionic surfactants have lower cmc values as compared to the cationic/anionic surfactants.

3.1. Counterion binding

The layer just adjacent to the surface of the ionic micelles is known as the Stern layer to which the counterions are bound strongly and migrate with the micelles in an electrical field. Counterion association (g_1) of the pure/mixed micelles was evaluated from the degree of dissociation (g_2 , obtained from the ratio of post- and pre-micellar slopes of the specific conductance (κ) vs. [surfactant] plots) [30]. Higher counterion binding was observed for the 14-E2-14 + SDS/SDBS system

(Table 1) than the rest of the surfactant mixtures (except for CPC). Stronger counterion association reduces the cmc .

3.2. Mutual interaction between the surfactants in mixed micelles

The theories suggested by Clint, Rubingh, Motomura and Maeda have been used to explain the physicochemical parameters obtained from the experiments (see "Supplementary materials" for definition of terms and the equations used to evaluate the parameters).

The nature of interactions between 14-E2-14 and the conventional surfactant molecules, in their binary mixtures, can be explained in terms of Clint equation which is based on the pseudophase thermodynamic formulation (Eq. (S1)) [31]. The experimental cmc (cmc_{12}) values are lower than cmc_{ideal} which is attributable to the nonideal behavior and the attractive interactions between the constituent surfactants of binary mixtures. The order of cmc values of the binary mixtures with 14-E2-14 is as follows: TTAC > SDS > SDBS > CPC > TX-100 > Brij 58.

Rubingh model [32], based on regular solution approach (RSA), is the first model used for the surfactant mixtures for treatment of nonideal mixing. It is mostly used even after development of more complex models due to its simplicity. Comparison of the values of X_1^m (micellar mole fraction of 14-E2-14) in the mixed micelle and X_1^{ideal} (the corresponding micellar mole fraction in ideal state) (Fig. 3, Table 1S), which were evaluated by using Eqs. (S2) and (S3), demonstrates that the mixed micelles contain less surfactant molecules in comparison to that in ideal state ($X_1^m < X_1^{ideal}$). Also, the values of X_1^m (Fig. 3) increase with increase in the mole fraction of 14-E2-14 for most of the binary mixtures which indicates that the mixed micelle formation is favored in comparison to the formation of micelles by single components, and the mixed micellar phase is enriched in gemini surfactant molecules.

Mutual interactions between the surfactants in mixed micelles are due to the difference in structures of both the components, e.g., length and type of the hydrophobic chains, and electrostatic interactions among the hydrophilic parts. It is quantified in terms of interaction parameter, β^m , which is $[W_{12} - (\frac{1}{2}W_{11} + \frac{1}{2}W_{22})]/RT$, W being the molecular interaction energy between the indicated constituents (Eq. (S4)). Negative β^m values indicate that the attractive interaction (synergism) between the components in the mixed micelle is higher than the self-attraction of the surfactants before mixing. Zero β^m value indicates ideal mixing while positive values show lesser attraction after mixing (antagonism). Negative β^m values were obtained throughout the study for all the mixed systems suggesting synergism in the mixed micelle formation. Higher absolute values of β_{av}^m for 14-E2-14 + anionic (SDS and SDBS) systems are because of the electrostatic attractive interactions between the positively charged ammonium groups of the dicationic gemini and the negatively charged sulfate/sulfonate head groups. Nature and position of the functional group (i.e., presence of an ester linkage $[-CO(O)-]$) in spacer also affect the micellization process which makes it more hydrophilic that prompts micelle formation at low concentration [33]. In 14-E2-14 + cationic (CPC and TTAC) systems, the β_{av}^m value is less than 14-E2-14 + anionic mixed systems due to electrostatic repulsion between the same charged head groups. Stronger interaction of 14-E2-14 with CPC as compared to TTAC is caused by the higher hydrophobicity owing to the presence of pyridinium ring and additional $-(CH_2-CH_2)-$ group in CPC. It is clear from the data shown in Table 1 that least synergism is observed for the mixed systems of 14-E2-14 + nonionic (Brij 58 and TX-100) surfactants.

Activity coefficients (f_1^m) in the mixed micelles, according to the RSA, were calculated by Eqs. (S5) and (S6). Both f_1^m and f_2^m are less than unity showing nonideality of the systems. The mixed systems show higher f_1^m value than f_2^m suggesting higher activity of 14-E2-14 than the conventional surfactants.

