Research Article

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Mitigation of eco-unfriendly and costly microbial induced corrosion using novel synthesized Schiff base cationic surfactants

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Abstract

BACKGROUND: Sulfate-reducing bacteria (SRB) are considered to be the major cause of microbial-induced corrosion. It contributes to many environmental and other costly industrial problems in the petroleum industry. Thus there is always a great need for producing new efficient biocides and biocorrosion inhibitors.

RESULTS: In this work, three Schiff base surfactants (coded Q12, Q14 and Q18) were synthesized and characterized using Fourier transform infrared and ^{1}H-nuclear magnetic resonance techniques. A mixed culture of SRB was collected from an oil field production tank located at the North Bahrya Petroleum Company (NORPETCO), Egypt. The antimicrobial effect of the newly synthesized surfactants was studied against sessile and planktonic SRB over their different growth phases by various methods: viable cell count via most probable number method, estimation of biogenic sulfide concentrations, weight loss of iron coupons in microbial growth medium and biofilm examination on coupon surfaces using scanning electron microscopy. The synthesized surfactants expressed a high inhibition effect on bacterial growth, recording a minimum inhibitory concentration of 750 mg L^{-1} for Q18 and 1000 mg L^{-1} for both Q12 and Q14, with a considerable decline in biogenic sulfide productivity from a dose of 500 mg L^{-1} until complete suppression at a dose of 1000 mg L^{-1}. Also the synthesized surfactants showed an effective metal corrosion inhibition at a concentration of 500 mg L^{-1}.

CONCLUSION: Schiff base cationic surfactants with long hydrophobic chains can be recommended as biocorrosion inhibitors for industrial application in the petroleum sector.

Keywords: sulfate-reducing bacteria; environmental concerns; biocide; corrosion inhibitor; vanillin Schiff base; cationic surfactants

INTRODUCTION

Microbiologically influenced corrosion was first recognized more than 100 years ago.[1] Awareness of this type of corrosion has increased rapidly in the past 10 years.[2,3] It is a major problem in the petroleum industry, water utilities and some other clinical settings, as it accounts for roughly 20% of total corrosion losses.[4]

Many microorganisms, including bacteria, archaea and fungi, have been found to contribute to corrosion. Published research studies on microbial corrosion focus mainly on bacteria. Sulfidogenic bacteria such as sulfate-reducing bacteria (SRB) have been recognized as one of most corrosive microorganisms.[4] Hence it is the most widely studied bacteria in the microbial corrosion literature, since sulfate is widely dispersed in anoxic environments and SRB have a massive negative impact.[5,6] SRB are strict anaerobes, but they can survive when exposed to oxygen for a period of time without growth.[5] In an open-to-air environment, SRB appear to be the bottom dwellers in mixed-culture biofilms. Upper-layer aerobic and facultative microorganisms provide a local anaerobic environment required to develop SRB. Although several SRB strains cannot tolerate oxygen exposure, some *Desulfovibrio vulgaris* and *Desulfovibrio desulfuricans* strains, for example, are reported to have aerobic respiration capabilities.[7]

In nature, a biofilm is usually a consortium of microorganisms that attach to metal or other surfaces.[8] Mixed culture of microbes can form synergistic biofilms that are more recalcitrant than biofilms of single-strain microbes.[9] Microbes embedded in a biofilm are called 'sessile', while those suspended in bulk fluid are called 'planktonic' cells. Some sessile microbes may leave biofilms to colonize new sites by secreting extracellular polymeric substances (EPS) consisting of proteins, polysaccharides and nucleic acids, to embed sessile microbes for the formation of biofilms.[10] Such make biofilms much more resistant to antimicrobial agents.[11]

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In the oil and gas industry biocides are widely, used but high doses are required to prevent biofilm formation.[12] Although many types of biocides and corrosion inhibitors are widely used, Egyptian petroleum companies still suffer from pitting corrosion problems induced by SRB. In order to overcome the microbial corrosion problem, this study aimed to; (1) synthesize and characterize three Schiff base cationic surfactants cationic surfactants, (2) investigate their antimicrobial activity against sessile and planktonic sulfate reducing bacteria which have been collected from an Egyptian oilfield, and finally (3) examine their efficient to mitigate microbial corrosion of carbon steel as one of the most widely used metals in petroleum industry.

MATERIALS AND METHODS

Materials

All the reagents were of analytical grade and used as received without further purification. Vanillin and fatty acids (lauric, myristic and stearic acid) were purchased from Sigma-Aldrich Chemicals Co., St. Louis, MO, USA. Benzyl chloride, N,N'-dimethylethelendiamine and reaction solvents (xylene and ethanol) were purchased from Algomhoria Chemical Co. (Cairo, Egypt). All constituents of the bacterial growth media were of high purity and were obtained from Loba-Chemie Co. (Mumbai, India)

Synthesis of Schiff base cationic surfactants

The desired cationic surfactants were prepared through the following three steps (Scheme 1).

Synthesis of fatty acid ester with vanillin

This was done according to Sayed *et al.*,[13] where three different fatty acids – lauric (2 g), myristic (2.3 g) and stearic (2.85 g) – were separately esterified with vanillin (1.52 g) in a 250 mL round flask containing 150 mL xylene as solvent and 0.01% *p*-toluenesulfonic acid as catalyst, until the azeotropic amount of water (1.8 mL) was removed using a Dean–Stark apparatus placed between the round flask and the condenser to receive the produced water. After completion of the reaction, the solvent was removed using a vacuum rotary evaporator. The catalyst was extracted from the reaction medium using petroleum ether. Subsequent purification was done by means of vacuum distillation to remove the excess and residual unreacted materials.

Synthesis of Schiff base compounds

Schiff base compounds were synthesized following the procedure established by Aiad *et al.*[14] Different alkyl Schiff bases were synthesized through a condensation reaction of the obtained esters from the previous step with *N*,N'-dimethylethylenediamine, in which equimolar amounts were refluxed in ethanol for 12 h. The reaction mixture was left to cool to ambient temperature and then filtered. The products were recrystallized twice from ethanol, washed with water and dried in a vacuum oven at 40 °C. The obtained Schiff bases in this step are:

- (*E*)-4-(((2-(dimethylamino)ethyl)imino)methyl)-2-methoxyphenyl dodecanoate
- (*E*)-4-(((2-(dimethylamino)ethyl)imino)methyl)-2-methoxyphenyl tetradecanoate
- (*E*)-4-(((2-(dimethylamino)ethyl)imino)methyl)-2-methoxyphenyl stearate

Quaternization of the prepared Schiff bases

Schiff bases were quaternized according to the method reported by Shaban *et al.*,[15] by which equimolar amounts of the prepared Schiff bases (from the previous step) were refluxed with benzyl chloride in absolute ethanol for 45 h. The solution was evaporated under reduced pressure. The solid residue was washed with diethyl ether three times to remove the unreacted materials to give the desired cationic surfactants. The obtained products were denoted Q12, Q14 and Q18 and their specific names are, respectively:

- (*E*)-*N*-benzyl-2-((4-(dodecanoyloxy)-3-methoxybenzylidene) amino)-*N*,*N*-dimethylethan-1-aminium chloride
- (*E*)-*N*-benzyl-2-((3-methoxy-4-(tetradecanoyloxy)benzylidene) amino)-*N*,*N*-dimethylethan-1-aminium chloride
- (*E*)-*N*-benzyl-2-((3-methoxy-4-(stearoyloxy)benzylidene) amino)-*N*,*N*-dimethylethan-1-aminium chloride

Confirmation of chemical structure of the prepared Schiff base cationic surfactants

The new prepared Schiff base cationic surfactants were characterized using Fourier transform infrared (FTIR) and ^{1}H-nuclear magnetic resonance (NMR) spectroscopy. The FTIR spectra were performed by NICOLET IS-10 FT-IR spectrophotometer using KBr pellet with spectrum of wave number range 4000–400 cm^{-1} with an accuracy of 2 cm^{-1} and the ^{1}H-NMR spectra were characterized using BRUCKER BioSpin GmbH technique.

