

Synthesis of Ester Based Cationic Pyridinium Gemini Surfactants and Appraisal of Their Surface Active Properties

Pankaj Patial · Arifa Shaheen · Ishtiaque Ahmad

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Abstract New pyridinium gemini surfactants have been synthesized by esterification of halogenated carboxylic acids with long chain fatty alcohols furnishing respective esters (dodecyl-2-chloroacetate, tetradecyl-2-chloroacetate, hexadecyl-2-chloroacetate, dodecyl-2-bromoacetate, tetradecyl-2-bromoacetate and hexadecyl-2-bromoacetate) followed by their subsequent treatment with 4,4'-trimethylene dipyridine resulting in the formation of title Gemini surfactants: 4,4'-(propane-1,3-diyl)bis[1-(2-(dodecyloxy)-2-oxoethyl)]; 4,4'-(propane-1,3-diyl)bis{1-(2-(tetradecyloxy)-2-oxoethyl)}; 4,4'-(propane-1,3-diyl)bis{1-(2-(hexadecyloxy)-2-oxoethyl)} dipyridinium chlorides; 4,4'-(propane-1,3-diyl)bis{1-(2-(dodecyloxy)-2-oxoethyl)}; 4,4'-(propane-1,3-diyl)bis{1-(2-(tetradecyloxy)-2-oxoethyl)} and 4,4'-(propane-1,3-diyl)bis{1-(2-(hexadecyloxy)-2-oxoethyl)} dipyridinium bromides. Their identifications are based on IR, ¹H-NMR, ¹³C-NMR, DEPT, COSY and Mass spectral studies. Their surface active properties were also evaluated on the basis of surface tension and conductivity measurements.

Keywords Dipyridinium gemini surfactants · Synthesis · Surface tension and conductivity

Introduction

The development of surfactants based on natural renewable resources is a concept that is gaining recognition in the cosmetic and detergent industries. A new class of gemini cationic surfactants is a response to the increasing consumer demand for the products that are both greener and more efficient. In order to achieve these objectives, it is necessary to use renewable low-cost materials that are available in large quantities and to design molecular structures that show improved performance, favorable properties and reduced environmental impact [1]. Several series of new surfactants have been designed using environmentally friendly processes and their production permits us to attain various products and by-products of the oleochemical industries or ones derived from marine resources [2, 3].

A wide range of original surfactants derived from renewable resources have been developed with potential applications notably, in detergent and cosmetic industries. The production of these entirely natural molecules may substitute the surfactants conventionally used.

Cationic surfactants, with almost 7 % of the total surfactant market, have many applications such as fabric softeners, asphalt additives, corrosion inhibitors, biocides, and textile auxiliaries. They adsorb strongly onto a wide variety of materials by an ion exchange mechanism [4–6]. However, cationic surfactants have higher aquatic toxicity than other surfactants and are also more irritating to the skin and to the eyes. The toxicity of these surfactants is believed to result from their tendency to adsorb on to negatively charged surfaces [6, 7]. Different approaches are taken to overcome this problem. One approach is to introduce an easily cleavable bond into the surfactant structure. The search for novel surfactants with higher

P. Patial · I. Ahmad (✉)
Department of Chemistry, Guru Nanak Dev University,
Amritsar 143005, India
e-mail: chemi_ahmad@yahoo.co.in

A. Shaheen (✉)
Department of Chemistry, Dr. B.R. Ambedkar National Institute
of Technology, Jalandhar, India
e-mail: chemarifa@gmail.com

efficiency and effectiveness gave birth to the concept of gemini surfactants. Gemini surfactants are made up of two monomeric surfactant molecules with their head groups chemically bonded together by a spacer [8, 9]. It was found that the surfactant properties of gemini-type surfactants, such as a low critical micelle concentration (CMC) value and surface tension lowering, were superior to those of the corresponding single-type surfactants [10–17]. Since the term was coined by Menger in 1991, many different types of gemini surfactants have been synthesized, and their physicochemical properties have been investigated [18, 19].

Keeping in view the past work and perception on cationic gemini surfactants, we have attempted to synthesize them from renewable raw materials like fatty alcohols and halo-carboxylic acids. Here we have chosen the greener approach to make the process environmentally friendly and cost effective too. The purpose of this work was to prepare and characterize the cationic gemini surfactants with ester bonds inserted between the hydrocarbon tails and the positively charged head groups and to evaluate their surface active properties.

Experimental Section

Materials, Methods and Instrumentation

Chloroacetic acid, bromoacetic acid and 4,4'-trimethylene dipyridine were purchased from Sigma-Aldrich Chemical Co. USA. Lauryl alcohol (dodecyl alcohol), Myristyl alcohol (tetradecyl alcohol), cetyl alcohol (hexadecyl alcohol) and silica gel for T.L.C. were purchased from S. D. Fine Chemicals Ltd; Mumbai, India. Sulfuric acid was purchased from Merck, Germany. IR spectra were recorded as a thin film on KBr Pellet on a Shimadzu 8,400 s FT-IR (Kyoto, Japan) instrument. Mass spectra were recorded on a Waters Q-T of Micro mass using ESI as an ion source at sophisticated analytical instrumentation facility (SAIF), Panjab University, Chandigarh. ¹H-NMR, DEPT (Distortionless enhanced polarization Transfer), COSY (correlation spectroscopy) and ¹³C-NMR spectra were recorded on a JEOL AL-300 (JEOL, Japan) and (Bruker Advance II 400 NMR spectrometer) system as a solution in CDCl₃, using tetramethylsilane (TMS) as an internal standard.