Another suitable model, i.e., Motomura's approach [34], was used for the evaluation of micellar composition (X_1^M) and other physicochemical

Table 1

Values of the critical micelle concentration (cmc , cmc_{12}), ideal cmc (cmc_{ideal}), counterion association (g_1), micellar mole fraction calculated using Motomura's model (X_1^M), interaction parameter (β^m) and activity coefficients (f_1^m and f_2^m) for pure and mixed gemini – conventional surfactant systems for different mole fractions at 303.15 K.

Surfactant	Mole fraction of 14-E2-14, $\alpha_{14-E2-14}$	cmc or cmc_{12} $10^{-3} \text{ mol kg}^{-1}$	cmc_{ideal} $10^{-3} \text{ mol kg}^{-1}$	g_1^a	X_1^M	β^m	f_1^m	f_2^m
14-E2-14 SDS	1.0	0.0014		0.64				
	0.0	8.02		0.66				
	0.2	0.0047	0.0068	0.73	0.6348	-8.11	0.8231	0.0030
	0.4	0.0025	0.0034	0.74		-8.82	0.8505	0.0014
	0.6	0.0011	0.0023	0.82		-12.76	0.6053	0.0003
	0.8	0.0011	0.0017	0.72		-12.01	0.7565	0.0002
						$(\beta_{av}^m = -10.43)^b$		
SDBS	0.0	2.76		0.63				
	0.2	0.0038	0.0068	0.77	0.4370	-8.23	0.7095	0.0054
	0.4	0.0022	0.0034	0.45	0.8314	-8.54	0.7801	0.0028
	0.6	0.0020	0.0023	0.63	0.9748	-6.43	0.9662	0.0040
	0.8	0.0012	0.0017	0.69	-	-9.73	0.8415	0.0007
						$(\beta_{av}^m = -8.23)^b$		
CPC	0.0	0.837		0.53				
	0.2	0.0030	0.0068	0.61	0.3830	-8.03	0.5969	0.0114
	0.4	0.0020	0.0034	0.71	0.6799	-7.94	0.7147	0.0066
	0.6	0.0017	0.0023	0.75	0.8917	-6.92	0.8757	0.0059
	0.8	0.0010	0.0017	0.89		-9.66	0.7422	0.0014
						$(\beta_{av}^m = -8.14)^b$		
TTAC	0.0	4.1		0.64				
	0.2	0.0059	0.0068	0.39	0.4427	-5.44	0.9552	0.0112
	0.4	0.0028	0.0034	0.47	0.8667	-6.98	0.9301	0.0036
	0.6	0.0019	0.0023	0.48		-7.70	0.9346	0.0018
	0.8	0.0013	0.0017	0.21		-9.87	0.8685	0.0005
						$(\beta_{av}^m = -7.50)^b$		
Brij 58	0.0	0.0046						
	0.2	0.0025	0.0031	0.61	0.4290	-0.96	0.7643	0.8075
	0.4	0.0013	0.0024	0.15	0.6671	-2.71	0.6277	0.3943
	0.6	0.0012	0.0019	0.40	0.8184	-2.35	0.7887	0.3343
	0.8	0.0010	0.0016	0.63	0.9232	-3.19	0.8085	0.1721
						$(\beta_{av}^m = -2.30)^b$		
TX-100	0.0	0.18						
	0.2	0.0032	0.0066	0.48	0.4293	-5.63	0.6531	0.0518
	0.4	0.0018	0.0034	0.57	0.6673	-6.39	0.6925	0.0248
	0.6	0.0014	0.0023	0.38	0.8186	-6.50	0.7717	0.0155
	0.8	0.0011	0.0017	0.49	0.9232	-7.65	0.7665	0.0063
						$(\beta_{av}^m = -6.54)^b$		

Standard uncertainties for temperature are 0.1 K.

^a g_1 values are obtained from conductometric plots.

^b Average values.

parameters. It is applicable to any kind of surfactant mixtures and is independent of counterions of the amphiphiles. According to this approach, mixed micelles are considered as macroscopic bulk phase and the related energetics of such systems can be evaluated in terms of excess thermodynamic quantities. Wherever possible, the X_1^M values were calculated using Eqs. (S7)–(S12). The X_1^M values quantified from the Motomura model (Table 1) also support the X_1^m values.

