Efficiency of cationic gemini surfactants with 3-azamethylpentamethylene spacer as corrosion inhibitors for stainless steel in hydrochloric acid

O. Kaczerewska, R. Leiva-Garcia, R. Akid, B. Brycki

PII: S0167-7322(17)31599-4
Reference: MOLLIQ 7940
To appear in: Journal of Molecular Liquids

Received date: 13 April 2017
Revised date: 9 August 2017
Accepted date: 23 September 2017

Please cite this article as: O. Kaczerewska, R. Leiva-Garcia, R. Akid, B. Brycki, Efficiency of cationic gemini surfactants with 3-azamethylpentamethylene spacer as corrosion inhibitors for stainless steel in hydrochloric acid. The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. Molliq(2017), doi:10.1016/j.molliq.2017.09.103

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.
Efficiency of cationic gemini surfactants with 3-azamethylpentamethylene spacer as corrosion inhibitors for stainless steel in hydrochloric acid

O. Kaczerewska¹,²*, R. Leiva-Garcia², R. Akid², B. Brycki¹

¹Laboratory of Microbiocides Chemistry, Faculty of Chemistry, Adam Mickiewicz University in Poznań, Umultowska 89b, 61-614 Poznań, Poland

²School of Materials, University of Manchester, Manchester, M139PL, UK

*corresponding author
e-mail address: olga.kaczerewska@wp.pl

Abstract

The corrosion inhibition efficacy of two cationic gemini surfactants with 3-azamethylpentamethylene spacer on AISI 304 stainless steel in 3 M HCl was investigated by polarisation measurements and electrochemical impedance spectroscopy (EIS). Following corrosion testing, the surface of stainless steel samples was studied by scanning electron microscopy (SEM). The results showed that the effectiveness of corrosion inhibition were up to 95 % depending on the C-chain length and the gemini surfactant concentration. The inhibitive action is due to an adsorption of inhibitor molecules onto the metal surface following a Langmuir adsorption isotherm model. The variation in the cathodic and anodic branches reveals that the surfactants tested act as mixed-type inhibitors. The highest inhibition efficiency was reached around the values of the critical micelle concentration. The results obtained from both polarisation and EIS measurements are in a good agreement.

Keywords

Corrosion inhibitors, gemini surfactants, potentiodynamic, EIS

1. Introduction

Cationic gemini surfactants are an interesting class of chemical compounds. These dimeric surfactants consist of two monomeric moieties linked by a spacer [1], which can be flexible (eg. polymethylene groups) or rigid (eg. benzene ring) [2]. Interest in gemini surfactants arises from their superior aggregation, surface and biological properties compared to conventional analogues. Dicationic compounds strongly reduce the surface tension [3],
exhibit lower critical micelle concentration (CMC) values [4] and so much higher biological activity [5]. In terms of concentration, they are about one to two orders of magnitude more efficient compared to conventional surfactants [1,6,7]. Moreover, from an environmental point of view, dicaticonic compounds are less hazardous than monomeric ones [8]. Due to their excellent properties, gemini surfactants can have many potential industrial applications such as cleaning agents and detergents, biocides, preservatives and solubilisation agents in textile dying [7,9–14]. They can be also applied in nanotechnology as gene delivery agents and supramolecular solvents [15–17]. Recently, greater attention has been paid to the use of gemini surfactants as corrosion inhibitors (CIs) for metals, especially in acidic environments [18–24]. The mechanism of corrosion inhibition is based on the adsorption of surfactant molecules onto the metal surface, replacing water molecules and forming a protective film [25,26]. The process is physicochemical. The electrostatic interactions between positively charged nitrogen atoms and negatively charged metal surface is related to physisorption [27]. Chemisorption is connected with donor-acceptor interactions [28]. Adsorption is favourable due to the presence of electron-rich structures such us heteroatoms with unbounded electrons (N, O, S, P) [29,30] and π electrons (benzene rings, multiple bonds) [22,24] as these can share electrons with the free d-orbitals of metals [27].

A key parameter for using surfactants as corrosion inhibitors is the critical micelle concentration value (CMC), a value related to the surfactant concentration when molecules start forming aggregates (micelles). Typically at this value, surfactants first adsorb onto an interface (air-water, water-metal surface) and then form micelles or multilayers. The CMC value depends on the chemical structure of the gemini surfactants. Increasing the length of the alkyl chain [31,32], the spacer [33] and the number of quaternary nitrogen atoms [34,35] decrease the CMC values. Also, heteroatoms or multiple bonds changes the aggregation properties of the molecules [7,36]. Therefore, the efficacy of corrosion inhibition can be influenced by a reasonable modification of gemini surfactant structure [22].

Corrosion in acidic environments is a serious problem in petrochemical, marine or chemical production [37,38] due to the use of hydrochloric acid solutions [29] for cleaning, pickling, descaling or oil well acidification [26,39]. Every year corrosion results in huge economic losses, decreasing operation efficiency and increasing the risk of accidents [40].

