

# Novel Ester-linked Anionic Gemini Surfactant: Synthesis, Surface-Active Properties and Antimicrobial Study

Manisha B. Ahire<sup>1</sup> · Sunil S. Bhagwat<sup>1</sup>

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**Abstract** A novel anionic gemini surfactant containing an ester bond in the spacer group was synthesized using cardanol as the raw material and characterized by IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR. The surface properties of the gemini surfactant were investigated and compared with its corresponding single chain surfactant counterpart. It was found that this novel gemini surfactant exhibited a low critical micelle concentration value (1.9 mM) and good efficiency in reducing surface tension of water (33.6 mN/m). The gemini surfactant was found to have antimicrobial activity against Gram-negative (*Escherichia coli* and *Pseudomonas aeruginosa*), Gram-positive (*Bacillus subtilis* and *Staphylococcus aureus*) bacteria and fungi (*Aspergillus niger*, *Aspergillus flavus*, *Candida albicans* and *Rhizopus stolonifer*). The gemini as well as the corresponding single chain surfactant showed good antimicrobial activity against all pathogenic microorganisms studied and can be employed as an antimicrobial agent. The synthesized novel anionic gemini surfactant possesses an excellent wettability and low foamability.

**Keywords** Anionic gemini surfactant · Synthesis · Cardanol · Critical micelle concentration · Wetting agent · Antimicrobial activity

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✉ Sunil S. Bhagwat  
ss.bhagwat@ictmumbai.edu.in

<sup>1</sup> Department of Chemical Engineering, Institute of Chemical Technology, Matunga, Mumbai 400 019, India

## Abbreviations

CMC	Critical micelle concentration (mM)
CSMS	Cardanol sulfonate monomeric surfactant
CSGS	Cardanol sulfonate gemini surfactant
SDBS	Sodium dodecyl benzene sulphonic acid
CTAB	Cetyl trimethyl ammonium bromide
TLC	Thin layer chromatography
<sup>13</sup> C NMR	Carbon nuclear magnetic resonance
<sup>1</sup> H NMR	Proton nuclear magnetic resonance
D <sub>2</sub> O	Deuterated water
DMSO-d <sub>6</sub>	Hexadeuterated dimethyl sulfoxide
CDCl <sub>3</sub>	Deuterated chloroform
IR	Infrared spectrometry
GC–MS	Gas chromatography mass spectroscopy

## List of symbols

$\gamma$	Surface tension (mN/m)
$\gamma_{CMC}$	Surface tension at CMC (mN/m)
$\Gamma_{max}$	Maximum surface excess concentration (mol/cm <sup>2</sup> )
$A_{min}$	Minimum surface area per molecule (nm <sup>2</sup> )
$C_{20}$	Concentration of surfactant required to reduce surface tension by 20 mN/m
$\lambda_{max}$	Wavelength maximum (nm)
$\beta_{cb}$	Counterion binding coefficient
$\alpha_{cb}$	Counterion dissociation coefficient
$\theta$	Contact angle (°)
$R$	Universal gas constant
$T$	Absolute temperature
$N_A$	Avogadro's number (6.022 × 10 <sup>23</sup> mol <sup>-1</sup> )

## Introduction

Gemini surfactants (dimer) are a new class of surfactants composed of two monomeric surfactant molecules chemically bonded together by a spacer at or near their head groups. The spacer can be hydrophobic or hydrophilic, flexible (alkyl or ether group) or rigid (aromatic moieties) in nature [1, 2]. Compared with conventional surfactants, gemini surfactants have much lower critical micelle concentrations (CMC), greater efficiency in decreasing surface tension and excellent wetting properties [3, 4]. These surfactants often possess better foaming, aggregation and rheological properties at low concentration. Geminis are known to have numerous applications such as solubilizing agents, antifoaming agents, emulsifiers, bactericidal agents, dispersants, detergents, etc. [5, 6]. Gemini surfactants invite attention for cosmetics and toiletries especially in shampoo and personal care products, because of their mildness, soft feeling and low skin irritation [7]. Gemini Surfactants are markedly more surface-active than their comparable conventional surfactants. Their outstanding physico-chemical properties and widespread applications have attracted chemists in search of new surfactants.

Gemini surfactants with enhanced wetting properties play an important role in personal care products, textiles, oil industry, paper industry, pesticide or herbicide formulations, paints and coatings. Anionic surfactants are often used as wetting agents in commercial applications [8, 9]. Amphiphilic compounds having dimeric moieties are well-known and effective antimicrobial agents [4].

Owing to environmental concern, it is essential to design biocompatible surfactants containing biodegradable functionalities such as ester and amide groups that can be easily degraded after use. Several investigations have recommended that surfactants containing ester bonds show good biodegradability as the polar bond contributes to the high water solubility. Therefore, readily cleavable gemini surfactants are more suitable for use compared to conventional surfactants. Although many chemists have reported studies of gemini or cleavable surfactants, only limited information is available regarding cleavable gemini surfactants [10–14].