3.3. Interaction of surfactants in mixed monolayer

Interfacial composition (X_1^{σ}) and interaction parameter (β^{σ}) at air–water interface can be evaluated by Rosen's model (Eq. (S13)) [2]. The X_1^{σ} values are lower than X_1^m indicating that the mixed monolayer contains less surfactant molecules than the mixed micelles. X_1^{σ} values are further used to calculate β^{σ} (repulsive or attractive) at the air–water interface with the help of Eq. (S14) (Table 2). Here too the mixed entities are formed synergistically. The activity coefficients, f_1^{σ} and f_2^{σ} , evaluated by using Eqs. (S15) and (S16), are less than one (Table 2) showing nonideality of the mixed systems at the interface.

3.4. Surface and interfacial properties

Maximum surface excess (i.e., surface saturation, Γ_{max}) is a measure of the extent of adsorption of various components at the interface.

Minimum area per surfactant head group adsorbed at the interface (A_{min}) provides the idea about close or loose packing of surfactant molecules at the air–water interface. In the submicellar region, Γ_{max} and A_{min} can be calculated using the following set of equations [35]:

$$\Gamma_{max} = -\frac{1}{2.303nRT} \left(\frac{\partial \gamma}{\partial \log C} \right) \quad (1)$$

$$A_{min} = \frac{10^{18}}{N_A \Gamma_{max}} \quad (2)$$

where n represents the number of ionic species whose concentrations at the interface vary with surfactant concentration in solution. Many researchers have considered $n = 2$ for ionic surfactants where surfactant ion and counterion are univalent, $n = 3$ for dimeric surfactant made up of divalent surfactant ion and two univalent counterions [36]. In the present work the n values are taken as 1, 2, and 3 for nonionic, anionic/cationic, and gemini surfactants, respectively. For gemini-nonionic, gemini-cationic/anionic mixed micelles, n values are 4 and 5, respectively. C is the concentration of surfactant, $d\gamma/d\log C$ slope of γ versus $\log C$ plot, N_A the Avogadro's number, and R and T have their usual significance.

Obviously, A_{min} decreases when Γ_{max} increases (Table 2). For pure surfactants the order of decrease of A_{min} is 14-E2-14 > SDBS > CPC > TTAC > SDS > TX-100 > Brij 58, and for surfactant mixtures of 14-E2-14 the order is TX-100 > TTAC > CPC > Brij 58 > SDS > SDBS.

