ORIGINAL ARTICLE



### Synthesis, Characterization, and Applications of Some New Trimeric-Type Cationic Surfactants

Waleed A. El-Said<sup>1</sup> · Ahmed S. Moharram<sup>1</sup> · Essam M. Hussein<sup>1</sup> · Ahmed M. El-Khawaga<sup>1</sup>

Received: 1 October 2017 / Revised: 17 February 2018 / Accepted: 19 February 2018 © 2018 AOCS

Abstract In recent years, trimeric surfactants have created excitement in the surfactant field because of their properties, which have been found to be better than monomeric or dimeric homologues. Only a limited number of trimeric surfactants have been synthesized and studied so far, probably owing to the difficulty in synthesis. In this article, we synthesized some novel star-shaped trimeric cationic surfactants based on the alkylation of the 3 hydroxyl groups of the phloroglucinol nuclei as a core (i.e., spacer) with 3 dodecyl or 3 octyl groups (as tails) for the surfactant. The chemical structures were confirmed by nuclear magnetic resonance, Fourier transform infrared, mass spectrometry, and elemental analysis; also the critical micelle concentration was determined by electrical conductivity measurements. These surfactants were used in the synthesis of mesoporous silica nanoparticles by the sol-gel method. The silica particles shape and size were determined using field emission scanning electron microscopy and highresolution transmission electron microscopy images. Furthermore, the corrosion inhibitor capability of these surfactants was investigated by monitoring the corrosion rate of iron sheets in 0.5 M hydrochloric acid in the presence and in the absence of different surfactants at 45°C based on the weight loss method. We have used cetyltrimethylammonium bromide (CTAB) as a positive control,

**Electronic supplementary material** The online version of this article (doi:10.1002/jsde.12041) contains supplementary material, which is available to authorized users.

Waleed A. El-Said waleed@sogang.ac.kr the obtained results showed a high inhibition efficiency at very low concentrations, and the prepared trimeric surfactants exhibited a higher anticorrosion efficiency than the CTAB surfactants.

**Keywords** Trimeric surfactant · Mesoporous silica · Cationic surfactant · Corrosion inhibitors

J Surfact Deterg (2018) 21: 343–353.

#### Introduction

Recent progress in the surfactant field has focused on the fabrication of different types of surfactants, including polymeric, Gemini, multifunctional, and biosurfactants. Gemini (dimeric) surfactants are composed of two conventional single-chain surfactants attached covalently to each other at the level of head groups with a spacer group (Menger & Keiper, 2000). These surfactants show unusual properties such as low values of both the critical micelle concentration (CMC) and Krafft temperatures, a complicated micellar shape, and great ability to decrease the surface tension of water (Moulik, 2002; Rosen & Tracy, 1998). All these properties have inspired scientists and researchers to increase the degree of oligomerization and to synthesize oligomeric surfactants (Laschewsky, Wattebled, Arotçaréna, Habib-Jiwan, & Rakotoaly, 2005; Zana, 2002). Oligomeric surfactants represent transitional structures between standard monomeric surfactants and polymeric ones. Although the properties of oligomeric surfactants have been found to be superior to that of Gemini analogs, a limited number of trimeric surfactants has been synthesized and studied (Gao, Millqvist-Fureby, Whitcombe, &

<sup>&</sup>lt;sup>1</sup> Department of Chemistry, Faculty of Science, Assiut University, Assiut 71516, Egypt

Vulfson, 1999; Murguía, Cabrera, Guastavino, & Grau, 2005; Yoshimura, Kimura, Onitsuka, Shosenji, & Esumi, 2004; Yoshimura, Koide, Shosenji, & Esumi, 2002). This may be accounted for the difficulty of synthesis and purification processes. However, the attempts have increased in the last few years, and some cationic and anionic trimeric surfactants have been synthesized and included in different applications (Hou, Cao, Deng, & Wang, 2008; Kampf, Wu, Wang, & Klein, 2016; Liang & Li, 2017; Zhang et al., 2017; Zhou et al., 2016).

Mesoporous silica nanoparticles (MSNP) can be defined as chemically and thermally stable nanomaterials having a well-defined and controllable morphology and porosity. These particles have external and internal surfaces that can be selectively functionalized with multiple organic and inorganic groups (Melde, Johnson, & Charles, 2008). The synthesis process of MSNP requires a silica source, a surfactant, and an acidic or basic medium (Melde et al., 2008). Any change in these parameters will affect the characteristics of the porous structure such as the pore diameter and volume, and the morphology of silica particles (Cai et al., 2001; Davidson, 2002; Lin, Kao, Mou, & Liu, 2000). These particles have a wide range of applications in areas such as catalysis (Fan et al., 2003), chemosensing or biosensing (Melde et al., 2008), gas adsorption (Melde et al., 2008), and drug delivery (Kwon et al., 2013). The preparation of MSNP via a sol-gel process is totally dependent on the soft template formed by surfactant micelles (Trewyn, Slowing, Giri, Chen, & Lin, 2007). The variety of micellar shapes and size of the trimeric surfactants (Danino, Talmon, Levy, Beinert, & Zana, 1995) inspired us to incorporate them in the preparation of MSNP.