Cashew nut shell liquid (CNSL) is a reddish brown colored, viscous, poisonous liquid obtained as a by-product from the extraction of cashew nut shells. Cardanol and anacardic acid are the major phenolic constituents present in natural CNSL (*Anacardium occidentale* species). Cardanol is a low cost, eco-friendly and biodegradable renewable biomass resource. It is a mixture of four different meta-alkyl phenols differing in the degree of unsaturation in the side chain: 5% saturated [3-(pentadecyl)-phenol], 49% monoene [3-(8Z-pentadecenyl)-phenol], 17% diene [3-(8Z,11Z-pentadecadienyl)-phenol] and 29%

triene [3-(8Z,11Z,14-pentadecatrienyl)-phenol]. It has both the characteristics of phenolic compounds and flexibility of aliphatic compounds and is widely used as raw material in polymer, adhesives, coatings and composite manufacturing industries [15–17]. Recently, many surfactants with high surface activity have been synthesized using cardanol. There are numerous reports published on monomeric surfactants prepared from cardanol, however, there are few reports on cardanol-based gemini surfactants [18]. This is the first report on an ester-linked anionic gemini surfactant with cardanol as starting material.

In the present study, a cardanol-based novel anionic gemini surfactant containing an ester linkage in the spacer group has been synthesized (Fig. 2) and its structure confirmed by TLC, IR,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR. The surface properties such as critical micelle concentration (CMC), surface tension, foam power and wettability were investigated. Also, the antimicrobial activity of newly synthesized anionic gemini surfactant against pathogenic bacteria and fungi are reported. The values obtained were compared with its corresponding monomeric surfactant.

## Experimental Section

### Materials and Methods

Cardanol (3-pentadecyl phenol) was obtained from the South Asia Cashew Corporation, Goa, India and vacuum distilled (at  $225 \pm 4$  °C, 0.005 mm Hg) before use. Adipic acid, chlorosulfuric acid, Sudan IV (M. S) dye, sulfuric acid, sodium hydroxide and sodium carbonate were of analytical reagent grade, purchased from S. D. Fine Chemicals Limited, India. All the solvents were of analytical reagent grade and used without further purification. Distilled water (conductance = 0.005 mS/cm) was employed in all experiments. Deuterated solvents such as  $\text{CDCl}_3$ ,  $\text{D}_2\text{O}$  and  $\text{DMSO-d}_6$  were purchased from Sigma Aldrich, India. A UV–Visible spectrophotometer (Agilent technologies Model-8453, India) was used for measurement of dye absorption spectra.

The structure of synthesized cardanol sulfonate monomer and novel ester-linked gemini surfactant were confirmed by using IR spectrometry (Bruker FTIR spectrometer),  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR (Agilent Technologies, 500 MHz). The two amphiphiles synthesized were designated as CSMS and CSGS.

### Synthesis of Cardanol Sulfonate Monomeric Surfactant (CSMS)

The schematic route for synthesis of amphiphile CSMS is shown in Fig. 1. Cardanol (12.4 mmol in 25 ml

dichloromethane) was charged to a three-necked round-bottom reaction kettle equipped with a water condenser and the solution was cooled in an ice bath to 0–5 °C. To this solution, chlorosulfuric acid (42.9 mmol) was added dropwise over a period of 1 h. The reaction mass was stirred for 3 h at room temperature [19]. The dichloromethane was separated from the reaction mass and the product was neutralized with ice cold 20% NaOH to pH = 8. The product obtained was washed with excess hexane and extracted with methanol, dried over anhydrous sodium sulfate and the solvent was evaporated using a rotary evaporator. The yield of the isolated product was 87%.

### Synthesis of Novel Ester-linked Cardanol Sulfonate Gemini Surfactant (CSGS)

The synthesis of the cardanol sulfonate gemini surfactant containing ester linkage in spacer group was carried out using a two-step procedure and the reaction steps used are summarized in Fig. 2.

In a typical experiment, a three-necked round-bottom reaction kettle fitted with a mechanical stirrer, Dean-Stark trap with water condenser and dropping funnel was charged with 20 mmol adipic acid and 40 mmol of concentrated sulfuric acid in toluene. The reaction mixture was refluxed for 10 min at 150–160 °C until the complete dissolution of the adipic acid. The reaction mass was cooled to room temperature before addition of cardanol (40 mmol), dissolved in 25 ml toluene. The reaction mass was refluxed at 110–115 °C for 6 h till the complete removal of water. The product was washed with excess hexane to remove unreacted cardanol and extracted with ethyl acetate, dried over anhydrous sodium sulfate and the solvent was evaporated using a rotary evaporator. The isolated product was further purified with a silica gel column and elution with hexane/ethyl acetate. The yield of the isolated product was 78%.

The cardanol gemini ester (4.2 mmol in 15 ml dichloromethane) prepared in the first step was charged into a three-necked round-bottom reaction kettle and stirred at 0–5 °C for 10 min. To this solution, chlorosulfuric acid

(25.2 mmol) was added dropwise over 30 min. The reaction mass was stirred for 3 h at room temperature. The dichloromethane containing an excess of unreacted sulfuric acid was separated from the reaction mass. The product obtained was neutralized with ice cold 10% Na<sub>2</sub>CO<sub>3</sub> to pH = 8. The neutralization reaction was carried out for an hour at room temperature. The product obtained was washed with excess hexane and extracted with methanol. The organic layer was concentrated using a rotary evaporator. The yield of the isolated product was 80%.