Synthesis of Dodecyl/Tetradecyl/Hexadecyl 2-Chloro/Bromo Acetate

The preparation of these esters from halogenated fatty acids has earlier been reported [20]. However, we herein report the modified procedure for their preparation with excellent yield, that too in a short time. Chloro/bromo

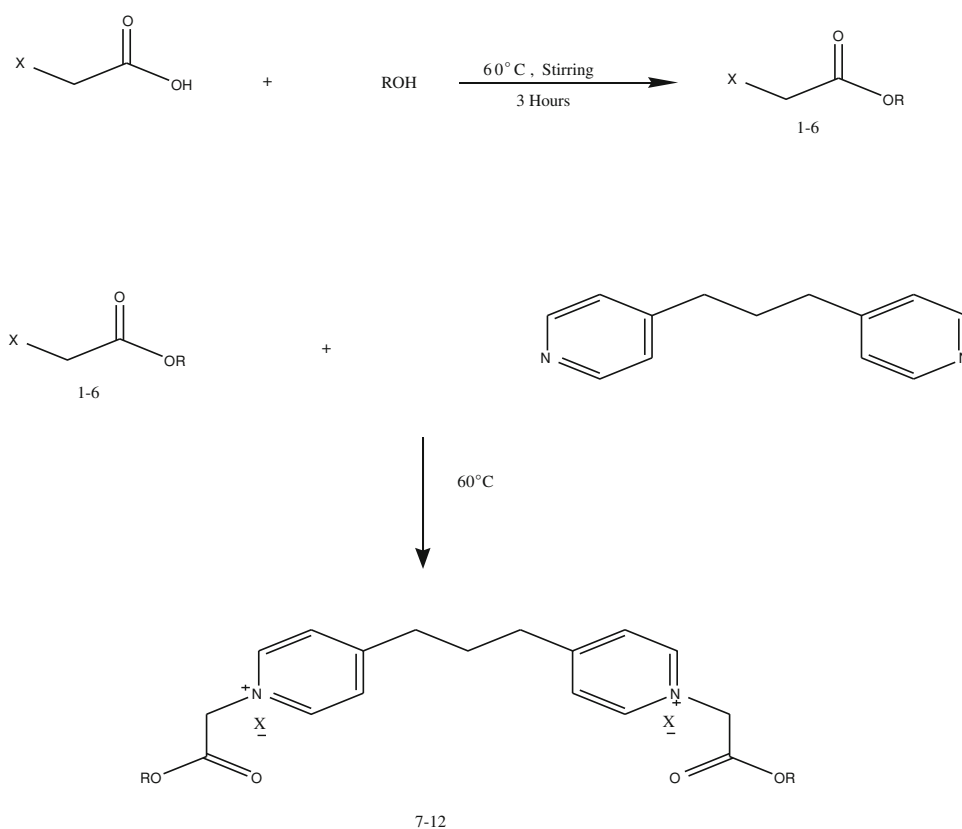
acetic acids (0.01 mol; 0.945 g for chloroacetic acid and 0.1389 g for bromo acetic acid) was added in a fatty alcohol (0.01 mol; dodecyl 1.863 g; tetradecyl 2.143 g; hexadecyl 2.422 g) followed by the addition of catalytic amount of sulfuric acid. The contents of the flask were then stirred for 2–3 h at 60 °C. The progress of the reaction was monitored by thin layer chromatography [silica gel G coated (0.25 mm thick) glass plates using hexane/ethyl acetate (98:2) as the mobile phase, the spots were visualized in iodine]. The reaction was completed in 3 h. In each case the crude reaction mixture was extracted with 50 ml of chloroform and washed repeatedly (3 × 25 ml) with water and then dried over sodium sulfate. Chloroform was removed from crude reaction mixture under reduced pressure in a rotary flash evaporator at 40 °C. The individual crude product was then purified using aqueous methanol i.e. (the crude compound was taken in a separating funnel and 10 ml of methanol was added with 2–3 drops of water which led to the settling of product at the bottom in its purest form). The yields of resulting esters are reported in parenthesis {hexadecyl-2-chloroacetate (**1**, 92 %), tetradecyl-2-chloroacetate (**2**, 92 %), dodecyl-2-chloroacetate (**3**, 91 %), hexadecyl-2-bromoacetate (**4**, 90.1 %), tetradecyl-2-bromoacetate (**5**, 94.4 %) and dodecyl-2-bromoacetate (**6**, 92 %)}.

Synthesis of Gemini Surfactants (7–12)

Each resulting ester (**1–6**) was immediately reacted with 4,4'-trimethylene dipyridine in 2:1 molar ratio (0.01 mol) at 60 °C for 1 h (for chloro esters) and 30 min (for bromo esters) i.e. for **1**, 6.378 g; for **2**, 5.817 g; for **3**, 5.256 g; for **4**, 7.267 g; for **5**, 6.706 g; for **6**, 6.145 g and 4,4'-trimethylene dipyridine (1.982 g) were taken. In each case the resulting crude product was crystallized with ether and subsequently recrystallized in cold acetone to get the pure compounds (**7–12**) which were characterized on the basis of IR, ¹H-NMR, ¹³C-NMR, COSY and DEPT experiments and mass spectral analysis as 4,4'-(propane-1,3-diyl) bis(1-(2-(hexadecyloxy)-2-oxoethyl) dipyridinium chloride (**7**); (4,4'-(propane-1,3-diyl)bis(1-(2-(tetradecyloxy)-2-oxoethyl)dipyridinium chloride (**8**); 4,4'-(propane-1,3-diyl)bis(1-(2-(dodecyloxy)-2-oxoethyl)dipyridinium chloride (**9**); 4,4'-(propane-1,3-diyl) bis(1-(2-(hexadecyloxy)-2-oxoethyl) dipyridinium bromide (**10**); 4,4'-(propane-1,3-diyl)-bis(1-(2-(tetradecyloxy)-2-oxoethyl)dipyridinium bromide (**11**) and 4,4'-(propane-1,3-diyl)bis(1-(2-dodecyloxy)-2-oxoethyl)dipyridinium bromide (**12**) (Scheme 1).