The ability of surfactants to adsorb at interfaces was the reason to use them as corrosion inhibitors. Corrosion of metals takes place in the presence of oxygen and moisture, which involves two electrochemical reactions: oxidation occurs at anodic sites and reduction occurs at cathodic sites (Kumar, 2008). Surfactants as corrosion inhibitors have many advantages, *e.g.*, a high anticorrosion efficiency, low toxicity, and easy production (Murira, Punckt, Schniepp, Khusid, & Aksay, 2008). In our previous work (El-Said, Moharram, Hussein, & El-Khawaga, 2018), we have synthesized three positional isomeric Gemini surfactants based on catechol, resorcinol, and quinol nuclei. The CMC of the three surfactants were determined; we have also used them as anticorrosion agents in the preparation of MPSNP.

In this paper, we reported on the synthesis of new trimeric cationic surfactants, which showed lower CMC values compared with the dimeric or monomeric analogs. Furthermore, the capability of using the developed trimeric surfactants as corrosion inhibitors was investigated and compared with cetyltrimethylammonium bromide (CTAB). The results show that the novel trimeric surfactants had a higher anticorrosion efficiency than the CTAB surfactants.

#### Experimental

#### Materials

*N*,*N*-Dimethylethylenediamine was purchased from Aldrich (Shanghai, China). 1-Bromooctane was purchased from Alfa Aesar (Karlsruhe, Germany). Dodecyl bromide was purchased from Fluka (Strasbourg, France). Tetraethyl orthosilicate (TEOS), CTAB, and hydrochloric acid (37%) were purchased from Merck (Darmstadt, Germany). These reagents were used as received without any further purification. All other chemicals were of analytical grade. All the aqueous solutions were prepared with deionized water (18.2 M $\Omega$  cm), which was purified with a Purite purification system (Cambridge, UK).

#### Methods

All melting points were uncorrected and determined using a Gallen-Kamp (Boston, Massachusetts, USA) melting point apparatus. Fourier transform infrared (FTIR) spectra of all synthesized compounds were measured using a KBr disc over 500-4000 cm<sup>-1</sup> on a Shimadzu IR-470 spectrophotometer (Kyoto, Japan). Nuclear magnetic resonance (NMR) spectra of surfactants were recorded at the LaNMR (NMR laboratory, Lille 2 University, France) on a Bruker Avance 300 (spectrometer operating at 300 MHz (<sup>1</sup>H) and 75 MHz (<sup>13</sup>C)). Chemical shifts are in parts per million (ppm) and referenced to the residual proton peaks in deuterated solvents. Datasets were analyzed using Bruker Topspin 3.2 software (Bremen, Germany). The <sup>1</sup>H NMR spectra of other compounds were recorded on a Varian EM-360 (60 MHz) (Palo Alto, California, USA) at the Faculty of Science, Assiut University, Egypt, and Varian Gemini (300 MHz) (Palo Alto, California, USA) at Micro Analytical Center, Cairo University, Egypt. The molecular weight of all prepared surfactants was analyzed using an Acquity UPLC-MS/MS (Waters) system, equipped with a Xevo triple quadrupole mass spectrometer with an ESI source (Milford, MA, USA). Transmission electron microscopy (TEM) images were recorded on a high-resolution TEM (HR-TEM) TECNAI G<sup>2</sup> spirit TWIN (Hillsboro, Oregon, USA) at an accelerating voltage of 120 kV using a VELETA camera (Muenster, Germany). The morphologies of the prepared silica samples were observed using a high brilliance LEO 1530 field emission scanning electron microscope (FE-SEM) (Oberkochen, Germany) at Istituto Di Struttura Materia, Montelibretti, Italy. The electrical Della

conductivity of all surfactant solutions was measured using a JENWAY model 4320 conductivity meter (Staffordshire, UK). The crystal structure of silica samples was characterized by wide-angle X-ray scattering (WAXS) using a Philips diffractometer (Model PW2103) (Almelo, Netherlands) with Cu K $\alpha$  radiation ( $\lambda = 1.54056$  Å). The diffraction patterns were recorded in the range of the diffraction angle  $2\theta$ from 4° to 80° with a step of 0.06°. The Brunauer -Emmett -Teller (BET) surface area and N<sub>2</sub> sorption isotherms of all prepared silica samples were obtained using a Quantachrome (Nova 3200 series) (Boyton Beach, Florida, USA) multigas adsorption apparatus. Thermal gravimetric analysis (TGA) was performed under an air atmosphere using DTG-60 simultaneous thermogravimetry/differential thermal analyzers (Shimadzu).