Evaluation of the synthesized surfactants as a biocide to control microbial-influenced corrosion

Surface activity of the synthesized surfactants

Surface tension (γ). The surface tension of the synthesized surfactant was determined with a K6 tensiometer instrument (Krüss Co., Hamburg, Germany), using ring method.[15] Distilled water was used for the preparation of different concentrations from Q12, Q14 and Q18. Concentrations from 0.01 to 10^{-6} mol L^{-1} were prepared and their surface tension was determined. All analyses were done in triplicate and the average was taken. Surface tension plots against the log of concentration were made and the critical micelle concentration (CMC) value for each compound was determined.

Effectiveness (π_{CMC}). The surface tension value (γ) at the π_{CMC} point was used to calculate the surface pressure (effectiveness) value according to the following equation[16]:

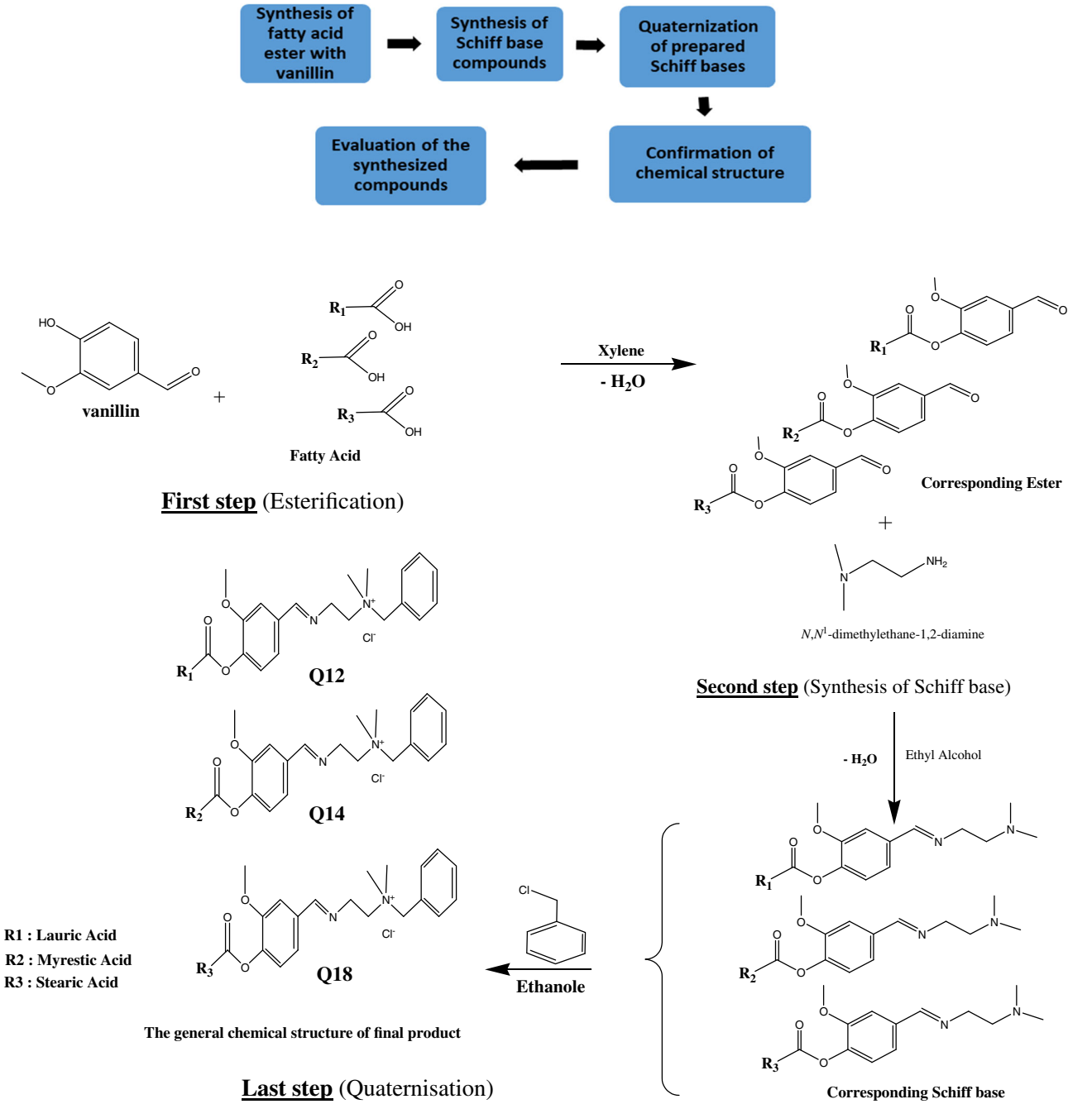
$$\pi_{CMC} = \gamma_0 - \gamma_{CMC} \quad (1)$$

where γ_0 represents the value of surface tension of pure distilled water. The second variable γ_{CMC} represents the value of surface tension of surfactant solution (Not distilled water) at the Critical Micelle Concentration. And CCMC represents the concentration of surfactant solution at CMC point.

The most effective surfactant is that which gives the greatest lowering in the surface tension at the C_{CMC} point.

Surface excess concentration (Γ_{max}). The surface excess concentration of the synthesized surfactant was determined according to Gibbs' adsorption equation:

$$\Gamma_{max} = \left(\frac{-1}{nRT}\right)\left(\frac{d\gamma}{d\ln C}\right) \quad (2)$$



Scheme 1. Steps in the synthesis of the cationic surfactant

where Γ_{max} is the surface excess concentration of surfactant ions, n is the number of species ions in solution, R is the gas constant, T is the absolute temperature, γ is the surface tension at a specific concentration and C is the concentration of a surfactant. A surfactant that reduces the surface energy is one that exists in excess concentration near the interface.

Minimum surface area (A_{min}). The area occupied by one molecule in nm^2 at the interface is defined as a minimum surface area (A_{min}). It is calculated as follows:[17]

$$A_{min} = \frac{10^{16}}{\Gamma_{max} N_A} \quad (3)$$

where N_A is Avogadro's number and Γ_{max} (mol cm^{-2}) is the maximal surface excess of the adsorbed surfactant molecules on to the interface.

