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Synthesis, Characterization and Solution Properties of Novel Cationic Ester-Based Gemini Surfactants

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Abstract: The present investigation involves the synthesis of a series of novel green ethylene oxide-linked diester-functionalized cationic gemini surfactants 2,2′-[(oxybis(ethane-1,2-diyl))bis(oxy)]bis(N-alkyl-N,N-dimethyl-2-oxo-ethanaminium) dichloride (C_m-DEG-C_m; $m = 12, 14, 16$). These compounds were characterized by ^{1}H-NMR, MS-ESI (+), FT-IR spectroscopy and elemental analysis; their solution properties were evaluated by surface tension and rheology measurements. The dimeric surfactant, C_m-DEG-C_m, possesses improved physicochemical properties as compared to its monomeric counterpart. Much lower critical micelle concentration (*cmc*) makes the cationic gemini surfactants more useful for the biomedical, pharmaceutical, industrial and academic sectors. Longer the alkyl chain of surfactants lower are the *cmc* values, the order is C_{16}-DEG-C_{16} $<$ C_{14}-DEG-C_{14} $<$ C_{12}-DEG-C_{12}. For all the three synthesized gemini surfactants no cloud point was noticed in between the temperatures 0 °C to 100 °C at the concentrations 0.002 mM, 0.02 mM and 0.2 mM of the aqueous surfactant solutions which is a beneficial factor for the use of these amphiphiles in various areas of application.

Keywords: cationic gemini surfactant; *cmc*; micelles; rheology.

1 Introduction

Nowadays, interest in the study of surfactant systems has increased as there is a concern for the researchers to understand the physical, chemical and structural

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properties of the organized assemblies. In the field surface science ample research has been done on the study of the physicochemical behaviour of pure, synthetic surfactants with relatively simple structures which is partially motivated by the significant role of the amphiphiles in biophysics, biotechnology and pharmacology. Surfactant self assembly remains an area in which the industrial applications and fundamental science are closely linked, and thus various cationic, anionic, zwitterionic, non-ionic surfactants have been synthesized and commercialized. A large number of papers discussing the synthesis of surfactants [1], their corrosion inhibition effect [2, 3], catalysis [4], use of surfactants for the synthesis of cationic nanoparticles [5], for electrochemical stability [6], etc. has been published. Some recent findings including the experimental as well as theoretical studies, phase behaviour [7] and rheological properties [8] of the surfactant systems, their biophysical applications [9] have been found in the literature. The wide industrial applications of the novel surfactants are the subject of current interest and the systems are being actively researched.

An exciting development in the field of surface chemistry was the emergence of dimeric or gemini surfactants. The name gemini was assigned by Menger and Littau to bis-surfactants with rigid spacer although later on the name was extended to other double-tailed surfactants irrespective of the nature of the spacers; the results of their investigations [10] have been received well by a large group of authors. Currently, the gemini surfactants attract much attention because of their superior aggregation capacity and versatile morphological behaviour. Unlike the conventional single head-single tail amphiphiles, geminis consist of two tails and two head groups bridged with a spacer [10–12]. Gemini surfactants can be visualized as the dimers in which two surfactant moieties are linked together by a spacer. The spacer can be either hydrophobic or hydrophilic, may vary in length and is attached to the two surfactant moieties at the position near their hydrophilic head groups, leaving the hydrophobic groups mostly intact. Properties of the gemini surfactants are different from those of the corresponding conventional surfactants and can be tuned by modifying the chemical nature and length of the spacer group [13]. Aggregation of gemini surfactants in aqueous solution, mostly the m-s-m type surfactants (m and s are the number of carbon atoms in alkyl chains and polymethylene spacer, respectively), has been examined extensively. Owing to their increased hydrophobicity, gemini surfactants show much lower *cmc* than their conventional counterparts, while the nature of the spacer can tune their size and shape [14, 15].

Amphiphiles have the tendency to get adsorbed at the surfaces and interfaces, and assemble in water at a particular threshold concentration, i.e. critical micelle concentration (*cmc*) to form micelles. Over the last few decades, researchers are in a great stride for the development of highly efficient surfactants with various functionalized molecular architectures. Due to their unique structure gemini surfactants, in recent times, have received considerable attention from industrial community. These amphiphiles have great potential for application in the petroleum industry, pharmaceutical, biotechnology, oil recovery and other sectors because of their superiority over typical conventional surfactants for having better interfacial properties, enhanced surface activity, much lower *cmc*, higher solubilizing capability and multifarious aggregate structures [16–22]. The surface and interfacial properties of the gemini surfactants are dependent on the nature of the head group as well as the spacer, length of hydrophobic chain, and their molecular arrangement.