Conductivity Measurements [21, 22]

The critical micelle concentrations (CMC) of these surfactants (**7–12**) were determined by the conductivity

Scheme 1 Scheme of reactions

method. The conductance as a function of surfactant concentration was measured at 25 °C. Measurements were performed with an Equiptronic Conductometer (Auto temperature conductivity meter model E.Q.661) with stirring to control the temperature. The solutions were thermostated in the cell at 25 °C. For each series of measurements, an exact volume of 25 ml Millipore water (resistivity 18 MΩ) was introduced into the vessel and the specific conductivity of the water was measured. For the determination of CMC, adequate quantities of concentrated stock surfactant solutions in water (i.e. 0.25, 2, 3, 0.25, 2 and 3 mM for surfactants **7**, **8**, **9**, **10**, **11** and **12**, respectively) were added in order to change the surfactant concentration from concentrations well below the critical micelle concentration (CMC) and repeated to verify our results. The intersection point of specific conductivity versus surfactant concentration was taken as the CMC. The degree of counterion binding (β) was calculated as $(1-\alpha)$, where $\alpha = S_{micellar}/S_{premicellar}$, i.e. ratio of the slope before and after CMC.

Surface Tension Measurements

Surface tension values were used to calculate CMC using a CSC Du Nouy interfacial tensiometer (Central Scientific Co., Inc.) equipped with platinum-iridium ring

(circumference 5.992 cm) at 25 °C. The tensiometer was calibrated using triple distilled water. For the determination of CMC and surface tension, adequate quantities of a concentrated stock solution (i.e. 0.25, 2, 3, 0.25, 2 and 3 mM, stock solution for surfactants **7**, **8**, **9**, **10**, **11** and **12**, respectively) were used. The data of this determination is presented in Table 1.

Where $X = \text{Cl}, \text{Br}$ and $R = \text{CH}_3(\text{CH}_2)_{11}-; \text{CH}_3(\text{CH}_2)_{13}-$ and $\text{CH}_3(\text{CH}_2)_{15}-$.

Results and Discussion

The structures of ester based gemini pyridinium surfactants (**7–12**) were established by IR, ¹H-NMR, ¹³C-NMR, COSY, DEPT and mass spectral data.

Spectral Results

The IR spectra of the pyridinium gemini surfactants (**7–12**) showed the absorption bands in the region at 2,915–2,849 cm⁻¹ indicating the presence of methylene groups. The absorptions at 1,741–1,730 cm⁻¹ indicate the presence of ester carbonyl group whereas other absorptions at 1,641–1,620 cm⁻¹ indicate the presence of C–N. The band at 1,570–1,540 cm⁻¹ very well established the

Table 1 Data reporting the CMC values by conductivity and surface tension measurements, degree of counter ion binding and surface tension at CMC at 25 °C

S. no.	CMC (mM) by conductivity measurements	The degree of counter ion binding (β) (%)	CMC by surface tension measurements in (mM)	Surface tension at CMC (mN/m)
7	0.059	36	0.057	62.4
8	0.144	42	0.105	58.8
9	0.359	56	0.381	40.8
10	0.036	50	0.035	68.4
11	0.121	53	0.085	60.1
12	0.172	59	0.167	58.7