Conductivity (K). Conductivity was determined according the method reported by Bao *et al.*[18] using the Cond 3210 SET 1, Probe TetraCon 325 (Wissenschaftlich-Technische Werkstattern)

apparatus for measuring the specific conductivity of the prepared cationic surfactants in aqueous solution at 25 °C in order to evaluate the C_{CMC} value and the degree of counterion dissociation (β). The C_{CMC} value calculated from the electrical conductivity was used to confirm the C_{CMC} value detected from the previous surface tension results, where the specific conductivity is linearly correlated with a surfactant concentration in both a premicellar and a postmicellar region. The intersection point between the two lines gives the C_{CMC} value, while the ratio between the two slopes gives the β value.

Standard free energy of micellization (ΔG^o_{mic}). Standard free energy of micellization per mole of CMC was evaluated as follows:

$$\Delta G_{mic}{}^{O} = (2-\beta)RT\ln C_{CMC} \quad (4)$$

where β is the degree of counterion dissociation, R is the gas constant, T is temperature and C_{CMC} is the molarity of the synthesized surfactant.

BIOCIDAL EFFECT OF THE SYNTHESIZED SURFACTANTS ON SRB

Formation water samples were collected from an oilfield production tank located at North Bahrya Petroleum Co. (NORPETCO), Egypt. The physicochemical characterization of the collected water samples is illustrated in Table 1. The cultivation study was performed as a mixed culture of the total endogenous sulfidogenic bacteria, and the antimicrobial activities of the synthesized surfactants were studied.

Water samples were collected by disposable syringe and *in situ* inoculated into prepared anaerobic selective media called modified Postgate's B medium, as reported by Postgate,[11] using the same water salinity as the water sample. The medium was inoculated with the water sample 10% (v/v) under anaerobic conditions and incubated for 14 days at 37 °C until black precipitates of iron sulfide appeared, which is the indicator of the presence of SRB. Positive vials were subcultured three times in order to obtain fresh active bacterial colonies to use as inocula for further experiments.

Experimental setup for microbial corrosion study

A customized experiment was used for this study, using two groups of bioreactors consisting of 125 mL glass serum bottles closed with rubber stoppers, containing carbon steel coupons with a composition (wt%) of 0.21 C, 0.035 Si, 0.025 Mn and 0.082 P, the remainder being Fe as the sole iron source. The first groups of iron coupons were designed having dimensions of 10 × 10 × 2 mm coated with inert Teflon, except the top surface, which had an area of 100 mm.[2] This surface was then exposed to the culture medium in order to study the activity of SRB and biofilm formation. The second group had dimensions of 20 × 60 × 2 mm and were used for weight loss experiments. All coupons were sequentially polished with 180, 400 and 600 grit sandpapers, rinsed with distilled water and then with isopropanol and finally, sterilized with UV light for l5 min.

Table 1. Physicochemical characterization of the collected formation water sample

Item	Concentration (mg L^{-1})
Sulfate	150
Iron	16.5
Magnesium	1020
Calcium	1040
Salinity as NaCl	53 000
Specific gravity	1.05504
pH	7.1
Temperature	35 °C

Table 2. Composition of Postgate C medium

Ingredient	Concentration (g L^{-1})
Sodium lactate	6.0
Na_2SO_4	4.5
NH_4Cl	1.0
Yeast extract	1.0
KH_2PO_4	0.5
Sodium citrate.$2H_2O$	0.3
$CaCl_2.6H_2O$	0.06
$MgSO_4.7H_2O$	0.06
$FeSO_4.7H_2O$	0.004
pH	7.4

In order to investigate the effect of the synthesized surfactants on SRB activity, 75 mL of modified Postgate's C growth medium[11] (Table 2) was used in this experiment in each reactor. Iron coupons were immersed in the medium and then sparged with nitrogen according to the modified Hungate's technique for anaerobes to ensure anaerobic conditions.[19] After autoclaving, a 3-day seed culture (10%, v/v) was used as inoculum and different concentrations (500, 1000, 1500, 2000 mg L^{-1}) of the prepared cationic surfactants were injected separately into each bioreactor except the control. All steps were performed in an anaerobic cabinet.

Samples were taken periodically from each reactor to estimate the biogenic sulfide, which is the metabolic product of sulfidogenic bacteria, using a spectrophotometer (model DR3900, Hach, Loveland, CO, USA) and to examine the viable bacterial counts using the most probable number (MPN) method[20] through different phases of the bacterial growth curve.

After the end of the incubation period (30 days), the metal coupons were removed from the bioreactors. The first group was fixed with 3% glutaraldehyde–phosphate-buffered saline (PBS; pH 7.3–7.4) for 6 h, washed twice with PBS (5 min each), rinsed with distilled water twice (5 min each) and then dehydrated using an ethanol gradient (50%, 75%, 95% and 99%) for 10 min before storage in a desiccator. After that, the entire surface area of coupons was examined by scanning electron microscopy (SEM) for biofilm observation; surface images of iron coupons were recorded using a Quanta FEG 250 scanning electron microscope (FEI Co., Hillsboro, OR, USA), available at the Egypt Desalination Research Center of Excellence (EDRC), Cairo.

The second group of coupons (weight loss coupons) were removed from the medium, polished using a hard plastic brush with hot water and then with ethanol to remove the corrosion products, dried and weighed accurately according to ASTM G1-72 (reapproved 2004 Standard, 2011). The test was replicated three times and total weight loss was calculated. The corrosion rate R and the inhibition efficiency (η %) were then calculated using the following equations:[21]

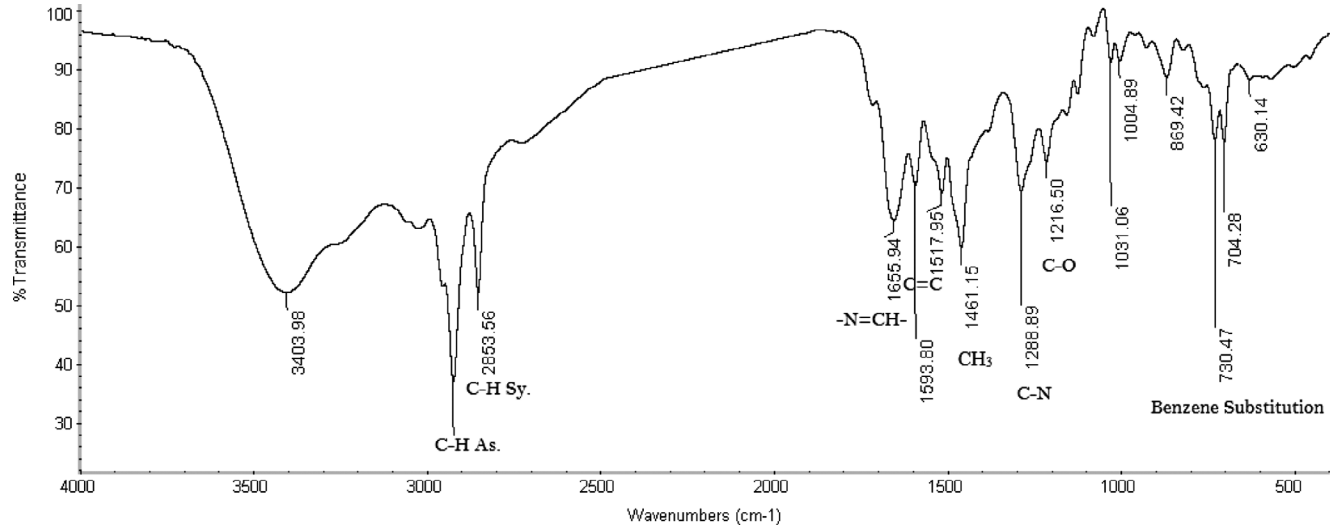


Figure 1. FTIR spectrum for Q18 surfactant.