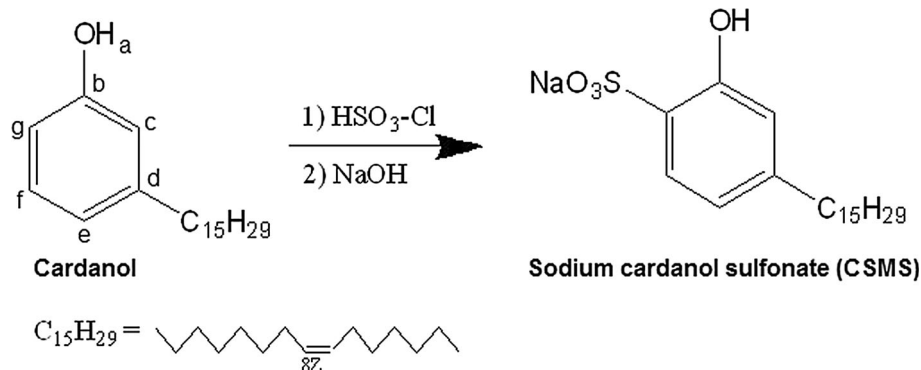
### Chemical Analysis

Cardanol—pale lemon color, liquid, FTIR—wavelength (cm<sup>-1</sup>) = 3341.9 (O–H, phenolic compound), 3006.29 (=C–H, aromatic ring), 2922.9 and 2852.88 (–C–H, aliphatic chain), 1588.69 (C=C, long aliphatic chain), 1455.32 (C=C, aromatic), 1263.1–1072.82 (C–O, phenol). GC–MS (*m/z*, relative intensity %) = 302.28 (*M*, 18), 206.18 (4), 161.11 (4), 133.09 (12), 120 (44), 108 (100), 91 (20), 77 (46), 55 (54). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS) δ ppm = 6.65 (2H, d, Ar–H<sub>c,g</sub>), 6.76 (1H, Ar–H<sub>e</sub>), 7.13 (1H, t, Ar–H<sub>f</sub>), 5.28 (1H, s, Ar–OH<sub>a</sub>), 4.89–5.42 (4H, m, side chain HC=CH), 0.90–2.79 (27H, alkyl side chain proton). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>, TMS) δ ppm = 155.4 (ArC–OH), 144.9 (ArC–alkyl chain), 112.45–130.22 (C=C, Ar and aliphatic chain), 13.80–35.8 (aliphatic chain).

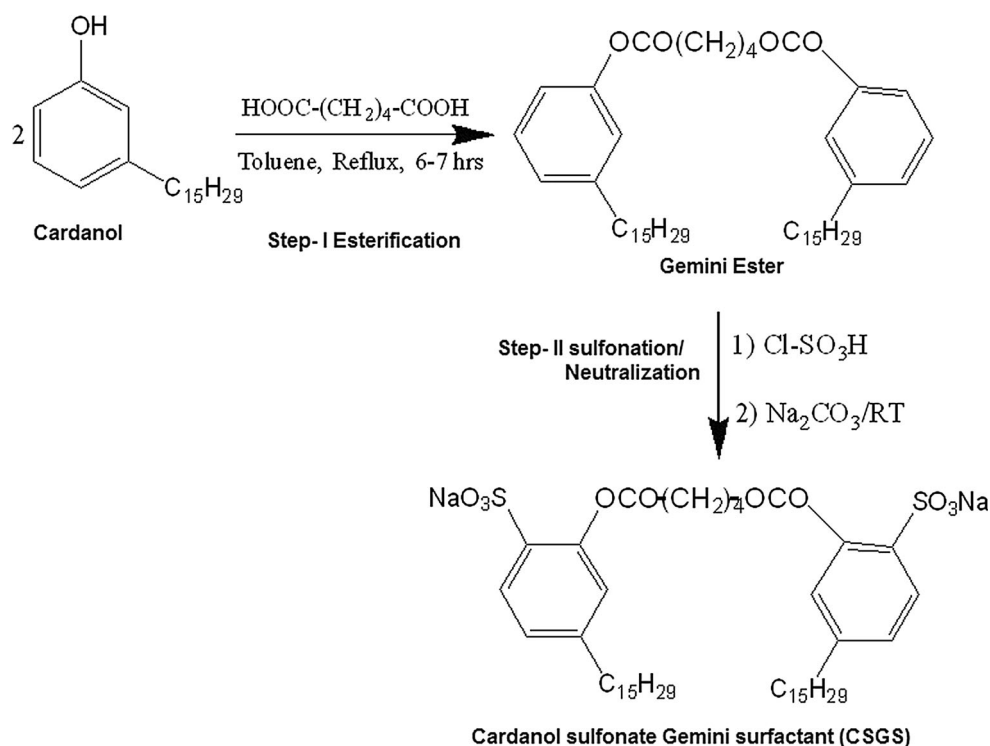
CSMS—yellow color, solid, hygroscopic, FTIR- wavelength (cm<sup>-1</sup>) = 3594.52, 3531.95 (O–H, phenolic compound), 3091.47 (=C–H, aromatic ring), 2927.92 and 2859.94 (–C–H, aliphatic chain), 1679.72–1584.56 (C=C), 1425 and 1182.37 (S=O, sulfonate), 1049.39 (C–O, phenol), 693.79 (C–S stretching). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, TMS) δ ppm = 8.10 (1H, s, Ar–OH<sub>a</sub>), 7.94 (1H, s, Ar–H<sub>f</sub>), 7.38–7.47 (2H, d, Ar–H<sub>c,e</sub>), 6.46–6.58 (2H, d, side chain), 0.74–1.92 (27H, aliphatic chain).