The continuous usage of cationic surfactants with poor biodegradability and higher toxicity are the major environmental concern. To overcome these problems, researchers have been synthesizing several easily degradable, less toxic, cleavable surfactants with soft-bonded functionality in their molecular architecture [23–31]. In this work, the authors have a particular interest in synthesizing oxy-diester-functionalized cationic gemini surfactants because the insertion of ester bonds between the polar head groups of a surfactant is a way to render it biodegradable more rapidly. Lower *cmc* values make the gemini surfactants useful for various applications where it is an advantage that the self-assembly in bulk and at interfaces occurs at low concentration.

2 Experimental section

2.1 Materials

The compounds N,N-dimethyldodecylamine, (TCI, Japan), N,N-dimethyltetradecyl amine (TCI, Japan), N,N-dimethylhexadecylamine (TCI, Japan), chloroacetyl chloride (CDH, India), diethylene glycol (TCI, Japan), ethyl acetate (Rankem, India), ether (Rankem, India) were used as received.

Synthesis of novel oxy-diester-linked cationic gemini surfactants (C_m-DEG-C_m)

A series of gemini surfactants, referred as C_m-DEG-C_m, were prepared and characterized systematically. Synthesis of gemini surfactants involves two main steps: preparation of oxy-diester-functionalized spacer part and its quaternization with alkyl amine [29, 31].

Preparation of oxybis(ethane-1,2-diyl)bis(2-chloroacetate)

For the preparation of oxy-diester spacer portion, chloroacetyl chloride was taken because of its bifunctional nature. It can easily form ester functionality with alcohol. This reaction involves nucleophilic substitution mechanism. The experimental set up includes three necked round bottomed flask (RBF) equipped with a magnetic stirrer, a thermometer, a condenser and a drying tube (calcium chloride). 0.22 mol of chloroacetyl chloride was taken in the RBF in inert N_2 atmosphere. Then 0.1 mol of diethylene glycol was slowly added to it with the quick fitted additional funnel in the same atmosphere. After the diethylene glycol was completely poured into the RBF, the reaction mixture was heated for 8 h at 50 °C. The elimination of byproduct (HCl gas) was done under reduced pressure. Thereafter, the final organic phase was washed with saturated brine till neutralization. The product was dissolved in diethyl ether and magnesium sulphate was added to it for drying. After few hours the dissolved compound was separated from magnesium sulphate and yielded the desired product, i.e. oxybis(ethane-1,2-diyl)bis(2-chloroacetate).

Preparation of 2,2′-[(oxybis(ethane-1,2-diyl))bis(oxy)]bis(N-alkyl-N,N-dimethyl-2-oxoethanaminium) dichloride

The respective N,N-dimethylalkylamine (m = 12, 14, 16) (0.21 mol) and oxybis(ethane-1,2-diyl)bis(2-chloroacetate) (0.1 mol) were taken in a three-necked round bottomed flask, then refluxed with ethyl acetate for 10 h. The solvent was removed from the crude reaction mixture under reduced pressure and subsequently recrystallized with ethyl acetate to obtain the desired cationic gemini surfactants 2,2′-[(oxybis(ethane-1,2-diyl))bis(oxy)]bis(N-dodecyl-N,N-dimethyl-2-oxoethanaminium) dichloride (C_{12}-DEG-C_{12}), 2,2′-[(oxybis(ethane-1,2-diyl))bis(oxy)]bis(N-tetradecyl-N,N-dimethyl-2-oxoethanaminium) dichloride (C_{14}-DEG-C_{14}) and 2,2′-[(oxybis(ethane-1,2-diyl))bis(oxy)]bis(N-hexadecyl-N,N-dimethyl-2-oxoethanaminium) dichloride (C_{16}-DEG-C_{16}) as white solid product. Reaction route for the synthesis is shown in Figure 1. Molecular structure and purity of the