$$R = \frac{W}{At} \quad (5)$$

$$\eta\% = \frac{R_o - R}{R_o} \times 100 \quad (6)$$

where W is the average weight loss, A the total area of the specimen, t is immersion time, and R_o and R are the values of the corrosion rate without and with addition of the cationic surfactant, respectively. In addition, the minimum inhibitory concentration (MIC) of the synthesized cationic surfactant against the target bacteria was tested. MIC is defined as the lowest concentration of a biocide that completely inhibits the microbial growth of the specific organism being tested.[4] The test was conducted according to ASTM D4412-84.[22]

RESULTS AND DISCUSSION

Confirmation of chemical structure of the synthesized cationic surfactants

FTIR analysis (Fig. 1) confirmed the expected functional groups. The prepared cationic surfactants had nearly the same main characteristic bands; for example, compound Q18 showed stretching vibration bands of —C—H aliphatic symmetric and asymmetric at 2853.56 cm^{-1} and 2924.47 cm^{-1} respectively. The presence

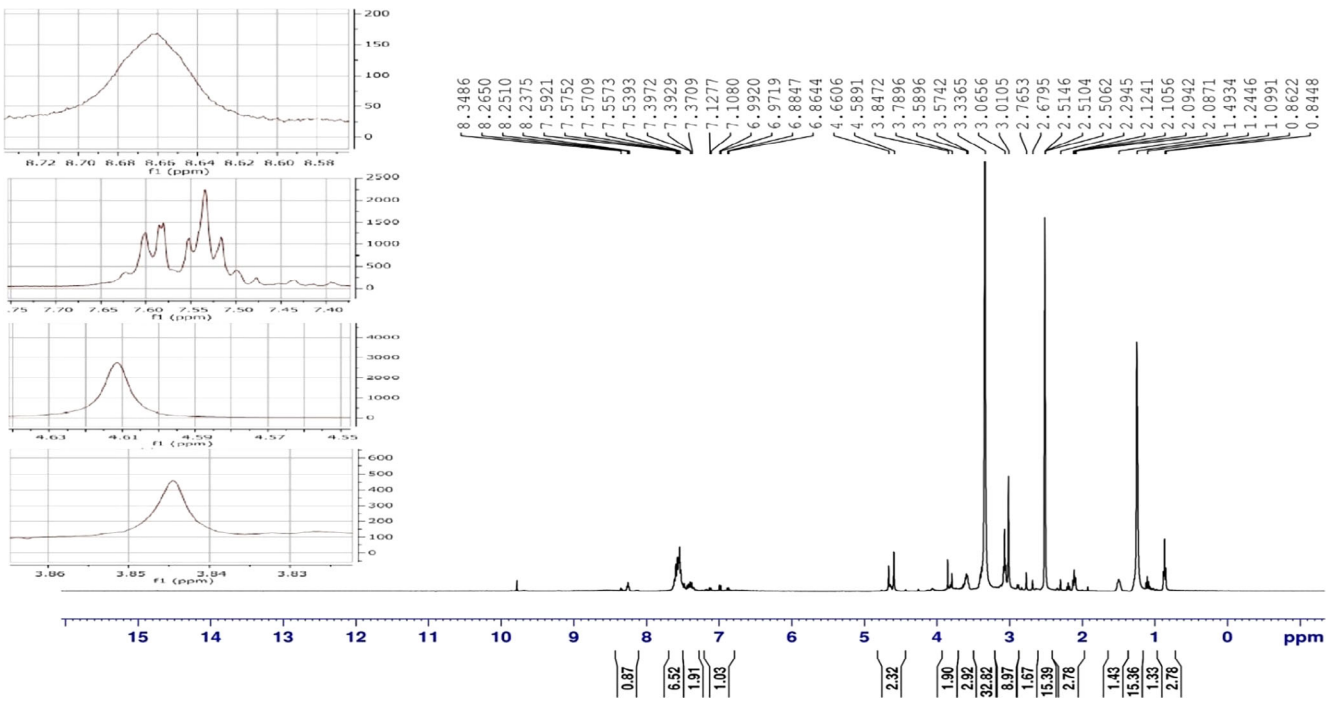


Figure 2. ^{1}H-NMR spectrum for Q18 surfactant.

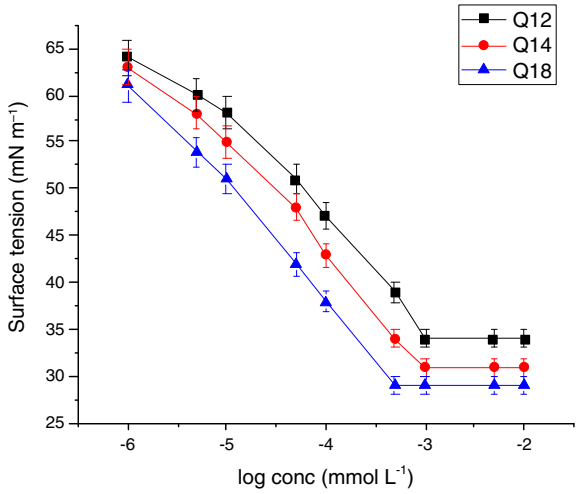


Figure 3. Surface tension of Q12, Q14 and Q18.