Cardanol gemini ester—brown-black color, liquid, FTIR- wavelength (cm<sup>-1</sup>) = 2925.43 and 2854.34 (–C–H, aliphatic chain), 1614.27 – 1573.43 (C=C), 1734.44 (C=O,

**Fig. 1** Schematic route for synthesis of CSMS



**Fig. 2** Schematic route for synthesis of CSGS



ester spacer group), 1015.23–1239.08 (C–O, ester).  $^1H$  NMR (500 MHz, DMSO- $d_6$ , TMS)  $\delta$  ppm = 7.02–7.92 (8H, Ar- $H_{c,e,f,g}$ ), 6.53 (4H, aliphatic chain), 0.82–3.4 (62H).  $^{13}C$  NMR (500 MHz, DMSO- $d_6$ , TMS)  $\delta$  ppm = 172.78 (2C, C=O, ester), 150.76–153.48 (2C, ArC–O), 145.99–146.21 (2C, ArC–alkyl chain) 115.62–138.92 (C=C, Ar and aliphatic chain), 14.22–29.55 (aliphatic chain)

CSGS—brown color, solid, FTIR—wavelength ( $cm^{-1}$ ) = 2924.39 and 2856.88 (C–H, aliphatic chain), 1637.34–1588.35 (C=C), 1764.98 (C=O, ester spacer group) 1435.39 and 1140.47 (S=O, sulfonate), 1049.39 (C–O, phenol), 619.30 (C–S stretching).  $^1H$  NMR (500 MHz,  $D_2O$ , TMS)  $\delta$  ppm = 8.28–8.29 (2H, Ar- $H_f$ ), 7.88 (4H, Ar- $H_{c,e}$ ), 6.40 (4H, aliphatic chain), 0.71–3.58 (62H) [20, 21].

### Critical Micelle Concentration Determination

The critical micelle concentration (CMC) was estimated by tensiometry, conductometry and dye solubilization method. The surface tension experiments were performed by a Wilhelmy plate method using a Krüss K11 tensiometer at room temperature ( $303 \pm 1$  K). The accuracy of the measurement was within  $\pm 0.2$  mN/m. The platinum plate used for the measurement was cleaned with acetone, washed thoroughly with distilled water and then heated using a piezo gas burner before use. The instrument was calibrated using distilled water having a surface tension value of  $71 \pm 1.0$  mN/m. Each surface tension value was a

mean average of three readings at an interval of 30 s. All the experiments were run in triplicate with an accuracy of  $\pm 0.3$  mN/m.

The conductivity of aqueous solutions of surfactants was measured using a Labtronics digital conductivity meter (Model LT 23, India). The instrument was standardized using 0.01 M potassium chloride having conductance 1.4 mS/cm.

The dye solubilization was studied using water insoluble Sudan IV dye. The ultraviolet, visible absorption spectra were recorded on a single beam UV–Visible spectrophotometer. The Sudan IV dye ( $\lambda_{max} = 514$  nm) shows a shift in the maximum wavelength ( $\lambda_{max} = 531$  nm) due to the presence of micelles. The typical procedure is to add an excess of powdered dye to aqueous surfactant solutions, stir the suspension until equilibrium, separate the non-solubilized dye by filtration or centrifugation and record the absorbance. Plot of surfactant concentration versus the absorbance at the maximum wavelength (Fig. 4) was used to estimate the CMC values of synthesized CSMS and CSGS.

### Wettability

The contact angle measurements were carried out by a static sessile drop method using a Krüss G-10 goniometer with an accuracy of  $\pm 2^\circ$ . The instrument consists of a horizontal stage to mount a solid or liquid sample, a micrometer pipette to form a liquid drop, an illumination

source and a telescope equipped with a protractor eyepiece. The contact angle measurements were performed by simply aligning a tangent of the sessile drop with the solid surface at the contact point and the reading was taken with a protractor eyepiece. Wettability of the aqueous CSMS and CSMS solutions (2 mM) on hydrophilic/hydrophobic surfaces such as glass, Teflon and stainless steel was studied.