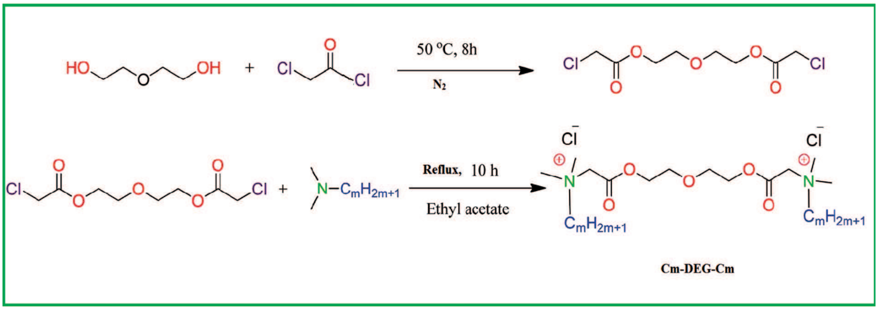

Fig. 1: Synthesis pathway of oxy-diester linked cationic gemini surfactants (C_m-DEG-C_m; m = 12, 14, 16).

products were analyzed by ^{1}H-NMR, MS-ESI (+), FT-IR spectroscopy and elemental analysis. The ^{1}H-NMR, MS-ESI (+) spectra are illustrated in Figures 2–7. The FT-IR spectral data are given in Table 1.

Determination of cloud points

For all the three synthesized oxy-diester-linked cationic gemini surfactants used in this study, at the concentrations 0.002 mM, 0.02 mM and 0.2 mM of the aqueous surfactant solutions, the temperature was increased to see whether there exists a cloud point. The surfactant solutions were taken in well stoppered tubes which were placed into temperature-controlled water bath. The temperature was raised slowly to see whether the clear solution became cloudy.

Viscosity measurements

Viscosity (η) of the gemini surfactant solutions was measured at fixed (100 s^{-1}) shear rate by using a modular compact rheometer (MCR 102 SN 81270415 FW3.70) equipped with conical shaped geometry at 35 °C after putting 2–3 drops of the surfactant solution on the measuring plate.

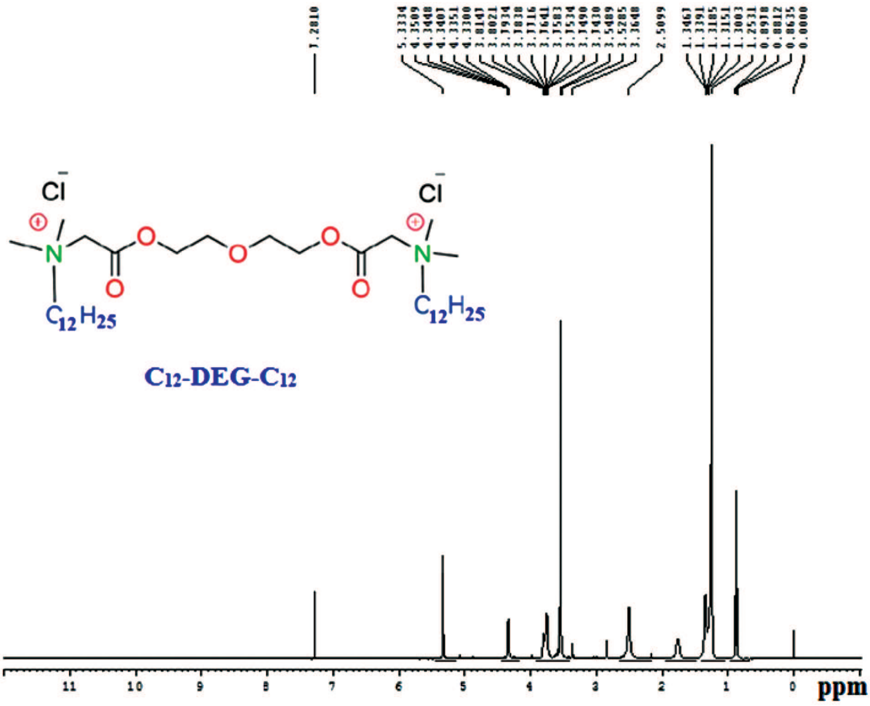

Fig. 2: ^{1}H-NMR spectrum (400 MHz) of 2,2′-[(oxybis(ethane-1,2-diyl))bis(oxy)]bis(N-dodecyl-N, N-dimethyl-2-oxoethanaminium) dichloride (C_{12}-DEG-C_{12}) in $CDCl_3$.