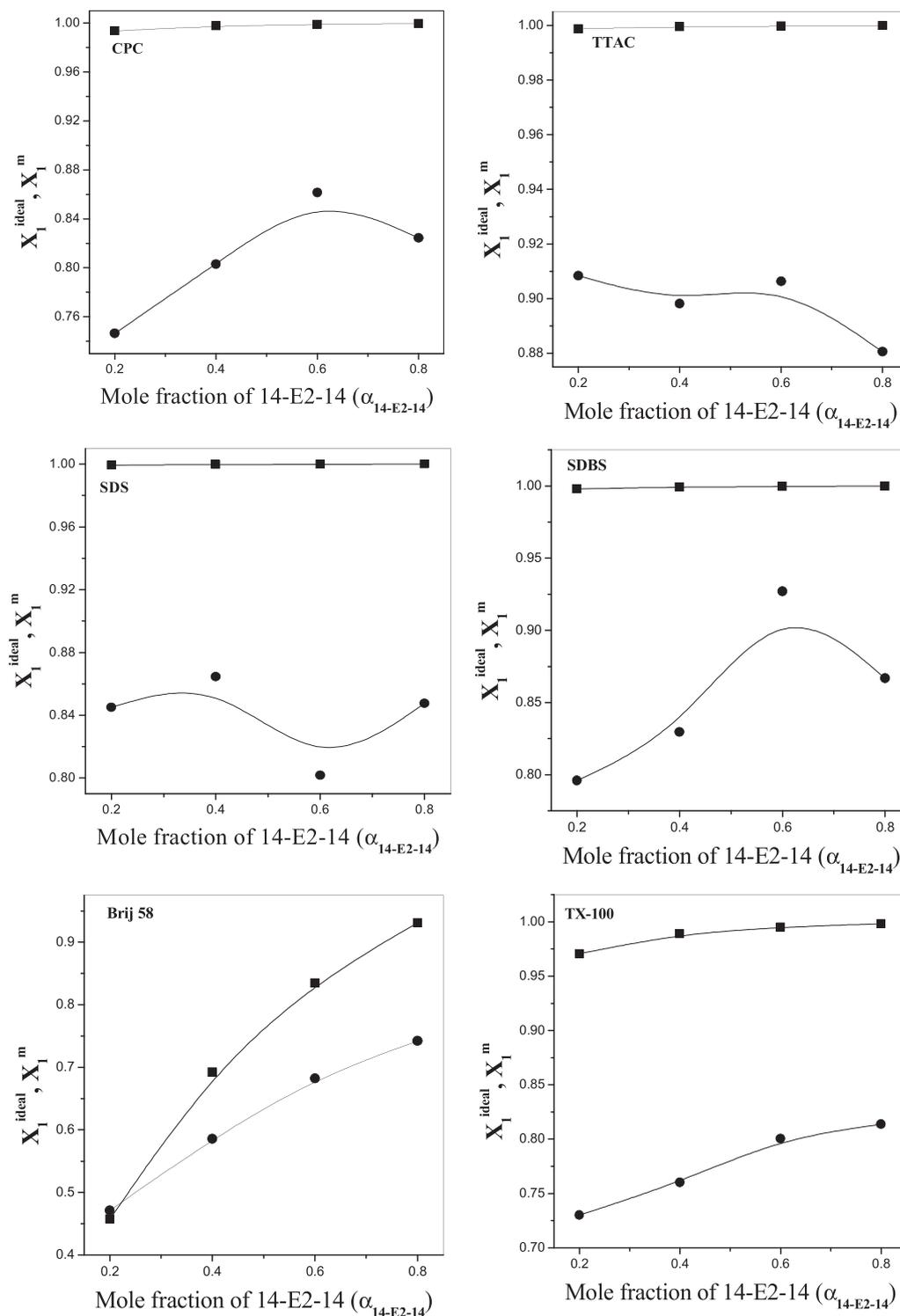


Fig. 3. Plots of X_1^m (•) and X_1^{ideal} (■) vs. the mole fraction of 14-E2-14 mixed with different conventional surfactants at 303.15 K.

Among all the binary solutions, the lowest A_{min} value was obtained for the 14-E2-14 + SDBS system. Due to the electrostatic attraction in 14-E2-14 + anionic surfactant mixtures, surfactant molecules are more tightly packed at interface lowering the A_{min} . A_{min} values increase with $\alpha_{14\text{-E2-14}}$ for 14-E2-14 + SDS/SDBS and 14-E2-14 + Brij 58, whereas for 14-E2-14 + TX-100 system Γ_{max} increases and thus A_{min} decreases with the increase of $\alpha_{14\text{-E2-14}}$. No trend is observed for the systems with cationic surfactants.

3.5. Thermodynamic properties of the gemini + conventional surfactant systems

Several types of forces such as electrostatic, covalent, hydrophobic and hydrogen bonding of various species are involved in adsorption of surfactants at the interface. Influence of such forces on the adsorption behavior is discussed here from a thermodynamic point of view.

Table 2

Values of interfacial mole fraction (X_1^s), interfacial interaction parameter (β^s), activity coefficients (f_1^s and f_2^s), surface pressure at cmc (Π_{cmc}), maximum surface excess concentration (Γ_{max}) and minimum area per head group (A_{min}) of the pure and mixed gemini – conventional surfactant systems at 303.15 K.

System	Mole fraction of 14-E2-14, $\alpha_{14-E2-14}$	X_1^s	β^s	f_1^s	f_2^s	$\Pi_{cmc}/mN \cdot m^{-1}$	$\Gamma_{max} 10^7/mol \cdot m^{-2}$	A_{min}/nm^2
14-E2-14	1.0					20.4	8.8	1.88
SDS	0.0					41.0	26.4	0.63
	0.2	0.7037	-3.07	0.7637	0.2185	33.3	10.3	1.61
	0.4	0.7430	-4.19	0.7584	0.0991	27.2	8.5	1.95
	0.6	-	-	-	-	23.7	6.9	2.42
	0.8	0.8459	-4.60	0.8964	0.0370	21.0	6.0	2.78
SDBS	0.0					40.4	12.5	1.33
	0.2	0.6951	-5.53	0.5980	0.0691	29.3	15.0	1.11
	0.4	0.8826	-2.55	0.9655	0.1377	18.4	10.6	1.56
	0.6	0.8647	-4.01	0.9292	0.0498	24.0	8.6	1.92
	0.8	-	-	-	-	20.8	8.4	1.98
CPC	0.0					24.9	16.5	1.01
	0.2	0.7090	-7.12	0.5470	0.0278	21.4	5.9	2.83
	0.4	0.7462	-7.66	0.6106	0.0141	26.4	8.6	1.92
	0.6	0.7580	-8.75	0.5988	0.0065	26.7	8.6	1.93
	0.8	-	-	-	-	12.7	6.9	2.42
TTAC	0.0					29.7	22.4	0.74
	0.2	-	-	-	-	13.3	4.6	3.61
	0.4	-	-	-	-	15.3	5.0	3.32
	0.6	-	-	-	-	15.9	4.7	3.50
	0.8	-	-	-	-	16.7	4.8	3.70
Brij58	0.0					29.7	32.1	0.52
	0.2	0.4052	-5.19	0.1592	0.4263	25.5	10.9	1.53
	0.4	0.4685	-4.16	0.3088	0.4014	22.7	9.6	1.73
	0.6	0.5366	-3.77	0.4443	0.3370	12.9	6.8	2.45
	0.8	0.6699	-2.05	0.7996	0.3981	9.9	4.9	3.36
TX-100	0.0					38.5	32.0	0.52
	0.2					22.0	3.8	4.38
	0.4					15.9	3.9	4.27
	0.6					14.9	4.1	4.05
	0.8					14.3	4.7	3.57