### Evaluation of Antimicrobial Activity

The antimicrobial efficacy of newly synthesized ester-linked gemini surfactant and its corresponding monomeric surfactant was determined by using the Kirby-Bauer disc-diffusion method as per NCCLS guidelines (National Committee for Clinical Laboratory Standards) [22]. The CSMS, CSMS and CTAB were tested against bacterial strains such as *Staphylococcus aureus* (*S. aureus*, ATCC 6538), *Escherichia coli* (*E. coli*, ATCC 10536), *Pseudomonas aeruginosa* (*P. aeruginosa*, ATCC 9027) and *Bacillus subtilis* (*B. subtilis*, ATCC 6633). The fungal strains used were *Aspergillus niger* (*A. niger*, ATCC 6275), *Candida albicans* (*C. albicans*, ATCC 14037), *Aspergillus flavus* (*A. flavus*, ATCC 9643) and *Rhizopus stolonifer* (ATCC 10231). CTAB was used as a conventional reference antibacterial agent. Amphotericin B discs (AP 20 mcg/disc) were used for antimicrobial susceptibility testing of fungal culture.

The CSMS, CSMS and CTAB (test samples) were in distilled water (100 mg in 500  $\mu$ L) and thoroughly homogenized in Vortex mixer. The test microbes of approximately  $10^7$ – $10^8$  CFU/ml were individually spread over the face of Trypticase soy agar (TSA) by a sterile cotton swab. Then 30  $\mu$ L test samples of above concentration were smeared on the sterile disc. The disc containing test preparation was placed on seeded plates. The plates were then incubated at 37 °C for 24 h. The antimicrobial activity was evaluated by measuring the diameter of the growth inhibition zone formed around each disc. After the incubation period, the zones of inhibition (mm) were measured by a calibrated ruler.

### Foamability Study

The foaming properties of synthesized CSMS and CSMS surfactants (2 mM) were determined by the standard Ross-Miles pour foam test method (ASTM designation D-1173-53). In this method, 50 ml surfactant solution was taken in the foam receiver provided with a water jacket and the solution height was adjusted with a stopcock. The foam pipette was filled with 200 ml of same surfactant solution. The pipette solution was allowed to fall into the foam receiver from a height of 90 cm. The foam height in the foam receiver was measured immediately after the last

drop of the solution fell from the pipette. The temperature ( $303 \pm 1$  K) was maintained with the help of a water jacket. The foamability was measured in terms of the height (mm) of the foam produced initially and the foam stability was measured in terms of the height (mm) after 5 min [16].

Foamability was also tested using a horizontal impinging jet apparatus [23]. In this method, surfactant solution with a constant flow rate is made to impinge horizontally on a specially designed flat surface covered with a thin layer of the same solution, which generates polydispersed foam. The fine bubbles get carried towards the bottom of the column, whereas larger ones drift to the top and intermediates accumulate in between. The fine foam is collected in the collector arm where the volume is noted. The rate of fine foam generation is taken as a measure of foamability. All the experiments were triplicated.

## Results and Discussion

### Surface Tension and CMC Measurements

The CMC value was estimated by fitting the surface tension curve at a premicellar concentration with the Szyszkowski Eq. (1) and at postmicellar concentration with linear graph. Figure 3 shows the graph of surface tension against concentration.

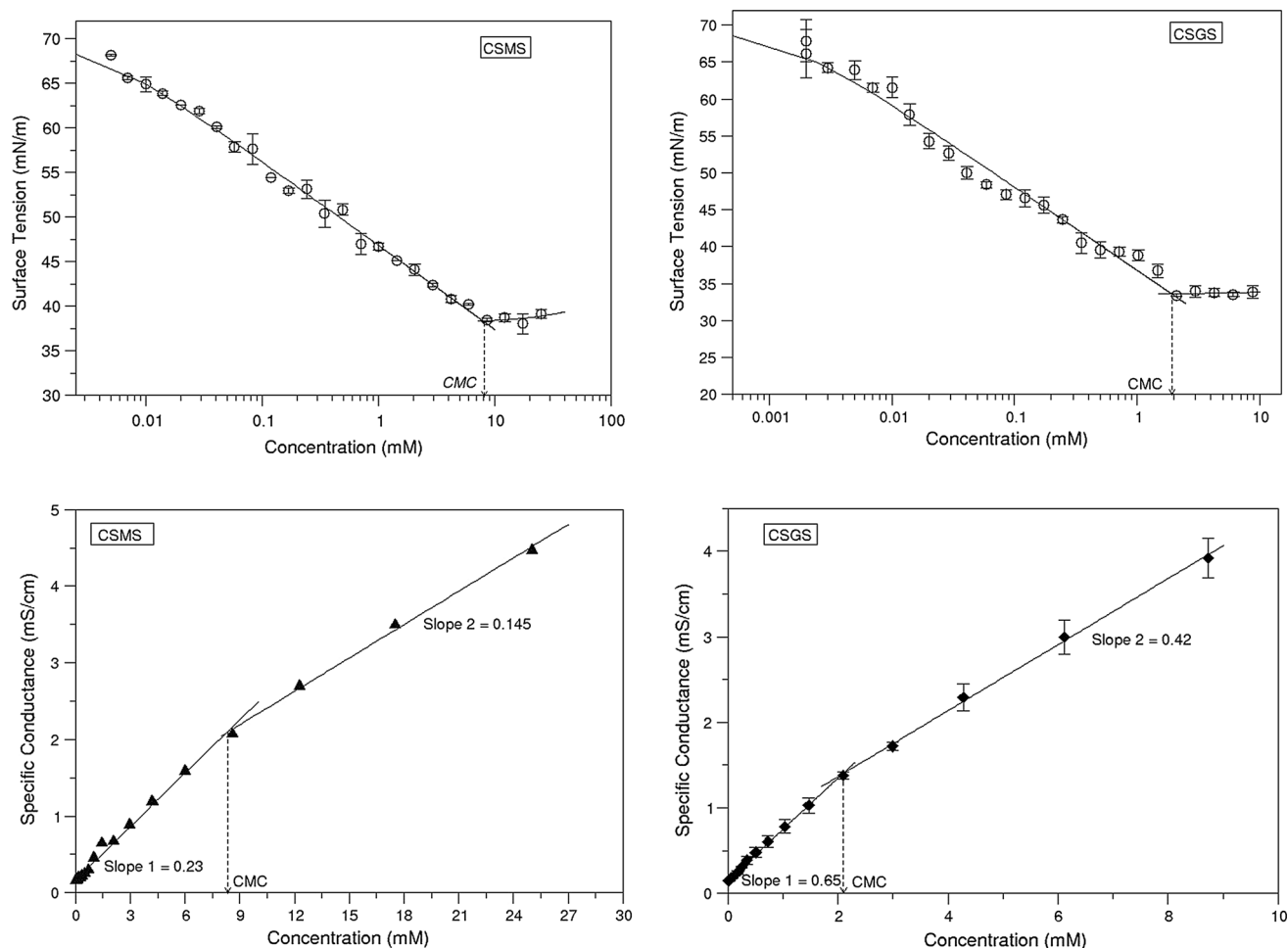
$$\pi = \gamma_0 - \gamma = nRT\Gamma_{\max} \times \ln(1 + K \times c) \quad (1)$$