#### **Organic Syntheses**

#### Synthesis of 1,3,5-Tris(ethoxycarbonylmethoxy)benzene (1)

The synthesis of this compound has been described in the literature (Lu et al., 2002). It was carried out by the reaction of an alkali metal phenolate with an alkyl halide in the presence of an inorganic base. Ethyl bromoacetate (26.7 g, 0.16 mol) was slowly added to a stirred mixture of anhydrous potassium carbonate (22.1 g, 0.16 mol) in 500 mL acetone at room temperature. Next, anhydrous phloroglucinol (5.04 g, 0.04 mol) in 100 mL of acetone was added dropwise over a period of 1 h. After addition, the mixture was refluxed overnight. The salts formed were removed by filtration and the solvent volume was reduced by rotary evaporation. After cooling to room temperature, the solution yielded (1) as a yellowish solid, which was recrystallized from ethanol to provide colorless crystals (yield 10.7 g (70%), m.p. 65–66°C).

FTIR ( $\nu$ ) (KBr) (cm<sup>-1</sup>): 2983.5 (CH str. Aliph.), 1749.7 (CO str.), 1221.3 (Ar. ether). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  1.305 (9H, t, -CH<sub>3</sub>, J = 9.60 Hz), 4.27 (6H, q, CH<sub>3</sub>-CH<sub>2</sub>, J = 9.60), 4.554 (6H, s, O-CH<sub>2</sub>), 6.142 (3H, s, ArH).

# *Synthesis of 2,2',2"-(Benzene-1,3,5-triyltris(oxy))tris*(N-(2-(*dimethylamino)ethyl*)*acetamide*) (2)

This amide compound was prepared simply *via* the reaction of the triester (1) with a primary amine in a 1:3.5 M ratio. Seven grams (18.2 mmol) of 1,3,5-tris(ethoxycarbonyl-methoxy)benzene (1) was dissolved in about 30 mL

Table 1 Physical properties of trimeric surfactants

absolute ethanol and 7 g (63.8 mmol) of N,Ndimethylethylenediamine was added, and then stirred under reflux overnight. The solvent and the excess of N,Ndimethylethylenediamine were removed by rotary evaporation and a pale yellow solid was obtained (yield 72.2%, m.p. 110–113°C).

FTIR ( $\nu$ ) (KBr) (cm<sup>-1</sup>): 3338 (NH str. Aliph.), 1682.8 (CO str.), 2949, 2860 (CH str. Aliph.). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  2.236 (18H, s, -CH<sub>3</sub>), 2.44 (6H, t, N-CH<sub>2</sub>, J = 8.00 Hz), 3.41 (6H, q, NH-CH<sub>2</sub>, J = 8.00 Hz), 4.44 (6H, s, O-CH<sub>2</sub>), 6.182 (3H, s, ArH), 7.0 (3H, s, NH).

#### Quaternization of 2,2',2"-(Benzene-1,3,5-triyltris(oxy)) tris(*N*-(2-(dimethylamino)ethyl)acetamide) with Alkyl Bromide (3 and 4)

This step involves the alkylation of the tri tertiary amine (2) with an alkyl halide. A solution of compound (2) (6.7 g, 13 mmol) and alkyl bromide (52.5 mmol) in 25 mL of absolute ethanol was refluxed for 1 day with continuous stirring. The solvent was removed *in vacuo* and excessive alkyl bromide was washed off with petroleum ether. The crude product was collected, dried, and recrystallized from ethanol as shown in Table 1.