Standard uncertainties for temperature are 0.1 K.

Table 3

Values of excess molar Gibbs energy of mixing (GEm), standard Gibbs energy of micellization (ΔG_m^0), standard Gibbs energy of adsorption ($\Delta adsG$) and minimum surface energy (G_{min}) for the pure and mixed gemini – conventional surfactant systems at 303.15 K.

System	Mole fraction of 14-E2-14, $\alpha_{14-E2-14}$	$-GEm/kJ \cdot mol^{-1}$	$-\Delta G_m^0/kJ \cdot mol^{-1}$	$-\Delta adsG/kJ \cdot mol^{-1}$	$G_{min}/kJ \cdot mol^{-1}$
14-E2-14	1.0		44.1	46.4	55.6
SDS	0.0		22.3	24.8	40.5
	0.2	2.7	40.3	43.5	35.8
	0.4	2.6	41.9	45.1	49.6
	0.6	5.1	44.7	48.2	68.1
	0.8	3.9	44.4	47.9	82.1
SDBS	0.0		24.9	28.2	22.5
	0.2	3.4	41.5	43.4	27.1
	0.4	3.0	42.8	44.6	47.8
	0.6	1.1	43.1	45.9	53.6
	0.8	2.8	43.8	46.3	58.9
CPC	0.0		28.4	30.5	37.0
	0.2	3.8	42.2	45.8	82.4
	0.4	3.3	43.2	46.2	50.4
	0.6	2.1	43.7	46.8	50.4
	0.8	3.5	44.4	46.2	84.0
TTAC	0.0		24.0	25.7	14.5
	0.2	1.7	40.2	43.1	123.8
	0.4	1.6	42.0	45.1	109.4
	0.6	1.7	43.3	46.6	114.9
	0.8	2.6	44.4	48.2	119.5
Brij58	0.0		41.1	42.0	12.2
	0.2	0.6	43.1	45.4	41.4
	0.4	1.7	44.2	46.6	49.9
	0.6	1.3	44.3	46.2	84.6
	0.8	1.5	44.9	46.9	121.1
TX-100	0.0		31.9	43.9	9.9
	0.2	2.8	41.5	49.9	182.0
	0.4	2.9	43.5	48.0	152.8
	0.6	2.6	44.3	48.0	135.3
	0.8	2.9	44.7	47.8	119.3

Standard uncertainties for temperature are 0.1 K.

The excess molar Gibbs energy of mixing, GEm , can be calculated using the values of X_i^m and f_i^m as per Eq. (3)

$$GEm = RT [X_1^m \ln f_1^m + (1 - X_1^m) \ln f_2^m] \quad (3)$$

Negative GEm (Table 3) shows the stability of the mixed micellar systems. The GEm values indicate more spontaneous mixed micellization of 14-E2-14 with SDS than with SDBS. It is also evident from the higher value of β^m .

Standard Gibbs energy of micellization

$$\Delta G_m^{\circ} = RT \ln X_{cmc} \quad (4)$$

measures the tendency of surfactant to form micelles (X_{cmc} indicates cmc of the mixture in the form of mole fraction). The values are found to be negative for all the systems; the order of the average ΔG_m° for the mixed systems in presence of the gemini surfactant is Brij 58 > TX-100 > CPC > SDS > SDBS > TTAC. The negative ΔG_m° values (Table 3) again support the occurrence of the mixed micellization process to be favorable.