presence of aromatic C=C in (7–12). The two terminal methyl protons of these gemini surfactants (7–12) are observed as a distorted triplet at δ 0.61–0.87 in their ^1H NMR spectra. Broad doublets in (7–12) are observed at δ 1.07–1.26 accountable for methylene protons of chain. Multiplet signals are observed at δ 1.29–1.65 due to presence of methylene protons next to terminal methyl groups. Multiplets are observed at δ 1.48–2.17 due to sandwiched methylene protons of spacer ($\text{PyCH}_2\text{CH}_2\text{CH}_2\text{Py}$). Triplets of a second type are observed at 2.67–2.99 due to α methylene proton of the spacer ($\text{PyCH}_2\text{CH}_2\text{CH}_2\text{Py}$). Triplets of a third type are observed at δ 4.01–4.21 due to α methylene proton. A doublet is observed at δ 5.84–6.04 due to methylene protons attached to nitrogen of pyridine. The two sets of ring protons of pyridine methine are observed as a doublet at δ 7.88–8.04 and δ 8.97–9.12. $^{13}\text{C}/\text{DEPT}$ NMR spectra displayed sp^3 carbon of terminal methyl group at δ 14.00–14.08. The carbons next to terminal methyl groups are observed in the range of δ 22.58–22.66. The carbons ($\text{COOCH}_2\text{CH}_2$) are observed at 25.63–25.69. The middle carbon of spacer i.e. ($\text{PyCH}_2\text{CH}_2\text{CH}_2\text{Py}$) is observed at 28.31–28.35. The chain carbons are observed at 29.10–29.90. The methylene carbons i.e. ($\text{CH}_2\text{CH}_2\text{CH}_3$) are observed at 31.83–31.89. The α methylene carbons of spacer i.e. ($\text{PyCH}_2\text{CH}_2\text{CH}_2\text{Py}$) are observed at 34.89–35.00. The methylene carbons attached to pyridine nitrogen are observed at δ 60.36–60.58. Other signals are observed at δ 67.26–67.35 due to methylene carbons α to carbonyl groups. Other structure revealing signals are observed at δ 127.78–127.90 due to ring carbons located β to nitrogen of pyridine. Other structure revealing signals are observed at δ 145.96–146.15 due to quaternary carbon joined to the methylene group of the spacer. More significant signals are observed at δ 162.74–162.85 due to ring carbons attached α to nitrogen of pyridine. The carbonyl carbons are observed at δ 166.61–166.78. All these data are in almost comparable with the previous report [23]. On all these accounts the structures of (7–12) are deduced as 4,4'-(propane-1,3-diyl)bis(1-(2-(hexadecyloxy)-2-oxoethyl)dipyridinium chloride (7); (4,4'-(propane-1,3-diyl)bis(1-(2-(tetradecyloxy)-2-oxoethyl)dipyridinium chloride (8); 4,4'-(propane-1,3-diyl)bis(1-(2-(dodecyloxy)-2-

oxoethyl)dipyridinium chloride (9); 4,4'-(propane-1,3-diyl)bis(1-(2-(hexadecyloxy)-2-oxoethyl)dipyridinium bromide (10); 4,4'-(propane-1,3-diyl)bis(1-(2-(tetradecyloxy)-2-oxoethyl)dipyridinium bromide (11) and 4,4'-(propane-1,3-diyl)bis(1-(2-(dodecyloxy)-2-oxoethyl)dipyridinium bromide (12). The structures of these gemini surfactants (7–12) are further consolidated by ESI-MS (positive ion) mass spectral data. Important peaks in these spectra are found at m/z 763.3, 764.4, 765.5, 707.4, 708.4, 651, 652.4, 763.3, 764.4, 765.5, 707.4, 708.4, 651, 652.4. These ion peaks account for the loss of proton and two chloride/bromide ions from the molecule leading to the formation of positively charged parent ion $\{\text{M}-2\text{Cl}-1\}^+/\{\text{M}-2\text{Br}-1\}^+$ and direct loss of two chloride/bromide ions from the molecule leading to the formation of $(\text{M}-2\text{Cl})^+ / (\text{M}-2\text{Br})^+$ positively charged ions.

(4,4'-(Propane-1,3-diyl)bis(1-(2-(hexadecyloxy)-2-oxoethyl)dipyridinium chloride(7). Brown solid, Yield is 92 %. Melting point 128 °C. IR (KBr pellet, cm^{-1}) 2,910, 1,744, 1,643, and 1,570. ^1H NMR (δ ppm CDCl_3): 0.67 (t, 6H, 2XCH_3), 1.07 (d, chain 56H, $2\text{X}(-\text{CH}_2-)_{14}$), 1.46(m, 4H, 2XCH_2 next to terminal methyl groups), 1.48 (m, 2H, $\text{PyCH}_2\text{CH}_2\text{CH}_2\text{Py}$), 2.82 (t, 4H, $\text{PyCH}_2\text{CH}_2\text{CH}_2\text{Py}$), 4.01 (t, 4H $2\text{XCO}_2\text{CH}_2$), 5.84(d, 4H, $2\text{XNCH}_2\text{CO}_2$), 7.88 (d, 4H, 4XCH ring protons β to nitrogen of pyridine), 8.97 (d, 4H, 4XCH ring protons α to nitrogen of pyridine). 75 MHz $^{13}\text{C}/\text{DEPT}$ NMR (δ ppm CDCl_3): 14.05(terminal methyl carbons), 22.63(CH_3CH_2), 25.67($\text{CH}_2\text{CH}_2\text{CO}_2$), 28.33 ($\text{PyCH}_2\text{CH}_2\text{CH}_2\text{Py}$), 29.31(chain methylene carbons), 31.86($\text{CH}_2\text{CH}_2\text{CH}_3$), 34.99($\text{PyCH}_2\text{CH}_2\text{CH}_2\text{Py}$), 60.36(CH_2CO_2), 67.26(CO_2CH_2), 127.79 (methine carbon β to nitrogen of pyridine), 145.96 (quaternary carbon of pyridine nucleus bearing spacer), 162.74 (methine carbon α to nitrogen of pyridine), 166.61(carbonyl carbon). ESI-MS positive ions m/z 763.3(100 %) $\{\text{M}-2\text{Cl}-1\}^+$, 764.4 (90 %) $(\text{M}-2\text{Cl})^+$.