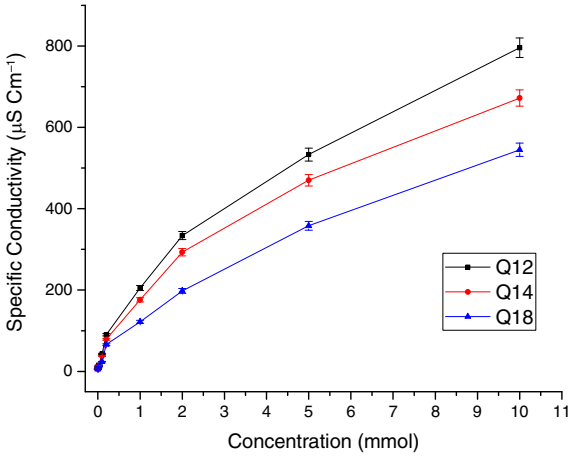


Figure 4. Specific conductivity of Q12, Q14 and Q18.

of bands at 1461.15 cm^{-1} for symmetric bending (CH_3) and the appearance of —N═CH— stretching at 1655.94 cm^{-1} proves the occurrence of the coupling reaction, and 1288.89, 1216.5, 1711.93 and 1517.97 cm^{-1} for C—N, C—O, C═O (carbonyl ester) and C═C aromatic stretching, respectively.[14,15]

The chemical structure of the synthesized cationic surfactants was also confirmed using ^{1}H-NMR spectra, which confirmed the distribution and number of protons. The spectrum of the synthesized cationic surfactant showed different characteristic peaks and had the following ^{1}H-NMR signals, as shown in Fig. 2. For the compound Q18, the^{1}H-NMR spectra depicted the following signals: δ = 0.88 ppm (t, 3H, CH_3 alkyl chain) terminal methyl group; δ = 1.27 ppm (m, 28H, $CH_3(CH_2)_{14}CH_2CO$) repeated methylene group; δ = 1.50 ppm (m, 2H, CH_2CH_2CO); δ = 2.1 ppm (t, 2H, CH_2CH_2CO); δ = 3.1 ppm (s, 6H, CH_2 $N^{\oplus}$ $(CH_3)_2$); δ = 3.35 ppm (t, 2H, $CH_2CH_2N^{\oplus}$ $(CH_3)_2$ CH_2); δ = 3.64 ppm (t, 2H, $CH_2CH_2N^{\oplus}$ $(CH_3)_2$ CH_2); δ = 3.84 ppm (s, 3H, CH_3—O); δ = 4.61 ppm (s, 2H, benzene ring CH2 $N^{\oplus}$); δ = 7.4–7.6 ppm (m, 8H, ph CH═N CH_2CH_2 $N^{\oplus}(CH_3)_2CH_2$ ph); δ = 8.66 ppm (s, 1H, ph CH═N CH_2 $N^{\oplus}(CH_3)_2CH_2$ ph. The data from the ^{1}H-NMR spectrum demonstrated the expected hydrogen proton distribution in the synthesized CMS, indicating no byproduct. For the compound Q14, the^{1}H-NMR spectra depicted the following signals: δ = 0.86 ppm (t, 3H, CH_3 alkyl chain) terminal methyl group; δ = 1.24 ppm (m, 28H, $CH_3(CH_2)_{14}CH_2CO$) repeated methylene group; δ = 1.49 ppm (m, 2H, CH_2CH_2CO); δ = 2.2 ppm (t, 2H, CH_2CH_2CO); δ = 3.33 ppm (s, 6H, CH_2 $N^{\oplus}$ $(CH_3)_2$); δ = 3.58 ppm (t, 2H, $CH_2CH_2N^{\oplus}$ $(CH_3)_2$ CH_2); δ = 3.78 ppm (t, 2H, $CH_2CH_2N^{\oplus}$ $(CH_3)_2$ CH_2); δ = 3.84 ppm (s, 3H, CH_3—O); δ = 4.58 ppm (s, 2H, benzene ring CH2 $N^{\oplus}$); δ = 7.3–7.59 ppm (m, 8H, ph CH═N CH_2CH_2 $N^{\oplus}(CH_3)_2CH_2$ ph); δ = 8.34 ppm (s, 1H, ph CH═N CH_2 CH_2 $N^{\oplus}(CH_3)_2CH_2$ ph. The data from the ^{1}H-NMR spectrum demonstrated the expected hydrogen proton distribution in the synthesized CMS, indicating no byproduct. For the compound Q12, the ^{1}H-NMR spectra depicted the following signals: δ = 0.86 ppm (t, 3H, CH_3 alkyl chain) terminal methyl group; δ = 1.24 ppm (m, 28H, $CH_3(CH_2)_{14}CH_2CO$) repeated methylene group; δ = 1.50 ppm (m, 2H, CH_2CH_2CO); δ = 2.1 ppm (t, 2H, CH_2CH_2CO); δ = 3.35 ppm (s, 6H, CH_2 $N^{\oplus}$ $(CH_3)_2$); δ = 3.59 ppm (t, 2H, $CH_2CH_2N^{\oplus}$ $(CH_3)_2$ CH_2); δ = 3.78 ppm (t, 2H, $CH_2CH_2N^{\oplus}$ $(CH_3)_2$ CH_2); δ = 3.84 ppm (s, 3H, CH_3-O); δ = 4.62 ppm (s, 2H, benzene ring CH2 $N^{\oplus}$); δ = 7.3–7.6 ppm (m, 8H, ph CH═N CH_2CH_2 $N^{\oplus}(CH_3)_2CH_2$ ph); δ = 8.4 ppm (s, 1H, ph CH═N CH_2 CH_2 $N^{\oplus}(CH_3)_2CH_2$ ph. The data from the^{1}H-NMR spectrum demonstrated the expected hydrogen proton distribution in the synthesized CMS, indicating no byproduct.

Surface activity of the synthesized surfactants

The objective of investigating the surface activity of the three synthesized cationic surfactants was to highlight the effect of their molecular structure on the adsorption behavior as well as their adsorption affinity on the interface and/or aggregate in micelles in the oil–water system, which is essential for their field application. Studying the adsorption and micellization behavior is therefore crucial and plays a major role in several interfacial applications of surfactant solutions, including solubilization, emulsification, corrosion inhibition and also the biological activity of these compounds.

The surface tension plots of the new synthesized surfactants in aqueous medium against the log of concentration are shown in Fig. 3. As can be seen, the surface tension significantly decreased with increase in the surfactant concentration in the aqueous medium until an inflection point was reached which corresponded to the critical micelle concentration. The surface tension

Table 3. Critical micelle concentration (C_{CMC}), surface tension (γ_{CMC}), maximum surface excess (Γ_{max}), minimum area (A_{min}), effectiveness (π_{CMC}), degree of counterion dissociation (β) and free energy of micellization (ΔG_{mic}) of the synthesized surfactants at 25 °C

Cationic surfactant	C_{CMC}(mmol L^{-1}	γ_{CMC}(mN m^{-1}	π_{CMC}(mN m^{-1})	$\Gamma_{max} \times 10^{10}$(mol cm^{-2})	A_{min}(nm^2)	β	ΔG_{mic}(kJ mol^{-1})
Q12	0.1	34	38	1.57	105.27	0.421048	−22.8234
Q14	0.12	31	41	1.82	91.06	0.442937	−22.3716
Q18	0.062	29	43	1.996	83.22	0.464827	−24.008

Table 4. The most probable number and biogenic sulfide concentration through the incubation period with different doses of synthesized cationic surfactant