# 2,2',2"-(Benzene-1,3,5-triyltris(oxy))tris(N-(2-(dimethyl (octyl)aminium)ethyl)acetamide) Tribromide (3)

<sup>1</sup>H NMR ( $d_6$ -Dimethyl sulfoxide [DMSO], 300 MHz):  $\delta$ 0.846 (9H, t, -CH<sub>3</sub>), 1.253 (30H, t, -(CH<sub>2</sub>)<sub>5</sub>-), 1.66 (6H, m,  $-(CH_2)$ -), 3.077 (18H, s, N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>), 3.39 (12H, t,  $N^+CH_2$ ), 3.55 (6H, q, NH-(*CH*<sub>2</sub>)-), 4.49 (6H, s, O-CH2-), 6.3 (3H, s, ArH), 8.51 (3H, t, NH). Mass Spectrometer Electrospray Ionization [MS-ESI] (m/z): Calcd.: 1090; Found: 465 ( $[M-2Br^{-}]^{+2}/2$ , 100), 283 ( $[M-3Br^{-}]^{+3}/3$ , 45), 1009 ([M-Br<sup>-</sup>], 15). Anal. Calcd. for C<sub>48</sub>H<sub>93</sub>Br<sub>3</sub>N<sub>6</sub>O<sub>6</sub> (1090): C, 52.89%; H, 8.60%; Br, 21.99%; N, 7.71%; O, 52.36%; 8.81%, Found: C, H, 8.28%; Br. 22.15%; N, 7.40%.

# 2,2',2"-(Benzene-1,3,5-triyltris(oxy))tris(N-(2-(dimethyl (dodecyl)aminium)ethyl)acetamide) Tribromide (**4**)

<sup>1</sup>H NMR (*d*<sub>6</sub>-DMSO, 300 MHz): δ 0.843 (9H, t, -CH<sub>3</sub>), 1.227 (54H, s, -(CH<sub>2</sub>)<sub>9</sub>-), 1.657 (6H, m, -(CH<sub>2</sub>)-), 3.078 (18H, s, N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>), 3.39 (12H, t, N<sup>+</sup>CH<sub>2</sub>), 3.55 (6H, q, NH-(*CH*<sub>2</sub>)--), 4.55 (6H, s, O-CH<sub>2</sub>--), 6.297 (3H, s,

Alkyl halide	Compound	Solvent of recrystallization	Color	Melting point (°C)	Yield (%)
Octyl bromide	3	Ethanol	White	104-106	67
Dodecyl bromide	4	Ethanol	White	122–124	61

ArH), 8.519 (3H, t, NH). MS–ESI (m/z): Calcd.: 1258.32; Found: 549 ([M-2Br<sup>-</sup>]<sup>+2</sup>/2, 100), 339 ([M-3Br<sup>-</sup>]<sup>+3</sup>/3, 20), 1178 ([M-Br<sup>-</sup>], 5). Anal. Calcd. for C<sub>60</sub>H<sub>117</sub>Br<sub>3</sub>N<sub>6</sub>O<sub>6</sub> (1258.32): C, 57.27%; H, 9.37%; Br, 19.05%; N, 6.685; O, 7.63%, Found: C, 58.16%; H, 9.28%; Br, 18.35%; N, 6.44%.

#### Determination of CMC *via* the Electrical Conductivity Measurements

The conductivity of the surfactant solutions in deionized water was measured as a function of concentration using a JENWAY model 4320 conductivity meter. Sufficient time was given to the system to equilibrate between successive additions. This method was used to determine both the CMC and the micelle ionization degree ( $\alpha$ ) of the surfactant.

#### Synthesis of MSNP

0.2 g of the trimeric surfactant (4) is dissolved in 40 mL deionized water followed by the addition of 1 mL of aqueous ammonia solution 25%. Three milliliters of TEOS was then added dropwise and stirred for 6 h at  $60^{\circ}$ C. The mesostructured product formed was cured at room temperature for a day. The products were filtered and dried at 90°C. The surfactant was removed by calcination at  $600^{\circ}$ C for 5 h.

# Corrosion Inhibition Efficiency Based on the Weight Loss Method

The corrosion tests were performed on iron (Fe) sheets (96.16% Fe and 3.84% C) in a square shape with a geometrical area of 3.75 cm<sup>2</sup>. These sheets were polished with emery papers followed by successive washing with deionized water and acetone, dried at 90°C, and finally allowed to stand for 5 h in 0.5 M HCl solution at 45°C in the absence and in the presence of different concentrations of the surfactants (10 and 50  $\mu$ M) (Zhang, Pan, & Gao, 2015). The weight difference of the Fe sheets was measured after washing with deionized water and acetone and then dried at 90°C.

#### **Results and Discussion**

#### **Organic Synthesis**

Compounds (1) and (2) were synthesized according to Scheme (1) and characterized using FTIR and  ${}^{1}H$  NMR.

#### Synthesis of 1,3,5-Tris(ethoxycarbonylmethoxy)benzene (1)

The FTIR spectrum of compound (1) is shown in Fig. 1a, which shows the disappearance of the OH-stretching band

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and the appearance of both CO ester groups and aliphatic CH-stretching bands at 1749 and 2983.5  $\text{cm}^{-1}$ , respectively. This confirmed the complete O-alkylation of phloroglucinol.