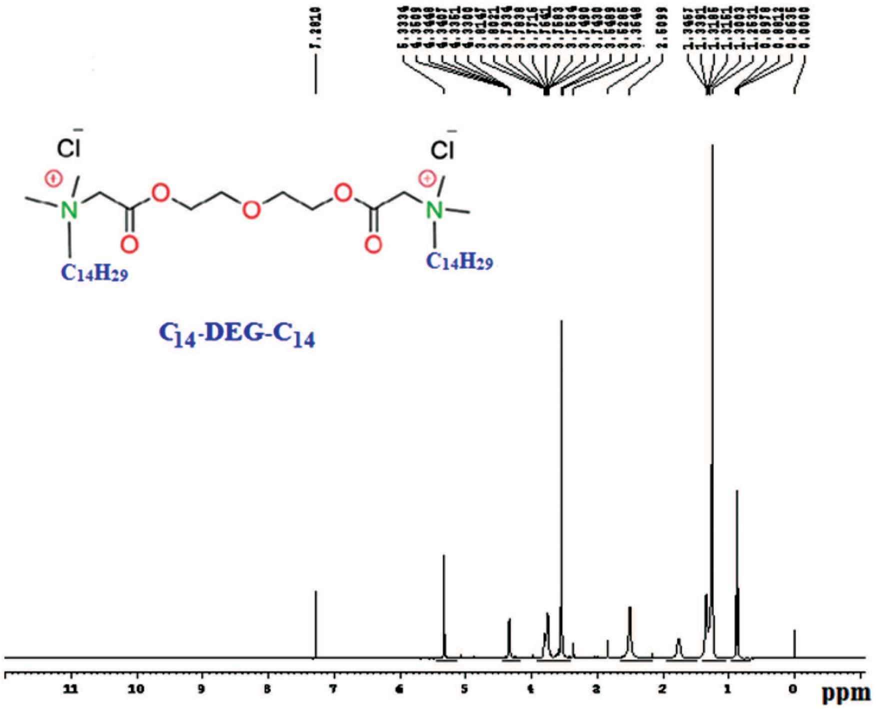

Fig. 3: ^{1}H-NMR spectrum (400 MHz) of 2,2′-[(oxybis(ethane-1,2-diyl))bis(oxy)]bis(N-tetradecyl-N, N-dimethyl-2-oxoethanaminium) dichloride (C_{14}-DEG-C_{14}) in $CDCl_3$.

Surface tension measurements

The amphiphiles lower the surface and interfacial tensions as a result of their accumulation at the air–water interface and the surface tension becomes constant at the critical micelle concentration (*cmc*). The *cmc* can be used as a criterion of purity of an amphiphile and for the prediction of other physical properties. *cmc* of the aqueous solution of gemini surfactants were measured by surface tension method based on the Du Nouy ring detachment principle at 30 °C. Double distilled water was used to prepare the aqueous solutions of C_m-DEG-C_m. The tensiometer was calibrated by deionized water with surface tension (γ) ranged from 71 to 72 mN m^{-1}. After each addition of the concentrated surfactant solution in pure water, the solutions were left for 5 min to attain the equilibrium before noting the γ value. The experiments were repeated to obtain the results of good reproducibility. With the addition of surfactant in water, its logarithmic concentration reduces γ almost linearly. After certain concentration (*cmc*), almost constant γ values were obtained that would change the slope considerably. Absence of