(4,4'-(Propane-1,3-diyl)bis(1-(2-(tetradecyloxy)-2-oxoethyl)dipyridinium chloride (8). Brown solid, Yield, 95.5 %. Melting point 122 °C. IR (KBr pellet, cm^{-1}) 2871, 1743, 1643, and 1570. ^1H NMR (δ ppm CDCl_3): 0.87 (t, 6H, 2XCH_3), 1.26 (d, chain 48H, $2\text{X}(-\text{CH}_2-)_{12}$), 1.65 (m, 4H, 2XCH_2 next to terminal methyl groups), 1.99 (m, 2H,

PyCH₂CH₂CH₂Py), 2.97 (t, 4H, PyCH₂CH₂CH₂Py), 4.19 (t, 4H, 2XCO₂CH₂), 6.04 (d, 4H, 2XCH₂CO₂), 7.96 (d, 4H, 4XCH ring protons β to nitrogen of pyridine), 9.12 (d, 4H, 4XCH ring protons α to nitrogen of pyridine). 75 MHz ¹³C/DEPT NMR (δ ppm CDCl₃): 14.05 (terminal methyl carbons), 22.63 (CH₃CH₂), 25.67 (CH₂CH₂CO₂), 28.35 (PyCH₂CH₂CH₂Py), 29.31 (chain methylene carbons), 31.87 (CH₂CH₂CH₃), 34.89 (PyCH₂CH₂CH₂Py), 60.39 (CH₂CO₂), 67.24 (CO₂CH₂), 127.89 (methine carbon β to nitrogen of pyridine), 145.85 (quaternary carbon of pyridine nucleus bearing spacer), 162.87 (methine carbon α to nitrogen of pyridine), 166.66 (carbonyl carbon). ESI-MS positive ions *m/z* 707.4 (100 %) {(M-2Cl)-1}⁺, 708.4 (51 %) (M-2Cl)⁺.

4,4'-(Propane-1,3-diyl)bis(1-(2-(dodecyloxy)-2-oxoethyl)dipyridinium chloride (**9**): Brown sticky solid, Yield, 92.5 %. Melting point 117 °C. The IR (KBr Pellet, cm⁻¹): 2915, 1746, 1639, and 1570. ¹H NMR (δ ppm, CDCl₃): 0.61 (t, 6H, 2XCH₃), 1.10 (d, chain 40H, 2X(-CH₂-)₁₀), 1.29 (m, 4H, 2XCH₂ next to terminal methyl groups), 1.69 (m, 2H, PyCH₂CH₂CH₂Py), 2.67 (t, 4H, PyCH₂CH₂CH₂Py), 4.19 (t, 4H, 2XCO₂CH₂), 5.92 (d, 4H, 2XCH₂CO₂), 7.75 (d, 4H, 4XCH ring protons β to nitrogen of pyridine), 8.98 (d, 4H, 4XCH ring protons α to nitrogen of pyridine). 75 MHz ¹³C/DEPT NMR (δ ppm, CDCl₃): 14.08 (terminal methyl carbons), 22.66 (CH₃CH₂), 25.69 (CH₂CH₂CO₂), 28.34 (PyCH₂CH₂CH₂Py), 29.33 (chain methylene carbons), 31.89 (CH₂CH₂CH₃), 34.95 (PyCH₂CH₂CH₂Py), 60.40 (CH₂CO₂), 67.30 (CO₂CH₂), 127.78 (methine carbon β to nitrogen of pyridine), 146.01 (quaternary carbon of pyridine nucleus bearing spacer), 162.68 (methine carbon α to nitrogen of pyridine), 166.62 (carbonyl carbon). ESI-MS positive ions at *m/z* (relative intensity %) 651.4 (100 %) {(M-2Cl)-1}⁺, 652.4 (60 %) (M-2Cl)⁺.

(4,4'-(Propane-1,3-diyl)bis(1-(2-(hexadecyloxy)-2-oxoethyl)dipyridinium bromide (**10**). Brown solid, Yield, 95.5 %. Melting point 145 °C, IR (KBr pellet, cm⁻¹) 2870, 1741, 1641, 1570 and 1514. ¹H NMR (δ ppm CDCl₃): 0.79 (t, 6H, 2XCH₃), 1.20 (d, chain 56H, 2X(-CH₂-)₁₄), 1.57 (m, 4H, 2XCH₂ next to terminal carbons), 1.82 (m, 2H, PyCH₂CH₂CH₂Py), 2.83 (t, 4H, PyCH₂CH₂CH₂Py), 4.11 (t, 4H, 2XCO₂CH₂), 5.98 (d, 4H, 2XCH₂CO₂), 7.93 (d, 4H, 4XCH ring protons β to nitrogen of pyridine), 9.06 (d, 4H, 4XCH ring protons α to nitrogen of pyridine). 75MHz ¹³C/DEPTNMR (δ ppm CDCl₃): 14.01 (terminal methyl carbons), 22.58 (CH₃CH₂), 25.63 (CH₂CH₂CO₂), 28.31 (PyCH₂CH₂CH₂Py), 29.46 (chain methylene carbons), 31.83 (CH₂CH₂CH₃), 34.91 (PyCH₂CH₂CH₂Py), 60.50 (CH₂CO₂), 67.36 (CO₂CH₂), 127.88 (methine carbon β to nitrogen of pyridine), 145.70 (quaternary carbon of pyridine nucleus bearing spacer), 163.05 (methine carbon α to nitrogen of pyridine), 166.23 (carbonyl carbon). ESI-MS