		Q12		Q14		Q18		Control[a]	
Conc. (ppm)	Incubation period(days)	MPN cells(mL^{-1})	Sulfide (mg L^{-1})	MPN cells(mL^{-1})	Sulfide (mg L^{-1})	MPN (cells mL^{-1})	Sulfide (mg L^{-1})	MPN cells(mL^{-1})	Sulfide (mg L^{-1})
Untreated (control)									
	Zero time	—	—	—	—	—	—	10	5
	10	—	—	—	—	—	—	2.4×10^8	230
	20	—	—	—	—	—	—	2.9×10^8	250
	30	—	—	—	—	—	—	4.6×10^6	236
500	Zero time	11	5	21	4	24	7	—	—
	10	7.5×10^3	66	3.8×10^4	70	1.1×10^3	36	—	—
	20	2.7×10^4	74	3.5×10^4	88	2.1×10^3	47	—	—
	30	1.5×10^2	71	9.3×10^2	80	1.2×10^2	42	—	—
1000	Zero time	43	7	64	5	9.2	4	—	—
	10	Nil	6	23	18	Nil	6	—	—
	20	Nil	7	11	14	Nil	6	—	—
	30	Nil	5	Nil	15	Nil	4	—	—
1500	Zero time	1.4×10^2	3	3.6×10^2	4	1.5×10^2	4	—	—
	10	Nil	4	Nil	5	Nil	4	—	—
	20	Nil	3	Nil	3	Nil	5	—	—
	30	Nil	2	Nil	4	Nil	3	—	—
2000	Zero time	92	4	11	3	23	6	—	—
	10	Nil	5	Nil	4	Nil	5	—	—
	20	Nil	5	Nil	4	Nil	6	—	—
	30	Nil	1	Nil	2	Nil	2	—	—

Cultures injected by the synthesized cationic surfactants Q12, Q14 and Q18.
[a] Control: culture medium with iron coupon and bacteria without surfactant.

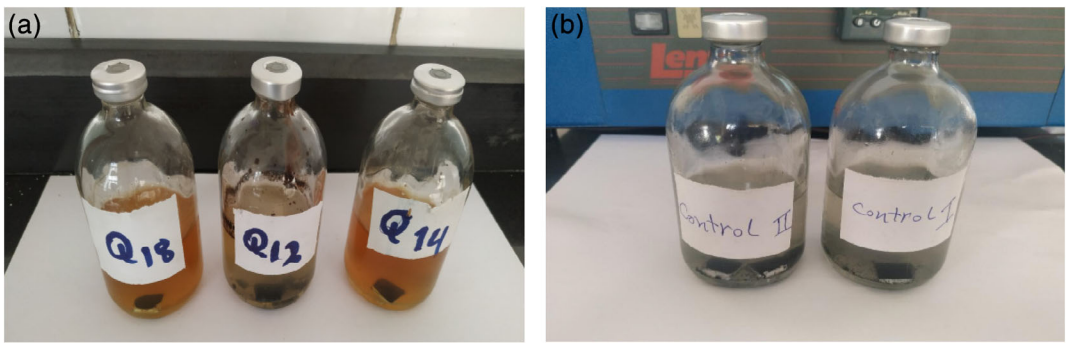


Figure 5. (a) Growth medium with iron coupons injected with 1000 mg L^{-1} synthesized surfactants Q12, Q14 and Q18 compared with control samples (b).

was 29, 31 and 34 mN m^{-1} for Q18, Q14 and Q12, respectively. A progressive fall in CMC values of investigated surfactants was noted in accordance with the lengthening of the alkyl chain (*n*). This is likely due to the enhancement of hydrophobicity with the number of methylene groups in chains that would make aggregation within the bulk solution easier for surfactant molecules.

The effectiveness is the difference between the surface tension of pure water and the surface tension of surfactant solution at the critical micelle concentration. From Table 3, it can be depicted that the surfactant Q18 was the most effective, as it gave the largest reduction in surface tension at CMC. This was attributed to the increase in alkyl chain length, which led to an increase in hydrophobicity, promoting migration of the methylene group to the surface to avoid interaction with the polar medium, hence leading to the recorded decrease in surface tension.[23]

Other important parameters to evaluate the surface activity of the surfactants are the maximum surface excess concentration (Γ_{max}) and the minimum surface area per molecule (A_{min}) at the air–water interface. These parameters give insight into the interfacial adsorption efficiency of the synthesized surfactants at the aqueous solution interface. It can be concluded from Table 3 that the values of Γ_{max} increased but the A_{min} decreased by increasing the hydrocarbon chain length, which might have made the

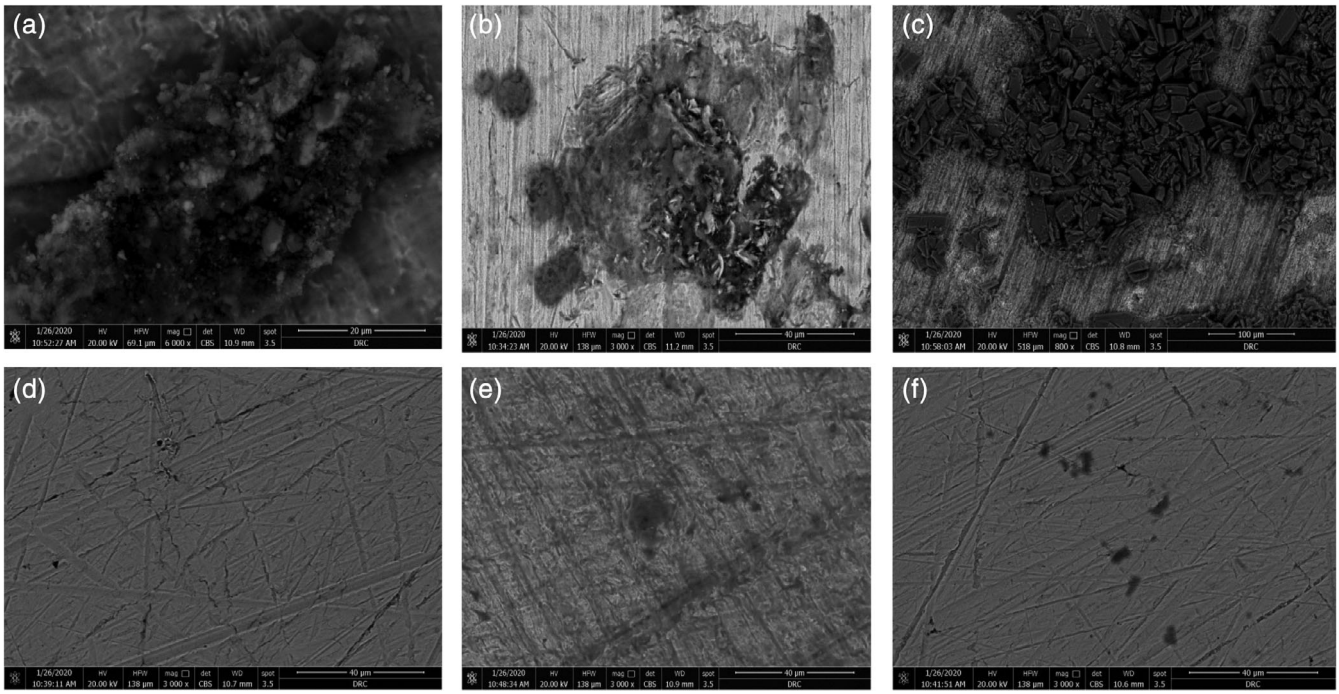


Figure 6. Surface of coupons inoculated with SRB in the absence (a, b, c) and presence of 100 mg L^{-1} cationic surfactants Q18 (d), Q14 (e) and Q12 (f) after 30 days of incubation.

surfactant molecules more tightly packed. The results revealed that by increasing the hydrophobic chain length, as in the case of compound Q18, hydrophobicity increased. Consequently, the surfactant molecules were directed towards the interface. The surface energy of the solution therefore decreased, which in turn led to an increase in the maximum surface excess. These observations were in line with previously reported data.[24] A large value of Γ_{max} implied the adsorption of more surfactant molecules on the solution surface, which also meant a lowering in surface tension. A low A_{min} value suggested the tight packing or full surface coverage by the prepared surfactants at the interface.[25] The decrease in surface tension and A_{min} value demonstrates that this compound might act also as an appropriate corrosion inhibitor.