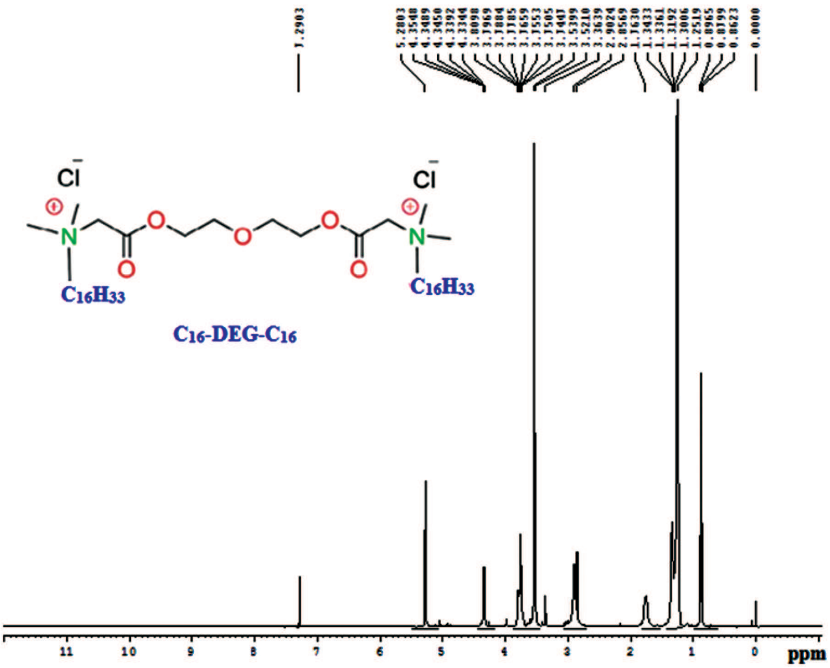

Fig. 4: ^{1}H-NMR spectrum (400 MHz) of 2,2′-[(oxybis(ethane-1,2-diyl))bis(oxy)]bis(N-hexadecyl-N,N-dimethyl-2-oxoethanaminium) dichloride (C_{16}-DEG-C_{16}) in $CDCl_3$.

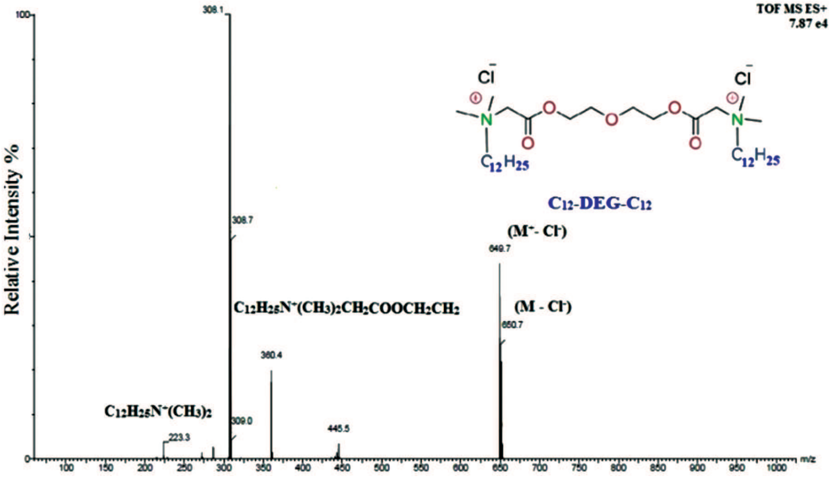

Fig. 5: ESI-MS (+) spectrum (relative intensity vs. m/z) of 2,2′-[(oxybis(ethane-1,2-diyl))bis(oxy)]bis(N-dodecyl-N,N-dimethyl-2-oxoethanaminium) dichloride (C_{12}-DEG-C_{12}).

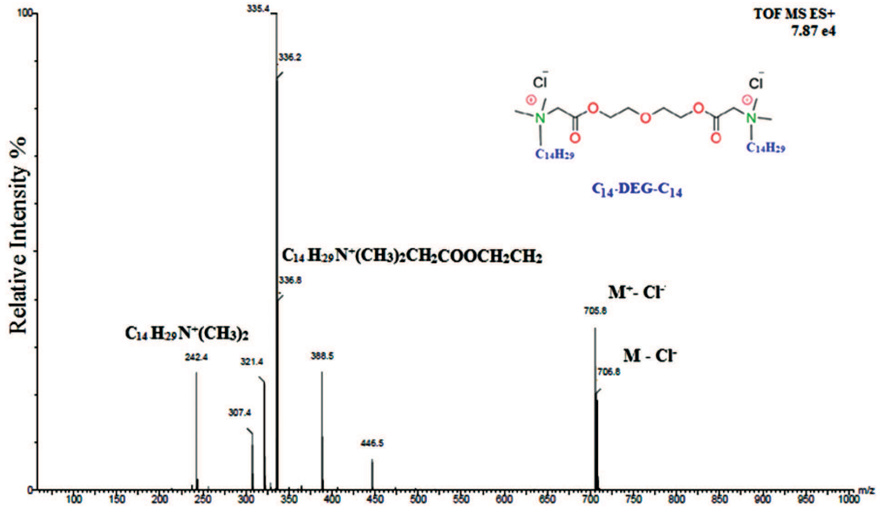

Fig. 6: ESI-MS (+) spectrum (relative intensity vs. m/z) of 2,2′-[(oxybis(ethane-1,2-diyl))bis(oxy)]bis(N-tetradecyl-N,N-dimethyl-2-oxoethanaminium) dichloride (C_{14}-DEG-C_{14}).