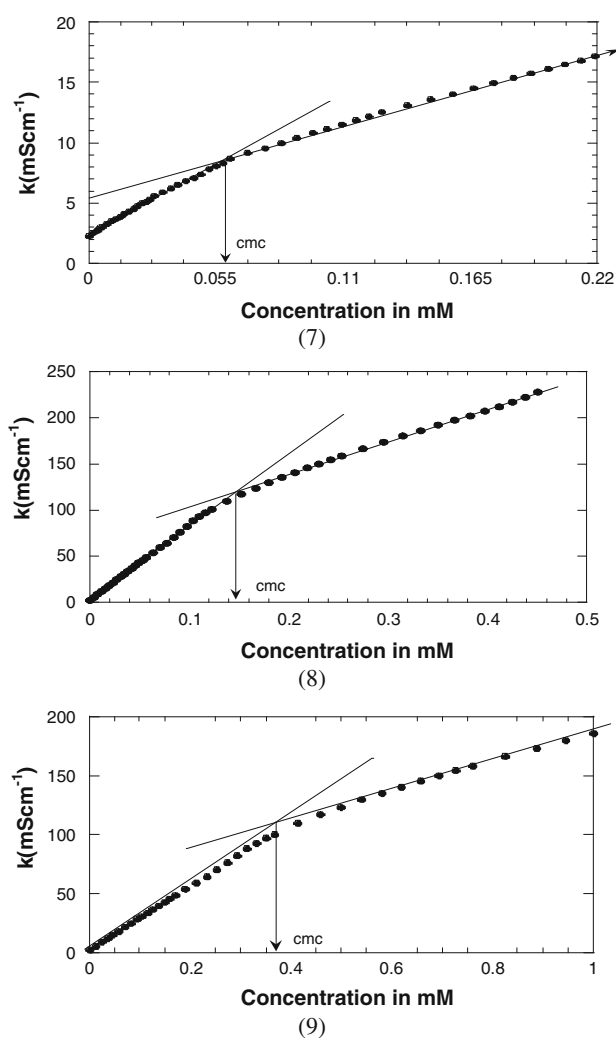


Fig. 1 Specific conductivity versus concentration plot of gemini surfactants **7**, **8** and **9**

Positive ions *m/z* 763.3 (20 %) {(M-2Br)-1}⁺, 764.4 (10 %) (M-2Br)⁺.

(4,4'-(Propane-1,3-diyl)bis(1-(2-(tetradecyloxy)-2-oxoethyl)dipyridinium bromide (**11**). Brown solid, Yield 93.4 %, Melting point 139 °C. IR (KBr pellet, cm⁻¹) 2,860, 1,742, 1,642 and 1,560. ¹H NMR (δ ppm CDCl₃): 0.87 (t, 6H, 2XCH₃), 1.26 (d, chain 48H, 2X(-CH₂-)₁₂), 1.64 (m, 4H, 2XCH₂ next to terminal methyl groups), 2.17 (m, 2H, PyCH₂CH₂CH₂Py), 2.99 (t, 4H, PyCH₂CH₂CH₂Py), 4.21 (t, 4H, 2XCO₂CH₂), 6.01 (d, 4H, 2XCH₂CO₂), 8.04 (d, 4H, 4XCH ring protons β to nitrogen of pyridine), 9.12 (d, 4H, 4XCH ring protons α to nitrogen of pyridine). 75 MHz ¹³C/DEPT NMR (δ ppm CDCl₃): 14.06 (terminal methyl carbons), 22.64 (CH₃CH₂), 25.68 (CH₂CH₂CO₂), 28.35 (PyCH₂CH₂CH₂Py), 29.21 (chain methylene carbons), 31.87 (CH₂CH₂CH₃), 35.01 (PyCH₂CH₂CH₂Py), 60.55 (CH₂CO₂), 67.43 (CO₂CH₂), 127.90 (methine carbon β to nitrogen of pyridine), 145.79

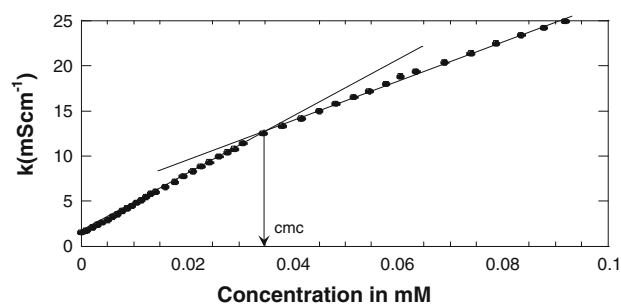
(quaternary carbon of pyridine nucleus bearing spacer), 163.01 (methine carbon α to nitrogen of pyridine), 166.25 (carbonyl carbon). ESI-MS positive ions m/z 707.4 (100 %) $\{(M-2Br-1)\}^+$ 708.4 (40 %) $(M-2Br)^+$.

(4,4'-(Propane-1,3-diyl)bis(1-(2-(dodecyloxy)-2-oxoethyl)dipyridinium bromide (**12**). Brown sticky solid, Yield 93.4 %, Melting point 131 °C. IR (KBr pellet, cm^{-1}) 2910, 1746, 1640 and 1574. ^1H NMR (δ ppm CDCl_3): 0.68 (t, 6H, 2XCH_3), 1.09 (d, chain 40H, $2\text{X}(-\text{CH}_2-)_{10}$), 1.49 (m, 4H, 2XCH_2 next to terminal methyl groups), 1.83 (m, 2H, $\text{PyCH}_2\text{CH}_2\text{CH}_2\text{Py}$), 2.72 (t, 4H, $\text{PyCH}_2\text{CH}_2\text{CH}_2\text{Py}$), 4.02 (t, 4H, $2\text{XCO}_2\text{CH}_2$), 5.94 (d, 4H, $2\text{XCH}_2\text{CO}_2$), 7.87 (d, 4H, 4XCH ring protons β to nitrogen of pyridine), 9.01 (d, 4H, 4XCH ring protons α to nitrogen of pyridine) 0.75 MHz $^{13}\text{C}/\text{DEPT}$ NMR (δ ppm CDCl_3): 14.05 (terminal methyl carbons), 22.63 (CH_3CH_2), 25.67 ($\text{CH}_2\text{CH}_2\text{CO}_2$), 28.34 ($\text{PyCH}_2\text{CH}_2\text{CH}_2\text{Py}$), 29.30 (chain methylene carbons), 31.86 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 34.98 ($\text{PyCH}_2\text{CH}_2\text{CH}_2\text{Py}$), 60.52