The <sup>1</sup>H NMR spectrum of compound (1) showed two characteristic signals of ethyl esters: The first is a triplet one at  $\delta = 1.305$  ppm, which represented nine protons of the three methyl groups. The second is a quartet at  $\delta = 4.27$  ppm, which represented six protons of the three methylene groups. The singlet signal at  $\delta = 4.554$  ppm represented six protons of the aromatic rings appeared as a deshielded signal at  $\delta = 6.142$  ppm (Fig. S1).

# Synthesis of 2,2',2"-(Benzene-1,3,5-triyltris(oxy))tris(N-(2-(dimethylamino)ethyl)acetamide) (2)

In the FTIR spectrum of compound (2), the CO band was shifted toward a longer wavelength ( $\nu = 1682.8 \text{ cm}^{-1}$ ), which indicated the formation of an amide linkage. The NH-stretching band appeared at 3310 cm<sup>-1</sup> (Fig. 1b). The chemical structure of compound (2) was confirmed using <sup>1</sup>H NMR as shown in Fig. S2. It displayed the characteristic signal of the amide protons at  $\delta = 7.0$  ppm with an integration value corresponding to three protons. This proved the complete amidation of the three ester groups of compound (1). Protons of aromatic rings appeared as a downfield signal at  $\delta = 6.182$  ppm.

Synthesis of 2,2',2"-(Benzene-1,3,5-triyltris(oxy))tris(N-(2-(dimethyl(octyl)aminium)ethyl)acetamide) Tribromide and 2,2',2"-(Benzene-1,3,5-triyltris(oxy))tris(N-(2-(dimethyl (dodecyl)aminium)ethyl)acetamide) Tribromide

The FTIR spectra of compounds (3) and (4) showed the CO-stretching band of the amide linkage at 1688.2 and 1683.3 cm<sup>-1</sup>, respectively. Both aliphatic and aromatic CHstretching bands could be seen clearly at 2942.8, 3026.7 and 2949.39, 3020.5 cm<sup>-1</sup>, respectively. The NH-stretching band appeared at 3310.1 and 3303.84 cm<sup>-1</sup>, respectively, as shown in Fig. 1c, d. The <sup>1</sup>H NMR spectra of compounds (3) and (4) recorded in  $d_6$ -DMSO are sufficient to confirm the chemical structure of the new trimeric surfactants and their purity. From the integrals, it is notable that the total number of protons in the sample is in agreement with that in the chemical formula of the expected product. Chemical shifts of all protons in compound (3) were illustrated in Fig. 2a, whereas chemical shifts of all protons in compound (4) were illustrated in Fig. 2b. The difference in the  ${}^{1}\text{H}$ NMR spectra between the trimeric surfactants (3) and (4) could be seen in the integration value of the signal (b), which corresponds to tail protons. The integration value of the signal (b) in the <sup>1</sup>H NMR spectra of trimeric surfactants (3) and (4) expressed 30 and 54 protons, respectively.



Scheme 1 Synthetic route of the trimeric surfactants



Fig. 1 FTIR spectra of (a) compound (1), (b) compound (2), (c) compound (3), and (d) compound (4)

The <sup>13</sup>C NMR spectra of trimeric surfactants (**3**) and (**4**) show 15 and 19 signals, respectively, which agreed exactly with the total number of chemically equivalent carbon atoms in each molecule. The chemical shifts of both the carbonyl group and unsubstituted aromatic carbons appeared at 168.53 and 95.74 ppm, respectively, as shown in Fig. 3a, b. These spectra are very similar to each other. The difference could be seen in the region from 20 to 35 ppm, which corresponds to carbon atoms in the tail. The MS–ESI spectra of trimeric surfactants (**3**) and (**4**) show the characteristic signals at the following *m/e* values shown in Eq. (1) (Fig. 3c, d):

$$\frac{m}{e} = \frac{[\mathbf{M} - n\mathbf{B}\mathbf{r}^{-}]^{+n}}{n}, n = 1, 2, \text{ or } 3$$
(1)

#### **Determination of CMC**

A sudden change in the electrical conductivity is indicative of a significant change in the nature of the solute species. This change is due to the aggregation of surfactant molecules to form micelles. The electrical conductivity measurements of aqueous solutions of trimeric surfactants (**3**) and (**4**) within the concentration range from 0.2 to 15.3 mM and from 0.013 to 0.68 mM are shown in Fig. 4a, b, respectively. The electrical conductivity values appeared as two linear functions with different slopes. The first linear

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function, which had a greater slope value demonstrated that these surfactants acted as strong univalent electrolytes in the concentration range below the CMC. Above the CMC, where micelles are present in solution, curves showed a decrease in slope values. The value of CMC is the intercept of two linear functions with different slopes. Both the CMC and micelle ionization degree ( $\alpha$ ) values are listed in Table 2. The CMC of the trimeric surfactant (**4**) was 0.324 mM. This is a smaller value than that of dimeric analogs with the same tail length (El-Said et al., 2018) and even smaller than the monomeric surfactants with a longer-chain tail (CTAB) (Li et al., 2006). It is notable that the increasing tail length from the octyl to dodecyl group decreased the CMC value by about one order of magnitude.