where  $\gamma_0$  is the surface tension of the pure water and  $\pi$  is the surface pressure,  $\Gamma_{\max}$  is the maximum surface excess concentration of surfactant,  $c$  is the concentration of the surfactant solution,  $R$  is the universal gas constant,  $T$  is the absolute temperature,  $K$  is the adsorption constant and  $n$  is the number of dissociating ionic species whose concentration at the interface varies with the change in the surfactant concentration in the solution [24]. In case of gemini surfactant having a divalent surfactant ion and two univalent counter ions, the value of  $n$  employed is 3.

The efficiency ( $pC_{20}$ ) of the synthesized anionic gemini surfactant was also estimated. The  $pC_{20}$  value is the negative logarithm of surfactant concentration ( $C_{20}$ ), required to reduce the surface tension by 20 mN/m.  $\frac{CMC}{C_{20}}$  compares micellization and adsorption phenomena [4]. The minimum surface area per molecule ( $A_{\min}$ ) for synthesized surfactants was calculated using Eq. (2).

$$A_{\min} = \frac{10^{16}}{\Gamma_{\max} \times N_A} \quad (2)$$

where  $N_A$  is Avogadro's number. CMC values, surface tension at CMC ( $\gamma_{CMC}$ ),  $C_{20}$ ,  $\Gamma_{\max}$  and  $A_{\min}$  are



**Fig. 3** CMC measurements by surface tension and conductivity method

**Table 1** Surface active parameters of CSMS and CSGS

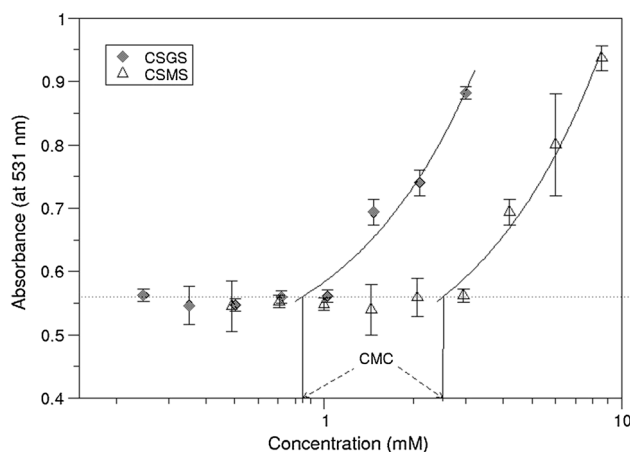
Surfactant	CMC (mM)	$\gamma_{\text{CMC}}$ (mN/m)	$^{10}10\Gamma_{\text{max}}$ (mol/cm <sup>2</sup> )	$A_{\text{min}}$ (nm <sup>2</sup> )	$C_{20}$ (mM)	$pC_{20}$	$\beta_{\text{cb}}$
Cardanol sulfonate*	8.4 <sup>a</sup>	38.4	0.67	2.47	–	4.5	–
CSMS	8.1 ± 0.5 <sup>a</sup> 8.34 ± 0.5 <sup>b</sup> 2.5 ± 0.15 <sup>c</sup>	38.2 ± 0.3	0.82	2.03	0.28	0.553	– 0.4
CSGS	1.9 ± 0.2 <sup>a</sup> 2.1 ± 0.3 <sup>b</sup> 0.84 ± 0.15 <sup>c</sup>	33.6 ± 0.2	0.65	2.55	0.044	1.36	– 0.36 –

\* The values were obtained from [17]