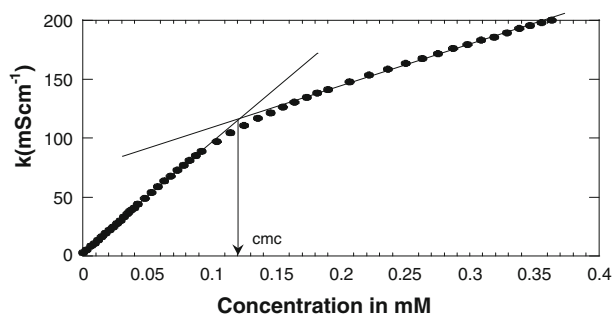
(CH_2CO_2), 67.41 (CO_2CH_2), 127.89 (methine carbon β to nitrogen of pyridine), 145.76 (quaternary carbon of pyridine nucleus bearing spacer), 163.01 (methine carbon α to nitrogen of pyridine), 166.24 (carbonyl carbon). ESI-MS positive ions m/z 651.4 (50 %) $\{(M-2Br-1)\}^+$, 652.4 (40 %) $(M-2Br)^+$.

Critical Micelle Concentration

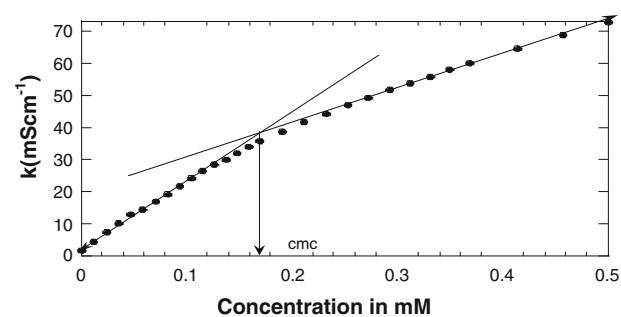
Gemini surfactants have astonishingly low CMC values, much lower than the corresponding single tail surfactants [24]. Only a few reports are available regarding synthesis and CMC values of gemini pyridinium surfactants [25, 26]. Critical micelle concentration and the degree of counter ion binding of these new pyridinium amphiphiles have been determined by the conductivity method. These new gemini pyridinium amphiphiles have low CMC values. It has been found that the CMC of these gemini amphiphiles decreases



(10)

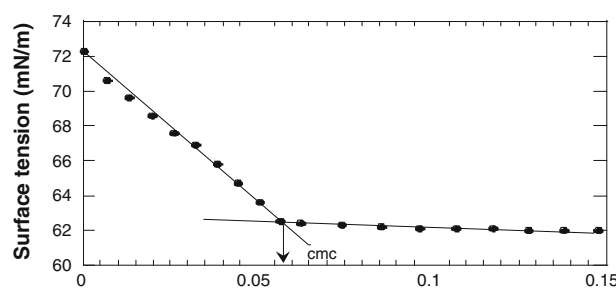


(11)

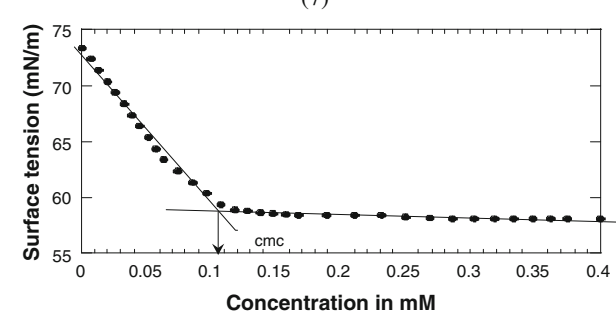


(12)

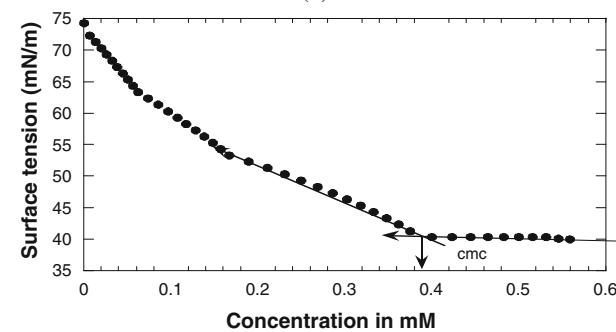
Fig. 2 Specific conductivity versus concentration plot of gemini surfactants **10**, **11** and **12**



(7)



(8)



(9)

Fig. 3 Plot of surface tension versus surfactant concentration of gemini surfactants **7**, **8** and **9**

with increasing chain length. The values of CMC and degrees of counter ion binding are given in Table 1. The graphs of the specific conductivity versus concentration have been plotted (Figs. 1, 2). It is found that the pyridinium gemini surfactants with bromine as a counter ion have low values of CMC as compared to the pyridinium gemini surfactants with chlorine as a counter ion [27].