The negative values of ΔG_{mic} for the synthesized surfactants demonstrated that both processes were spontaneous and represented a tendency of the synthesized surfactant molecules to be adsorbed at the interface.[26] There was an increase in ΔG_{mic} negative value by increasing the hydrophobic chain of the surfactant molecule (Table 3). This result means that compound Q18 might have been adsorbed at the interface faster than Q14 and Q12. The critical micelle concentrations have also been evaluated by conductivity measurement and its values were in agreement with the CMC values determined from the surface tension values. Figure 4 shows the variation in conductivity with concentration for Q18, Q14 and Q12 surfactants. The CMC values were determined from the break points in the curves of specific conductivity (K) versus surfactant concentration (C). In addition, the ratio between the two slopes gave the β values.

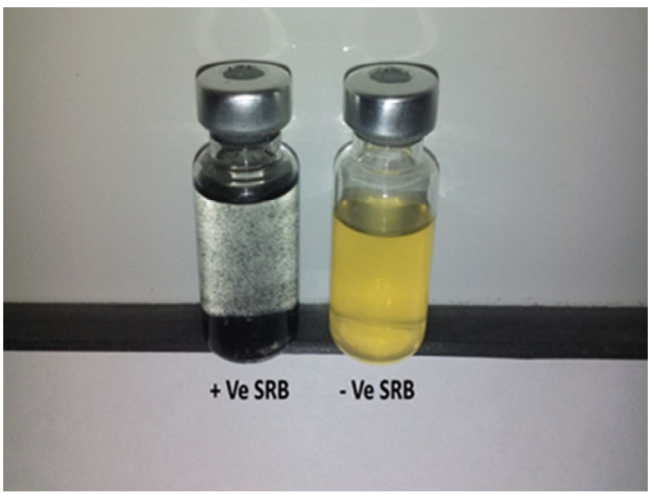


Figure 7. Another colorimetric factor elucidating planktonic SRB growth in Postgate medium B with and without surfactant treatment.

Table 5. Minimum inhibitory concentration of the synthesized cationic surfactants against planktonic SRB

	MPN		
Dose (ppm)	Q12	Q14	Q18
Negative control	1.4×10^7	1.4×10^7	1.4×10^7
250	1.1×10^4	1.2×10^5	1.6×10^5
500	2.3×10^3	2.8×10^4	7.5×10^2
750	1.2×10^2	1.6×10^3	Nil
1000	Nil	Nil	Nil
1500	Nil	Nil	Nil
2000	Nil	Nil	Nil

Table 6. Weight loss, corrosion rate and corrosion inhibition efficiency of the newly synthesized cationic surfactants

Synthesized cationic surfactant	Dose(mg L^{-1})	Weight loss(mg)	Corrosion rate R(mg cm^{-2} d^{-1})	Inhibition efficiency η(%)
Q12	250	56.4	0.07	81.3
	500	14.6	0.018	95.2
	1000	14.1	0.017	95.4
	1500	12.2	0.015	96
	2000	10.3	0.012	96.6
Q14	250	63.1	0.077	79.3
	500	15.4	0.019	94.9
	1000	12.6	0.015	95.8
	1500	11.7	0.014	96.1
	2000	11.3	0.0138	96.3
Q18	250	39.3	0.048	87
	500	10.6	0.013	96.5
	1000	8.1	0.01	97
	1500	5.8	0.007	98.1
	2000	4.5	0.005	98.5
Control	—	306.00	0.375	—
Blank	—	2.00	0.002	—

Biocidal effect of the synthesized cationic surfactants on SRB

In this area of study, investigations of antimicrobial activity of synthesized surfactants were carried out by different methods. Table 4 illustrates the bacterial cell count by most probable number method along different phases of growth with different doses of synthesized cationic surfactant; the results revealed that the three synthesized surfactants have a high inhibition effect from 4.6×10^6 cells mL^{-1} for control until the bacterial cell count was reduced to 1.5×10,^{2} 9.3×10^2 and 1.2×10^2 cells mL^{-1} for Q12, Q14 and Q18, respectively, after 1 month of cultivation with a dose of 500 mg L^{-1}. Moreover, the synthesized surfactants revealed a complete inhibition effect with higher surfactant doses.

The results of biogenic sulfide productivity showed growth and sulfate reduction behavior for SRB by oxidizing organic compounds or by using hydrogen (electron donor) to reduce sulfate to sulfide.[27] The MPN results were in agreement with sulfide concentration measurements, as shown in Table 4. There was a considerable decline in the biogenic sulfide concentration from a dose of 500 mg L^{-1} until achieving a complete suppression at doses of 1000 mg L^{-1} after 30 days of incubation in the three synthesized surfactants, but Q18 was the most effective . Inhibition of sulfide productivity is a critical main effect in the MIC process; it has been stated that, in addition to its precipitation in the form of FeS on the metal surface, hydrogen sulfide may increase metal corrosion as a source of bound protons.[28]

Figure 5 shows the growth medium and iron coupons in bottles with and without surfactants after the end of the incubation period. The turbidity indicating microbial growth, FeS precipitate and deterioration of the C-steel coupons are obvious in the absence of surfactants, unlike the case in the presence of surfactants.