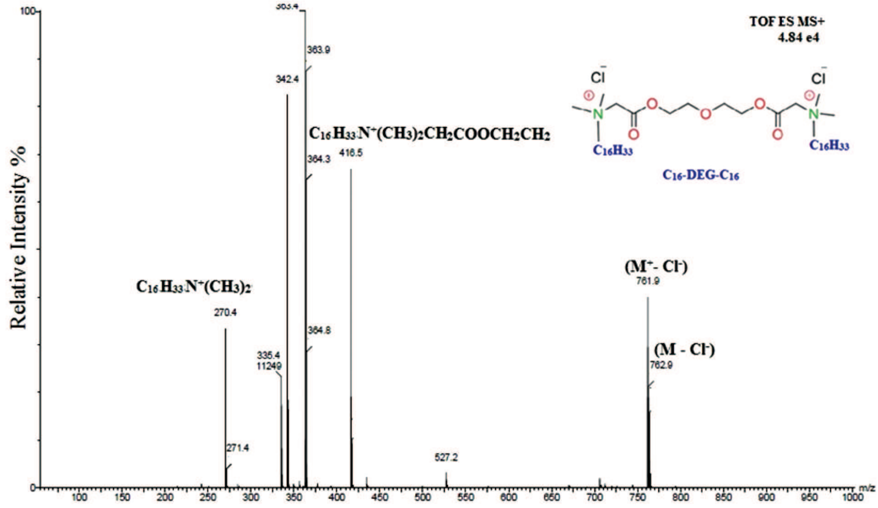

Fig. 7: ESI-MS (+) spectrum (relative intensity vs. m/z) of 2,2′-[(oxybis(ethane-1,2-diyl))bis(oxy)]bis(N-hexadecyl-N,N-dimethyl-2-oxoethanaminium) dichloride (C_{16}-DEG-C_{16}).

minima in the surface tension versus log [surfactant] plots was taken as additional evidence regarding the purity of the surfactants.

Tab. 1: Analytical data of MS-ESI (+), ^{1}H-NMR, IR and elemental analysis of cationic gemini surfactants (C_m-DEG-C_m, m = 12, 14, 16).

C_m-DEG-C_m	MS-ESI (+) m/z (%)	^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm)	IR ν (cm^{-1}) (KBr)	Elemental analysis (%)
C12-DEG-C12	(M-Cl^-) 650.7 (observed), (M^+-Cl^-) 649.7 (observed), ($C_{12}H_{25}N^+(CH_3)$ $CH_2COOCH_2CH_2$) 309 (observed), ($C_{12}H_{25}N^+(CH_3)$) 223.3 (observed)	0.864–0.897 (t, 6H, $-2 \times CH_3$, alkyl chain), 1.253–1.346 (m, 40H, $-2 \times (CH_2)_{10}$, alkyl chain), 2.509 (s, 4H, $-2 \times CH_2$–O–CH_2, spacer), 3.364–3.548 (s, 12H, $-2 \times N^+(CH_3)_2$), 3.743–3.814 (m, 4H, $-2 \times N^+CH_2$), 4.330–4.350 (m, 4H, $-2 \times CH_2OOC$, spacer), 5.333 (s, 4H, N^+CH_2COO)	2921, 2852 (C–H), 1749 (C=O), 1466 (C–O), 1127 (C–N)	C 58.68, H 10.77, N 4.02
C14-DEG-C14	(M-Cl^-) 706.8 (observed), (M^+-Cl^-) 705.8 (observed), ($C_{14}H_{29}N^+(CH_3)$ $CH_2COOCH_2CH_2$) 336.8 (observed), ($C_{14}H_{29}N^+(CH_3)$) 242.4 (observed)	0.830–0.897 (t, 6H, $2 \times CH_3$, alkyl chain), 1.252–1.347 (m, 48, H, $-2 \times (CH_2)_{12}$, alkyl chain), 2.104 (s, 4H, $-2 \times CH_2$–O–CH_2, spacer), 3.519–3.623 (s, 12H, $-2 \times N^+(CH_3)_2$), 3.715–3.818 (m, 4H, $-2 \times N^+CH_2$), 4.321–4.342 (m, 4H, $-2 \times CH_2OOC$, spacer), 5.404 (s, 4H, N^+CH_2COO)	2920, 2852 (C–H), 1747 (C=O), 1465 (C–O), 1126 (C–N)	C 60.66, H 11.09, N 3.87
C16-DEG-C16	(M-Cl^-) 761.9 (observed), (M^+-Cl^-), 762.9 (observed), ($C_{16}H_{33}N^+(CH_3)$ $CH_2COOCH_2CH_2$) 364.8 (observed), ($C_{16}H_{33}N^+(CH_3)$) 271.4 (observed)	0.862–0.896 (t, 6H, $2 \times CH_3$, alkyl chain), 1.251–1.343 (m, 48, H, $-2 \times (CH_2)_{14}$, alkyl chain), 2.856 (s, 4H, $-2 \times CH_2$–O–CH_2, spacer), 3.521–3.539 (s, 12H, $-2 \times N^+(CH_3)_2$), 3.744–3.809 (m, 4H, $-2 \times N^+CH_2$), 4.334–4.354 (m, 4H, $-2 \times CH_2OOC$, spacer), 5.280 (s, 4H, N^+CH_2COO)	2918, 2851 (C–H), 1749 (C=O), 1468 (C–O), 1129 (C–N)	C 61.22, H 11.15, N 3.60