The Degree of Counterion Binding (β)

The ratio of the slopes of the specific conductivity versus concentration curve above and below CMC gives degree of counterion dissociation α (i.e. $\alpha = S_{micellar}/S_{premicellar}$) and $(1-\alpha)$ gives the degree of counterion binding, β . It is an important parameter because it manifests the counterions that are contained in the Stern layer to counterbalance

the electrostatic force that opposes micelle formation. Quagliotto et al. [22] determined the β value for a series of gemini bispyridinium bromides having different spacers where they had shown that a different spacer is responsible for a different β value. The β value signifies the ability of counter ion to bind micelles. We, in our study, on new series of gemini pyridinium surfactants (7–12), have found that the β value decreases with increases in hydrophobicity [22].

Surface Tension Measurements

The CMC of new pyridinium gemini surfactants were calculated by using surface tension measurements. The graphs of the surface tension versus concentration are shown for gemini surfactants (7–12). A clear break is observed in all the pyridinium gemini surfactants (Figs. 3, 4). It is observed from the graphs that pyridinium gemini surfactants having bromine as a counter ion have low CMC values as compared to the pyridinium gemini surfactants having chlorine as a counter ion. The CMC values are reported in Table 1 for all the gemini surfactants. The values of CMC found by both the conductivity method and surface tension method correspond well with each other.

Conclusions

In the present study we have described a new protocol for the synthesis of six new ester based cationic gemini pyridinium surfactants starting from renewable long chain fatty alcohols through an environmentally friendly, energy saving and cost effective process. All the gemini cationic surfactants (7–12) are produced in excellent yields and these surfactants have been examined and are found to have good surface active properties. The results show that gemini pyridinium surfactants with longer hydrophobic chains have lower CMC values than those with shorter hydrophobic chains. Also it is found that gemini surfactants having bromine as a counter ion have lower CMC values as compared to gemini surfactants having chlorine as a counter ion. In a previous report [28] ester-containing gemini surfactants are more readily degradable than their non-ester counterparts. In addition, pyridinium cationic gemini surfactants may show good antimicrobial properties, DNA binding capability if tested properly.

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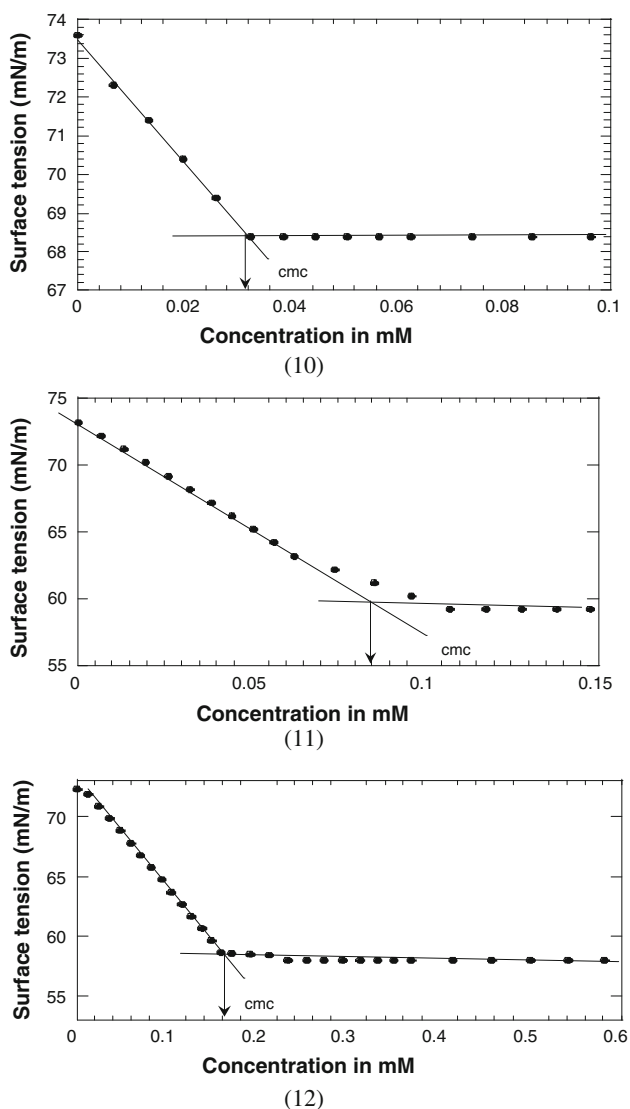


Fig. 4 Plot of surface tension versus surfactant concentration of gemini surfactants 10, 11 and 12

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Author Biographies

Pankaj Patial obtained his M.Sc. degree in Industrial Chemistry in 2008 from Guru Nanak Dev University, Amritsar, India. He is currently working on his Ph.D. in the field of Surfactant Chemistry from Guru Nanak Dev University, Amritsar, India.

Arifa Shaheen obtained her Ph.D. in Analytical Chemistry in 2009 from Guru Nanak Dev University, Amritsar, India. She is currently working as an Assistant Professor in Department of Chemistry at Dr. B.R. Ambedkar National Institute of Technology, Jalandhar, India.

Ishtiaque Ahmad obtained his Ph.D. degree in Organic Chemistry in 1979 from Aligarh Muslim University, Aligarh, India. He retired in 2010 as Professor in Chemistry from Guru Nanak Dev University, Amritsar, India. Currently he is the Principal of Shiv Shankar Institute of Engineering and Technology, Patti, India.