The efficiency of synthesized surfactants in mitigating the microbial corrosion process was also confirmed by examining the metal surface under SEM. Figure 6(A–C) displays severely corroded carbon steel surfaces, with the formation of extra polymeric substances (EPS; Fig. 6A,B), in addition to different forms of corrosion products, e.g. iron sulfide (Fig. 6C), at the end of the incubation period (30 days), in the absence of surfactants. Bacterial colonization, with the concomitant formation of EPS and iron sulfide deposits as the result of bacterial growth and the formation of biofilms on the metal surface, were very obvious in the absence of the three prepared surfactants. On the other hand, minimal corrosion damage on the surface of other steel samples was observed at the end of the incubation period (30 days) in growth medium injected with synthesized surfactants at a concentration of 1000 mg L^{-1} (Fig. 6D–F). The surface was free from biofilm and iron sulfide and coated entirely with the surfactant molecules where the polishing marks were still visible. This result indicated an effective surfactant protective film formation over the metal surface and revealed the highest inhibition efficiency of surfactant on the sessile SRB. Biofilm formation is known to subsequently alter electrochemical processes on the steel surface.[29] These alterations include H_2S production, pH changes, iron sulfide formation and also EPS production. These factors are collectively known to enhance and accelerate the microbial corrosion process.[30]

In order to study in depth the antimicrobial effect of the three synthesized surfactants against planktonic SRB, a separate experiment was conducted in order to estimate the MIC of these compounds against consortia of planktonic SRB. In the control sample (positive SRB, Fig. 7), black color was seen in the culture vials due to the existence of planktonic SRB. The SRB converts sulfate to sulfide, and the sulfide then reacts with iron present in the medium and forms FeS. But in the presence of synthesized cationic surfactants SRB growth was suppressed and the black color disappeared (negative SRB, Fig. 7).

The data in Table 5 represent the most probable number of SRB in the presence of different concentrations of the three synthesized surfactants (Q12, Q14 and Q18). The data show that the best inhibition efficiency was noted in compound Q18, where the count reduced from 1.4×10^7 for control to 7.5×10^2 bacterial cells mL^{-1} at a dose of 500 mg L^{-1} and complete inhibition occurred at 750 mg L^{-1}. As it contained the longest alkyl chain (C18), the hydrophobic moiety for the synthesized surfactants

Table 7. Comparison of inhibition efficiency of the synthesized cationic surfactants with those of previously published cationic and anionic surfactants

Inhibitor name	Inhibition efficiency (%)	Reference
Cationic gemini surfactant (NCGS)	97	42
Cationic gemini surfactant (SCGS)	96	43
Cationic monomeric surfactant (CMS)	92	24
Cationic gemini surfactant (CGS)	94	
Sodium dodecyl benzene sulfonate	84	44
Sodium dialkyl 3,6,9,12,15,18,21,24-octaoxahexacosane-1,26-diyl bis (phosphate) anionic surfactant	94.4	45
Three new Schiff base compounds	94–96	46
Three gemini cationic surfactants	83.6–90.2	47
Three ionic liquid-based gemini cationic surfactants	90.5–94	48
Series of Schiff base cationic surfactants	96.3–98.5	This study

increased. It has been found that with increase of hydrophobic chain carbon length antibacterial activity increased. Thus the difference in biological activity might be dependent on the length of the hydrophobic portion and also the interfacial properties for the synthesized surfactants. A similar observation was reported by Rosen *et al.*[31] However, the contrary was reported by Shaban *et al.*[32]

Moreover, the antimicrobial action of the synthesized surfactants also depends on the presence of a quaternary group as a hydrophilic portion, which influences the adsorption of the surfactant molecules on the surface of the bacterial cell and acts by interrupting the cell membrane.[33] Cationic surfactant is known as a type of surfactant where the head part bears a positive charge and is characterized by its high efficiency as a biocide as well as a corrosion inhibitor, as it is partially or completely adsorbed at the interface (metal/liquid) and protects the metal surface from bacterial growth.[34] Thus the mode of action of that type of compound (surfactant) on various microorganisms can be related to the adsorption of surfactant molecules on the outer cell membrane of the microorganisms due to their amphipathic characteristics, as well as the similarity between the hydrophobic chain to the lipid layer and the building units of the cell membranes. In addition, the cytoplasmic membrane consists of a phospholipid bilayer where proteins are anchored and is the target of cationic surfactants. The outer surface in the bacterial cell wall carries a negative charge; the cationic antimicrobial surfactants interact and are adsorbed on to the cell surface. As a result of this adsorption, the surfactant molecules penetrate the cell membrane, causing cell damage. The positive charges of cationic molecules, moreover, neutralize the negative charges on the bacterial cell membranes and migrate into the cytoplasmic membrane of the cell. Accordingly, the selective permeability that characterizes the outer cell membrane is deactivated completely; such interaction disorganizes growth, which is sufficient to cause fluidity loss of the membrane, causing cell death. This mechanism is also called electrostatic interaction, as has been reported previously.[35–38] In general, the newly synthesized cationic surfactants showed good antimicrobial effect against SRB as a consortium, with compound Q18 revealing maximum activity.

The data in Table 6 demonstrate the weight loss and microbial corrosion rate due to SRB growth and microbial corrosion inhibition efficiency in the absence and presence of different doses of the three synthesized cationic surfactants.

The corrosion rate was 306 mg cm^{-2} d^{-1} in control sample (i.e. in the presence of SRB and absence of surfactants), which was significantly higher than the blank sample (i.e. in the absence of SRB and surfactants) and treated samples (i.e. in the presence of SRB and surfactants). It has been found that the efficiency of the newly synthesized cationic surfactants decreased the corrosion rates of C-steel in the SRB culture medium, and its inhibition efficiencies were dependent on its concentration. Also, it is clear that the gradual increase in surfactant concentration from 250 to 2000 mg L^{-1} decreased the bio-corrosion rate. The increase of efficiency η with increasing surfactant concentration might have contributed to surfactant molecule adsorption on a steel surface, which might have increased the metal surface coverage.[39] Consequently, that protected the metal surface from SRB activity. Also, to understand what was happening in the absence of surfactants (control sample), it was important to shed light on the cathodic depolarization theory, whereby SRB cultivated in an anaerobic environment can utilize the hydrogen or organic compounds (as an electron donor), with sulfate (as an electron acceptor) being reduced to sulfide, and the following overall corrosion reaction occurs:

$$4Fe + SO_4^{2-} + 4H_2O \rightarrow 3Fe(OH)_2 + FeS + 2OH^-$$

According to this reaction, SRB enhances the corrosion rate of metal by their continuous consumption of atomic hydrogen accumulating at the cathodic site by hydrogenase enzymes. Consequently, this leads to an increase in metal dissolution and accumulation of corrosive sulfide.[40,41]

CONCLUSION

In this study, the synthesized cationic surfactants played a role in microbial corrosion inhibition as well as functioning as bactericides. As they inhibit both SRB growth and sulfide formation, they consequently prevent microbial corrosion. The inhibition efficiency of the three synthesized Schiff base cationic surfactants for carbon steel corrosion was comparative to, and even better than, many ordinary cationic or anionic surfactants, as listed in Table 7. Nevertheless, further toxicity and biosafety studies should be undertaken to assure the benign effect of the prepared surfactants against the non-target organisms, for safe application in real fields. The current study proved that the prepared cationic surfactants with longer hydrophobic chains expressed an efficient bactericidal effect and a pronounced promising anti-biocorrosion behavior. Thus they are recommended for application in petroleum and other industrial facilities. Consequently, further studies are underway to improve and enhance the efficiency of these promising compounds, and, moreover, to approve its feasibility, profitability and ecofriendly behavior relative to conventional commercial applied biocides and corrosion inhibitors. An environmental risk assessment and cost analysis for such an enhanced novel biocide and corrosion inhibitor will be conducted.

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