<sup>a</sup> Tensiometry, <sup>b</sup> conductometry and <sup>c</sup> dye micellization method

summarized in Table 1. It is expected that the gemini surfactants have a lower CMC than their corresponding monomeric surfactants. The CMC of the pure CSMS and CSGS from surface tension plot was obtained as 8.1 and 1.9 mM respectively. The lower  $C_{20}$  value for CSMS and

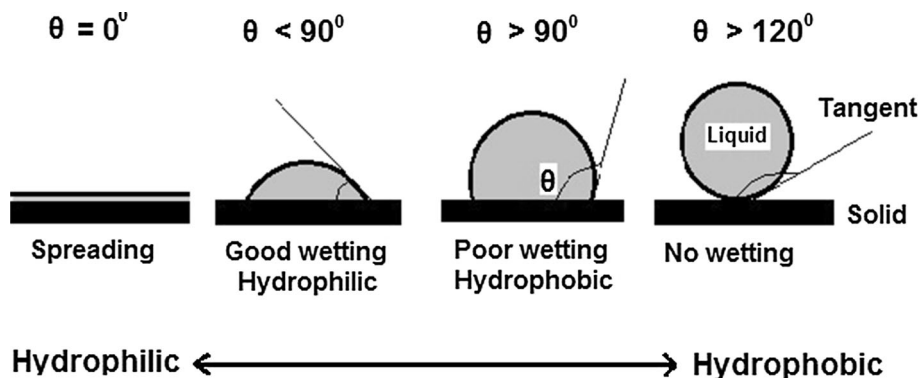
CSGS indicated that cardanol based surfactants are efficient in reducing surface tension. Higher  $\frac{\text{CMC}}{C_{20}}$  ratio obtained for CSMS (28.9) and CSGS (43.2) indicates that adsorption is facilitated more than micellization. It also indicates the presence of a larger hydrophilic head group area [4].



**Fig. 4** Determination of CMC by dye micellization

Conductivity measurements were carried out for CSMS and CSGS to calculate the CMC and the plot is shown in Fig. 3. The CMC value was obtained from the intersection point of two straight lines. These values are in good agreement with the CMC values obtained from the surface tension method. The slope in the premicellar region ( $s_1$ ) is greater than that in the postmicellar region ( $s_2$ ) and the ratio  $\frac{s_2}{s_1}$  gives the counterion dissociation constant,  $\alpha_{cb}$  and counterion binding coefficient,  $\beta_{cb}$  ( $1 - \alpha_{cb}$ ) [25]. The degree of binding ( $\beta_{cb}$ ) is related to the surface area per head group in the ionic micelle. The lower the value of  $\beta_{cb}$ , higher would be the surface head group area [4]. CSMS and CSGS have low  $\beta_{cb}$  which indicates a larger surface head group area as mentioned in Table 1.

**Fig. 5** Illustration of contact angles formed by sessile drop on a smooth solid surface



**Table 2** Contact angles of aqueous CSMS and CSGS surfactants

Sample	Concentration (mM)	Glass	Contact angle ( $\theta$ )	
			Teflon	Stainless steel
Pure water	–	30	$113 \pm 3$	$80 \pm 2$
CSMS	2	$25 \pm 1$	$76 \pm 2$	$41 \pm 2$
CSGS	2	$20 \pm 2$	$52 \pm 1$	$30 \pm 2$

The dye solubilization is one of the methods used for determination of the CMC. Plot of absorbance of the solubilized dye ( $\lambda_{max} = 531 \text{ nm}$ ) as a function of surfactant concentration is shown in Fig. 4. The inflection point in  $\lambda_{max}$  is taken as the CMC [26]. The dye solubilization is related to the structure of both surfactant and dyes. The CMC values obtained from dye micellization are lower than the CMC values obtained from tensiometry and conductometry (Table 1). It was observed that CSMS and CSGS have higher dye solubilization power. The reason for the good performance of these surfactants is that they allow dyes to be assimilated not only in the inner hydrocarbon part of the micelle but also in the head group shell which resulted in a lower CMC value [27].

**Wetting Power**

Contact angle measurements are commonly used to evaluate the degree of spreading/wettability of a liquid on a surface [28]. Wetting agents that lower the surface tension of the liquid, allow easier spreading or penetration into the solid if it is porous [29]. Figure 5 shows that a small contact angle ( $\theta$ ) is noticed when the liquid spreads on the surface, while a large contact angle is noticed when the liquid beads on the surface. When the contact angle of the pure water is smaller than  $90^\circ$ , the solid surface is considered to be hydrophilic; when the contact angle of the pure water is greater than  $90^\circ$ , the solid surface is hydrophobic [30]. It was observed that the CSGS has a very low contact angle  $20^\circ$ ,  $52^\circ$  and  $30^\circ$  on glass, Teflon and stainless steel respectively. The contact angle of CSMS