3 Results and discussion

Three diester-functionalized cationic gemini surfactants were synthesised, the chemical structure was characterized by several analytical tools and the analytical data are compiled in Table 1. The physicochemical properties of C_m-DEG-C_m were examined by means of *cmc*.

Critical micelle concentration

Figure 8 shows the plots of γ versus logarithm of the concentration of the synthesized gemini surfactants. The gemini surfactants exhibit high aggregation capacity and can form micelles in a micromolar concentration range. Decrease in *cmc* is observed as the alkyl chain gets longer (Table 2). As the hydrophobic part gets larger, the surfactant molecules become more lipophilic and thus have higher propensity to move from the bulk aqueous phase onto the air–water interface. The insertion of ether functional group in the spacer portion possibly affects the aggregation behaviour on the monolayer and in bulk. With the increase of chain length, the *cmc* values were found to decrease, C_{12}-DEG-C_{12} $>$ C_{14}-DEG-C_{14} $>$ C_{16}-DEG-C_{16}. Nature of the spacer and hydrophobicity of the gemini surfactants play a significant role in lowering the surface tension. The ethylene oxide group present

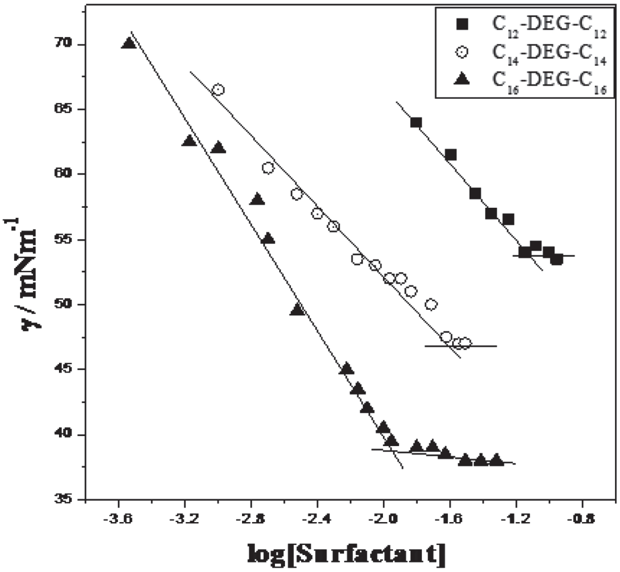

Fig. 8: Surface tension (γ) versus log [Surfactant] of the cationic gemini surfactants (C_m-DEG-C_m; m = 12, 14, 16).

Tab. 2: Properties of the oxy-diester-linked cationic gemini surfactants (C_m-DEG-C_m; m = 12, 14, 16).

Surfactant	Molecular formula	Molecular weight (g mol^{-1})	Melting point (°C)	*cmc* (mM)	γ_{cmc} (mN m^{-1})
C_{12}-DEG-C_{12}	$C_{36}H_{74}N_2O_5Cl_2$	685	90	0.075	53.87
C_{14}-DEG-C_{14}	$C_{40}H_{82}N_2O_5Cl_2$	741	94	0.025	46.90
C_{16}-DEG-C_{16}	$C_{44}H_{90}N_2O_5Cl_2$	797	98	0.011	38.85

in between the polar head groups might be participating in the hydrogen bonding with water.