#### Synthesis of MSNP

The synthesis of mesoporous silica using the sol-gel method is based on the formation of liquid-crystalline mesophases of surfactant molecules that serve as templates for the *in situ* polymerization of TEOS. Trimeric surfactant (4) was used in the synthesis of MSNP (S1) as discussed previously. The surfactant concentration (0.5 g 100 mL<sup>-1</sup> H<sub>2</sub>O) used in this synthesis process reached a value that is greater than its CMC value. HR-TEM and FE-SEM images clarified that these particles were monodispersed spherical



Fig. 2 <sup>1</sup>H NMR of (a) compound (3) and (b) compound (4)

nanoparticles with a diameter of about 60 nm, as shown in Fig. 5a, b, respectively.

The silica nanoparticles sample differs from that prepared with the corresponding Gemini surfactants, which all gave hollow sphere MSNP with different diameters depending on the used isomer used (El-Said et al., 2018). The WAXS pattern of (S1) shown in Fig. 5c confirms that (S1) has an amorphous nature. The TGA, conducted under an air atmosphere, of the silica sample before calcination showed four main steps. The first one (15.61–149.49°C; -5.115 wt.%) was attributed to the desorption of water molecules on the silica surface and the next two steps, which the most significant weight have loss (150.78-600°C; -29.8 wt.%), were attributed to the decomposition of the trimeric surfactant (4) present in pores, this was confirmed by the TGA curve of the trimeric surfactant (4). The fourth step, which started at 495.7 °C with a weight loss of -5.66% could be a result of the removal of water molecules from the hydroxyl groups on the silica and a small amount of residual organic material (Fig. 6a, b). This analysis helped us to determine the calcination temperature of the silica sample. The nitrogen adsorption/ desorption isotherm of MSNP is shown in Fig. 6c. The observed curve had a hysteresis loop that follows type IV, which is typical for porous materials. The surface area ( $S_{\text{BET}}$ ) calculated using the BET equation is about 448.23 m<sup>2</sup> g<sup>-1</sup>, and the pore volume is 0.31 cm<sup>3</sup> g<sup>-1</sup>. The average pore diameter is 2.76 nm.

#### Corrosion Inhibition by the Weight Loss Method

The corrosion inhibition efficiency of these trimeric surfactants (3) and (4) was measured based on the treatment of Fe sheets with 100 mL of 0.5 M HCl solution at  $45^{\circ}$ C. The



Fig. 3 (a)  ${}^{13}$ C NMR of the trimeric surfactant (3), (b)  ${}^{13}$ C NMR of the trimeric surfactant (4), (c) the MS–ESI spectrum of the trimeric surfactant (3), and (d) the MS–ESI spectrum of trimeric surfactant (4)

percentage values of the corrosion rate (*R*) and inhibition efficiency ( $\eta$ ) obtained using the weight loss method for different concentrations of the inhibitor are summarized in Table 3. The corrosion rate and inhibition efficiency were calculated from Eqs. 2 and 3:

$$R = \frac{(w_1 - w_2)}{(A^*t)}$$
(2)

$$\eta = [(R_{\rm o} - R_c)R_{\rm o}] * 100 \tag{3}$$



Fig. 4 Electrical conductivity measurements of (a) the trimeric surfactant (3) and (b) the trimeric surfactant (4)

Surfactant	CMC (mM)	α(%)	References
Trimeric (3)	4.41	74.3	Current work
Trimeric (4)	0.324	60	Current work
СТАВ	0.9	23	Li, Zhang, Zhang, & Han, 2006; Vautier-Giongo & Bales, 2003
Ortho dimeric	0.43	38.2	El-Said et al., 2018
Meta dimeric	0.65	43.8	El-Said et al., 2018
Para dimeric	1.51	43.4	El-Said et al., 2018

Table 2 CMC and  $\alpha$  values of trimeric surfactants (3) and (4)

where  $w_1$  and  $w_2$  are the sample weight (g) before and after immersion in HCl, respectively; A is the total geometrical area (cm<sup>2</sup>) of the Fe sheets; t is the corrosion time (h); and  $R_a$  and  $R_c$  are the corrosion rate in the absence and in the presence of surfactants, respectively. The results showed that these trimeric surfactants had a high anticorrosion efficiency ( $\eta$ ), which is more than 95% at a concentration of 50  $\mu$ M. This is a good result for a trimeric surfactant with a tail containing eight or 12 carbon atoms in comparison with CTAB, which has a tail of 16 carbon atoms. Under the same conditions, CTAB showed an inhibition efficiency of 81.86% at a concentration equal to 50  $\mu$ M.