**Table 3** Antimicrobial activity of synthesized surfactants against pathogens (Kirby–Bauer disc diffusion method)

Type	Microbes name	Zone of inhibition (mm)			
		CSMS	CSGS	CTAB	Amphotericin B
Bacteria					
Gram-positive	<i>S. aureus</i>	16	10	15	–
	<i>B. subtilis</i>	14	9	16	–
Gram-negative	<i>P. aeruginosa</i>	9	9	10	–
	<i>E. coli</i>	10	10	14	–
Fungi					
	<i>A. niger</i>	No zone	10	–	11
	<i>C. albicans</i>	No zone	9	–	11
	<i>Rhizopus stolonifer</i>	No zone	9	–	9
	<i>A. flavus</i>	No zone	9	–	9

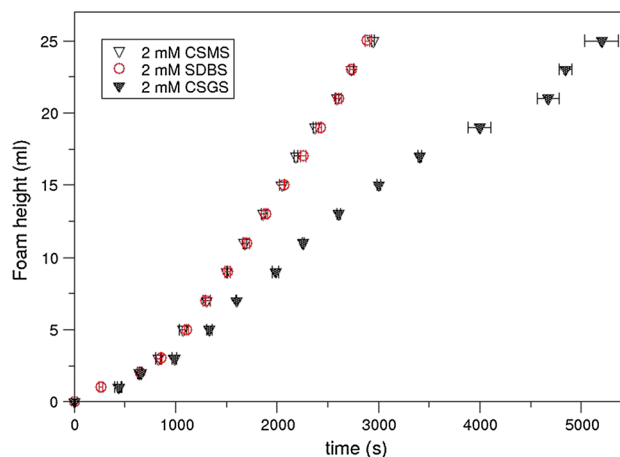
**Table 4** Foaming parameters of CSGS, CSMS and SDBS surfactants

Surfactant	Concentration (mM)	Ross-miles pour test method		Horizontal impinging jet method Foamability (ml/s) × 10 <sup>2</sup>
		Foam height (mm) 0 min	Foam stability (%) 5 min	
CSGS	2	13.3 ± 0.6	64 ± 0.6	0.5
CSMS	2	17.7 ± 1.1	85 ± 1	0.92
SDBS	2	39.3 ± 0.6	89 ± 3	0.9

on glass, Teflon and stainless steel was found to be 25°, 76° and 41° respectively. The contact angle results were taken as an average of five measurements and are listed in Table 2. The synthesized ester-linked gemini surfactant (CSGS) as well as its corresponding monomeric surfactant (CSMS) derived from cardanol possess excellent wetting properties and can be used as wetting agents.

### Antimicrobial Activity

A zone of inhibition signifies the presence of antimicrobial activity. The larger the zone of inhibition, the greater the diffusible antimicrobial activity. The antibacterial and antifungal activity of the CSGS and CSMS was assessed. Results of inhibition zone values are presented in Table 3. CSGS showed favorable antifungal activity in disc diffusion method, whereas absence of growth inhibition zone was observed in case of CSMS. An equivalent antifungal activity was observed with CSGS against *C. albicans*, *A. niger*, *A. flavus* and *Rhizopus stolonifer* in comparison with Amphotericin B. Both CSGS and CSMS were exhibited antibacterial activity comparable to CTAB. It was found that CSGS showed good antibacterial activity against both Gram-positive and Gram-negative bacteria as well as antifungal activity against all fungi studied. Hence, it can be employed as antimicrobial agents against plant, animal and human microbial pathogens.

**Fig. 6** Foamability plots for SDBS, CSMS and CSGS surfactants (Horizontal impinging jet method)

### Foamability

The foaming efficiency of the CSMS and CSGS was evaluated by the well-known Ross-Miles method as well as the horizontal impinging jet method. Foamability of the surfactant solution is a very important property both in the consumer and non-consumer goods industries. Generally anionic surfactants are known to be highly foaming surfactants [31]. The foam capacity and foam stability of the CSGS, CSMS and SDBS are mentioned in Table 4. The foam produced with CSMS is as stable as that observed



with SDBS. It can be seen from Fig. 6 that CSMS and SDBS show similar foaming properties suggesting CSMS can be used as an alternative to SDBS. However, the foamability studies revealed that the synthesized ester-linked gemini surfactant falls in the class of low foam producing surfactant and thus may be used in a variety of applications such as washing machine laundry, spray cleaners or additives in oilfield applications.

## Conclusions

A novel anionic gemini surfactant derived from cardanol containing ester-linkage in spacer group was synthesized. The surface activity of the gemini surfactant is higher than its corresponding single chain surfactant. The synthesized gemini surfactant shows excellent wettability and antimicrobial potency and has low foamability. It can be used as an antimicrobial agent for treatment against infectious organisms. This novel ester-linked gemini surfactant is suggested as having an extensive potential for industrial applications.

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**Manisha B. Ahire** received her M.Sc. (Organic chemistry) from the University of Pune, India in 2010 and currently pursuing her Ph.D. at the Institute of Chemical Technology, Mumbai, India. Her research interests are synthesis and applications of Gemini surfactants.

**Sunil S. Bhagwat** received his Ph.D. in chemical engineering from the University of Bombay (Mumbai), in 1989. At present, he is a professor of Chemical engineering at the Institute of Chemical Technology (ICT), Mumbai and a consultant to various chemical industries in India. He is currently on the editorial board of the Journal of Surface Science and Technology. His research interests are surfactants, interfacial science and engineering as well as energy and exergy engineering.