The standard Gibbs energy of adsorption at air/solution interface ($\Delta adsG$) [37] is correlated to ΔG_m° as

$$\Delta adsG = \Delta G_m^{\circ} - \frac{\Pi_{cmc}}{\Gamma_{max}} \quad (5)$$

where Π_{cmc} ($= \gamma_w - \gamma_{cmc}$) is the surface pressure at cmc , γ_w and γ_{cmc} are the surface tensions of pure water and surfactant solution at cmc . For all the systems, higher $\Delta adsG$ than the ΔG_m° (Table 3) shows more spontaneity to interfacial adsorption vis-à-vis micelle formation. Maximum value of $\Delta adsG$ was obtained for the gemini + TX-100 system whereas the gemini + SDBS surfactant mixture had a minimum value.

G_{min} is the work required to relocate the surfactant molecules from the bulk phase to the interface of the surfactant solution

$$G_{min} = \gamma_{cmc} A_{min} N_A \quad (6)$$

The lowest G_{min} of the gemini-anionic surfactant mixtures indicates that a thermodynamically stable surface, with synergistic interactions, is formed which is evident also by their interaction parameter values.

3.6. Maeda approach

In addition to the electrostatic interactions between the head groups, steric repulsions due to different hydrophobic chain lengths of surfactants can also be taken into account. According to Maeda [38] and Ruiz and Aguiar [39], hydrophobic chain-chain and hydrophilic head group-head group interactions of the surfactant molecules are found in mixed micelles.

Table 4
 ΔG_{Maeda}° and B_1 values for the 14-E2-14 + nonionic binary surfactant systems at 303.15 K.

System	Mole fraction of 14-E2-14, $\alpha_{14-E2-14}$	$-\Delta G_{Maeda}^{\circ}/\text{kJ} \cdot \text{mol}^{-1}$	B_1
14-E2-14	1.0	–	–
Brij 58	0.2	15.6	–2.17
	0.4	17.0	–3.92
	0.6	16.9	–3.57
	0.8	17.4	–4.41
TX-100	0.2	16.3	–10.51
	0.4	16.6	–11.28
	0.6	16.8	–11.39
	0.8	17.3	–12.54

Standard uncertainties for temperature are 0.1 K.

Accordingly,

$$\Delta G_{Maeda}^{\circ} = RT \{ B_0 + B_1 X_1^m + B_2 (X_1^m)^2 \} \quad (7)$$

The independent term B_0 is related to the cmc of the nonionic component as

$$B_0 = \ln cmc_2 \quad (8)$$

B_1 is a parameter related to the standard Gibbs energy change due to the exchange of a nonionic constituent in the nonionic pure micelle with an ionic constituent. The last coefficient, $B_2 = -\beta^m$ (the interaction parameter β^m in negative sign). Further, the two parameters B_1 and B_2 are related to the pure components' cmc values

$$B_1 + B_2 = \ln \left(\frac{cmc_1}{cmc_2} \right) \quad (9)$$

Using cmc and β^m , B_1 was evaluated with the help of Eq. (9), which are: 14-E2-14 + Brij 58, –2.17, –3.92, –3.57, –4.41; 14-E2-14 + TX-100, –10.51, –11.28, –11.39 and –12.54. Higher B_1 values indicate more chain-chain interaction and higher stability of the mixed micelles. The ΔG_{Maeda}° values, calculated from Eq. (7), are recorded in Table 4 which show comparable values.

4. Conclusions

The surface and micellar properties of the gemini surfactant ethane-1,2-diyl bis(*N,N*-dimethyl-*N*-tetradecylammoniumacetoxo)dichloride (14-E2-14) and its binary mixtures with six conventional surfactants were investigated. For the pure/mixed surfactant micelles, the cmc values were measured employing conductivity and surface tension methods. Various theoretical models have been used to obtain the physicochemical parameters and explanations are provided for the synergistic interactions between 14-E2-14 and the monomeric surfactants in the mixed systems. For all the binary systems, the cmc values for different mole fractions of the gemini were found to be less than ideal cmc indicating synergistic interaction between the surfactants. Low toxicity of the cleavable/biodegradable surfactant 14-E2-14 makes it particularly interesting for mixed micellization study. Due to its low toxicity to membranes, it can be considered as a suitable surfactant in drug formulations.

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Appendix A. Supplementary materials

Supplementary materials associated with this article can be found in the online version, at <http://dx.doi.org/10.1016/j.molliq.2015.06.064>. Surfactant structures, various spectra of 14-E2-14, equations used for the evaluation of physicochemical parameters of the mixed systems. Conductivity and tensiometry plots of all the mixed systems.

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