#### Conclusions

In this paper, we synthesized novel trimeric surfactants based on the phloroglucinol nucleus. The chemical structure of these surfactants was confirmed. The CMC and  $\alpha$  values were determined using the electrical conductivity



Fig. 5 (a) HR-TEM image of the silica sample prepared using the trimeric surfactant (4), (b) the FE-SEM image of the silica sample prepared using the trimeric surfactant (4), and (c) WAXS of the silica sample (S1) prepared using the trimeric surfactant (4)



Fig. 6 (a) TGA of the silica sample prepared using the trimeric surfactant (4), (b) TGA of the trimeric surfactant (4), and (c) the  $N_2$  sorption isotherm of the silica sample (S1) prepared using the trimeric surfactant (4)

Surfactant	$R (\mathrm{mg} \ \mathrm{cm}^{-2} \ \mathrm{h}^{-1})$	Н	Conc. (µM)	
_	11.96	0	0	
CTAB	2.17	81.86	50	
3	1.82	84.81	10	
	0.49	95.93	50	
4	2.05	82.83	10	
	0.52	95.65	50	

**Table 3** Corrosion rate (*R*) and inhibition efficiency ( $\eta$ ) of trimeric surfactants (**3**) and (**4**)

Prof. Aldo Capobianchi (Istituto Di Struttura Della Materia, Montelibretti, Italy) for FE-SEM measurements.

#### References

- Cai, Q., Luo, Z.-S., Pang, W.-Q., Fan, Y.-W., Chen, X.-H., & Cui, F.-Z. (2001) Dilute solution routes to various controllable morphologies of MCM-41 silica with a basic medium. *Chemistry of Materials*, 13:258–263.
- Danino, D., Talmon, Y., Levy, H., Beinert, G., & Zana, R. (1995) Branched threadlike micelles in an aqueous solution of a trimeric surfactant. *Science*, **269**:1420–1421.
- Davidson, A. (2002) Modifying the walls of mesoporous silicas prepared by supramolecular-templating. *Current Opinion in Colloid & Interface Science*, 7:92–106.
- El-Said, W. A., Moharram, A. S., Hussein, E. M., & El-Khawaga, A. M. (2018) Design, synthesis, anticorrosion efficiency, and applications of novel Gemini surfactants for preparation of small-sized hollow spheres mesoporous silica nanoparticles. *Materials Chemistry and Physics*, 211:123–136.
- Fan, J., Yu, C., Gao, F., Lei, J., Tian, B., Wang, L., ... Zhao, D. (2003) Cubic mesoporous silica with large controllable entrance sizes and advanced adsorption properties. *Angewandte Chemie International Edition*, **42**:3146–3150.
- Gao, C., Millqvist-Fureby, A., Whitcombe, M. J., & Vulfson, E. N. (1999) Regioselective synthesis of dimeric (Gemini) and trimeric

has the smallest CMC value for the preparation of MSNP. The resulting silica sample was monodispersed spherical nanoparticles with a diameter of about 60 nm as shown in HR-TEM and FE-SEM images. The mesoporosity of this silica sample was elucidated using the  $N_2$  sorption isotherm. The anticorrosion efficiency of these trimeric surfactants was measured using the weight loss method, which showed a high inhibition efficiency at a very low concentration.

measurements. We used the trimeric surfactant (4), which

Acknowledgements The authors thank Dr. Nicolas Lebegue (Lille 2 University, France) for the NMR measurements. Also, we thank

sugar-based surfactants. *Journal of Surfactants and Detergents*, 2: 293–302.