Cloud Point

Cloud point (CP) is one of the most important physical properties for understanding many processes in the chemical industries [32, 33]. Above CP, the water solubility of the surfactant is reduced resulting in a cloudy dispersion. Usually, cloud points range from 0 °C (freezing point) to 100 °C (boiling point) in water though there are some exceptions. With the increase of temperature intermicellar repulsions decrease and at some point the system starts to demix. During the transfer of monomers into micelles the net heat change is due to the disruption of water structure around the nonpolar tails of the surfactant molecules and incorporation of the monomers into the micelles.

Even though the gemini surfactants used in this study are cationic, the clouding behaviour – a general characteristic of nonionic surfactants – was expected because of the presence of the oxy-diester-linked spacers. Clouding is a result of the dehydration of the hydrophilic parts of the amphiphiles. Compounds which are water-structure breakers increase the CP while water-structure makers decrease the CP. The ester groups are highly hydrated; the oxy-diester linkage makes the spacer hydrophilic whereas the twin-tail part remains hydrophobic. Nature and position of the functional group (i.e. presence of the oxy-diester linkage in spacer part) affect the micellization process making it more hydrophilic which prompts the micelle formation at low concentration. Oxygen atoms of the spacer can form hydrogen bond with the water molecules reducing unfavourable contact of the hydrocarbon part with water and hydration in the vicinity of spacer reduces the electrostatic repulsion between the head groups. These hydrogen bonds break easily with the rise in temperature. No clouding behaviour was observed in between the temperatures 0 °C to 100 °C for all the three gemini surfactants at the concentrations 0.002 mM, 0.02 mM and 0.2 mM of the aqueous surfactant solutions. This is an advantage as CP sometimes poses a hindrance to the use of surfactant.

Tab. 3: Viscosity of the gemini surfactant solutions at fixed shear rate (100 s^{-1}).

S. no.	**[Surfactant]**	**Viscosity (Pa s)**		
		C12-DEG-C12	**C14-DEG-C14**	**C16-DEG-C16**
1	0.5 × *cmc*	0.00066	0.00071	0.00071
2	1 × *cmc*	0.00071	0.00071	0.000717
3	10 × *cmc*	0.00070	0.00072	0.000712
4	100 × *cmc*	0.00075	0.00075	0.00075

Rheology
Table 3 shows the values of viscosity at different concentrations of the gemini surfactants at 35 °C at fixed shear rate (100 s^{-1}). For all the three surfactants the increase in viscosity with the surfactant concentration was negligible although a small increase in viscosity was noticed at the concentration 100 times higher than the *cmc*. Surfactant solutions containing spherical micelles are isotropic in nature and of low viscosity [34]. The presence of reasonably long rod-shaped micelles in the solution could impart higher viscosity to the solution [35]. Our result indicates that up to the surfactant concentration which is 100 times higher than its *cmc*, there is no change in the micellar shape and only small spherical micelles are formed. Spacers of these surfactants are hydrophilic and, like the nonionic surfactants, form small spherical micelles.

4 Conclusions

Three dicationic ester-linked gemini surfactants of similar head as well as spacer groups but of different hydrophobic tail length were prepared in the lab and were characterized systematically which showed high purity of the synthesized gemini surfactants. The gemini surfactants have much lower *cmc*s than the monomeric analog having same number of carbon atoms in the hydrophobic tail part, *cmc*s of the gemini surfactants were found to decrease with the increase of chain length, the order is C_{12}-DEG-C_{12} > C_{14}-DEG-C_{14} > C_{16}-DEG-C_{16}. Nature and position of the functional groups affect the micellization process. Presence of oxy-diester linkage in the spacer makes it more hydrophilic favouring the micelle formation at low concentration. No cloud point was observed for any of the surfactants at the temperature range used here. From the rheology studies it was observed that the increase in viscosity with the increase of surfactant concentration is insignificant though at higher surfactant concentration the change is little prominent. The novel ester-functionalized gemini surfactants can provide an approach to control the architecture of the surfactant assemblies and, therefore, will benefit the engineering and scientific communities.

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