- Hou, Y., Cao, M., Deng, M., & Wang, Y. (2008) Highly-ordered selective self-assembly of a trimeric cationic surfactant on a mica surface. *Langmuir*, 24:10572–10574.
- Kampf, N., Wu, C., Wang, Y., & Klein, J. (2016) A trimeric surfactant: Surface micelles, hydration–lubrication, and formation of a stable, charged hydrophobic monolayer. *Langmuir*, **32**: 11754–11762.
- Kumar, A. (2008) Corrosion inhibition of mild steel in hydrochloric acid by sodium lauryl sulfate (SLS). *E-Journal of Chemistry*, 5: 275–280.
- Kwon, S., Singh, R. K., Perez, R. A., Abou Neel, E. A., Kim, H.-W., & Chrzanowski, W. (2013) Silica-based mesoporous nanoparticles for controlled drug delivery. *Journal of Tissue Engineering*, 4:1–18. https://doi.org/10.1177/2041731413503357
- Laschewsky, A., Wattebled, L., Arotçaréna, M., Habib-Jiwan, J.-L., & Rakotoaly, R. H. (2005) Synthesis and properties of cationic oligomeric surfactants. *Langmuir*, 21:7170–7179.
- Li, W., Zhang, M., Zhang, J., & Han, Y. (2006) Self-assembly of cetyl trimethylammonium bromide in ethanol–water mixtures. *Frontiers of Chemistry in China*, 1:438–442.
- Liang, Y., & Li, H. (2017) A comparison of trimeric surfactant intercalated montmorillonite with its Gemini modified one: Characterization and application in methyl orange removal. *Journal of Molecular Liquids*, 227:139–146.
- Lin, H.-P., Kao, C.-P., Mou, C.-Y., & Liu, S.-B. (2000) Counterion effect in acid synthesis of mesoporous silica materials. *The Journal of Physical Chemistry B*, **104**:7885–7894.
- Lu, J., Zeng, Q.-d., Wang, C., Zheng, Q.-y., Wana, L., & Bai, C. (2002) Self-assembled two-dimensional hexagonal networks. *Journal of Materials Chemistry*, 12:2856–2858.
- Melde, B. J., Johnson, B. J., & Charles, P. T. (2008) Mesoporous silicate materials in sensing. *Sensors*, 8:5202–5228.
- Menger, F. M., & Keiper, J. S. (2000) Gemini surfactants. Angewandte Chemie International Edition, 39:1906–1920.
- Moulik, S. K. H. A. S. P. (2002) Gemini surfactants: A distinct class of self-assembling molecules. *Current Science*, 82:1101–1111.

- Murguía, M. C., Cabrera, M. I., Guastavino, J. F., & Grau, R. J. (2005) New oligomeric surfactants with multiple-ring spacers: Synthesis and tensioactive properties. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **262**:1–7.
- Murira, C. M., Punckt, C., Schniepp, H. C., Khusid, B., & Aksay, I. A. (2008) Inhibition and promotion of copper corrosion by CTAB in a microreactor system. *Langmuir*, 24:14269–14275.
- Rosen, M. J., & Tracy, D. J. (1998) Gemini surfactants. Journal of Surfactants and Detergents, 1:547–554.
- Trewyn, B. G., Slowing, I. I., Giri, S., Chen, H.-T., & Lin, V. S. Y. (2007) Synthesis and functionalization of a mesoporous silica nanoparticle based on the sol–gel process and applications in controlled release. Accounts of Chemical Research, 40:846–853.
- Vautier-Giongo, C., & Bales, B. L. (2003) Estimate of the ionization degree of ionic micelles based on Krafft temperature measurements. *The Journal of Physical Chemistry B*, **107**:5398–5403.
- Yoshimura, T., Kimura, N., Onitsuka, E., Shosenji, H., & Esumi, K. (2004) Synthesis and surface-active properties of trimeric-type anionic surfactants derived from tris(2-aminoethyl)amine. *Journal* of Surfactants and Detergents, 7:67–74.
- Yoshimura, T., Koide, Y., Shosenji, H., & Esumi, K. (2002) Preparation and surface-active properties of telomer-type anionic surfactants from maleic anhydride. *Journal of Surfactants and Detergents*, 5:257–262.
- Zana, R. (2002) Dimeric and oligomeric surfactants. Behavior at interfaces and in aqueous solution: A review. Advances in Colloid and Interface Science, 97:205–253.
- Zhang, R., Huo, J., Peng, Z., Feng, Q., Zhang, J., & Wang, J. (2017) Emulsification properties of comb-shaped trimeric nonionic surfactant for high temperature drilling fluids based on water in oil. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 520:855–863.
- Zhang, T., Pan, Z., & Gao, H. (2015) Novel synthesized Gemini surfactant as corrosion inhibitor for carbon steel in HCl solution. *Jour*nal of Surfactants and Detergents, 18:1003–1009.
- Zhou, C., Wang, D., Cao, M., Chen, Y., Liu, Z., Wu, C., ... Wang, Y. (2016) Self-aggregation, antibacterial activity, and mildness of cyclodextrin/cationic trimeric surfactant complexes. ACS Applied Materials & Interfaces, 8:30811–30823.