Stainless steels are widely used in industry as construction materials for piping, tanks and vessels etc, [25,38] because of their good corrosion resistance due to the presence of a passive layer (mixed oxide layer) on its surface. Despite the good properties of stainless steel, corrosion may occur and the use of protection systems is needed [41]. One option would be
the use of cationic gemini surfactants, however, there is a lack of information on their performance as corrosion inhibitors for stainless steels. Therefore, in this paper, the efficiency of cationic gemini surfactants with a 3-azamethyl pentamethylene spacer as corrosion inhibitors of stainless steel in 3 M hydrochloric acid is studied by electrochemical techniques and surface morphology analysis by scanning electron microscopy (SEM).

2. Materials and Experimental Techniques

2.1. Cationic surfactants

Gemini surfactants, 3-azamethyl-1,5-pentamethylene-bis(N-dodecyl-N,N-dimethylammonium bromide) (3N-12) and 3-azamethyl-1,5-pentamethylene-bis(N-octadecyl-N,N-dimethylammonium bromide) (3N-18) have been prepared by a method previously described in the literature [7,42]. The chemical structure of the synthesised surfactants is presented in Figure 1.

2.2. Stainless steel

The working electrode was made of stainless steel (AISI 304). The chemical composition of the working electrode in (weight %) being: Cr 17-20, Mn <2, Ni 8-11, C <0.08, Fe balance.

2.3. Electrolytes

The test electrolyte, 3 M HCl was prepared by dilution of analytical grade HCl (32 %) with deionised water. Solutions with different concentrations of inhibitors were prepared from the stock solution of 3 M HCl. The range of concentrations for the compound with twelve carbon atoms in the alkyl chain was: 0.1-2 mM and for the one with eighteen carbon atoms was 0.005-0.1 mM. The concentration chosen were based upon CMC values of the surfactants previously determined by the authors using conductometry methods [43]: 1.06 mM for 3N-12 and 0.076 mM for 3N-18. All experiments were carried out at room temperature in a naturally aerated test solution.

2.4. Electrochemical methods

Electrochemical tests were carried out using a conventional three-electrode cell with a platinum counter electrode, a saturated calomel electrode (SCE) as a reference electrode and a working electrode of stainless steel AISI 304 plate (2.5x2.5 cm). All polarisation curves were recorded using a potentiostat (Versastat™ 4.0). Individual separate anodic and cathodic
potentiodynamic polarisation measurements were obtained by changing the electrode potential automatically from (cathodic) OCP to -300 mV vs the OCP and (anodic) OCP to +300 mV vs OCP, respectively, with a scan rate 0.5 mV s$^{-1}$. Linear polarisation resistance measurements (LPR) were obtained by changing the potential from -20 to 20 mV versus the measured OCP with a scan rate of 10 mV min$^{-1}$. Electrochemical impedance spectroscopy (EIS) measurements were carried out using a potentiostat (Versastat$^\text{TM}$ 4.0). Impedance spectra were obtained over a frequency range of 100 kHz to 10 mHz with a 10 mV sine wave as the excitation signal at open circuit potential. SCE and platinum electrodes were used as the reference and counter electrodes respectively.

2.5. Surface morphology

The morphology of the 304 stainless steel surface after the corrosion test was also studied by scanning electron microscopy (SEM) using a FEI Quanta 200 operating at 20 kV and different magnifications.

3. Results and discussion

3.1. Open circuit potential

Open circuit potential measurements were obtained at room temperature for the stainless steel samples in 3 M HCl without (blank) and with the addition of different concentrations of either 3N-12 or 3N-18 gemini surfactants; Figure 2 shows the trend in the OCP with time. The OCP of the blank solution was $-401$ mV$_{SCE}$ after 1 hour, reaching $-355$ mV$_{SCE}$ after 24h. Adding inhibitors shifted the potential towards more positive values than the values for the blank solution. The stainless steel potential in the blank solutions changed from $-401$ mV$_{SCE}$ to $-355$ mV$_{SCE}$ after 24 hours of immersion. 3N-18 appeared to be the most efficient as the potential increased from $-348$ mV$_{SCE}$ to $-313$ mV$_{SCE}$ (after 24 hours at 0.01 mM). While 1 mM was the best concentration of 3N-12 which shifted OCP from $-352$ mV$_{SCE}$ to $-330$ mV$_{SCE}$.

3.2. Potentiodynamic polarisation measurements

Figure 3 and 4 display the potentiodynamic anodic and cathodic polarisation curves of stainless steel in 3M hydrochloric acid in the presence and absence of the selected inhibitors. It is noticeable that both anodic metal dissolution and cathodic hydrogen evolution reactions were reduced by adding the inhibitors. There is a positive shift for the anodic overvoltage and the cathodic overvoltage compared to the blank solution indicating that the synthesised cationic surfactants act as mixed inhibitors. Moreover, the shape of the branches is similar to
the plots of the blank solution which suggests the corrosion mechanism has not changed and the inhibitors act by an adsorption process onto both anodic and cathodic active sites of the surface [22]. The values of anodic Tafel slope ($b_a$), cathodic Tafel slope ($b_c$), corrosion current density ($i_{corr}$), polarization resistance ($R_p$), corrosion potential ($E_{corr}$) and inhibition efficiency (IE%) were calculated and are listed in Table 1. Here it is observed that $b_a$ values for the inhibited solution are higher when compared to the $b_a$ values of the blank solution, while the $b_c$ values are compared to the blank solution. These results prove that the surfactants act as mixed inhibitors [22]. It was observed that current corrosion density values decreased after adding inhibitors. For the blank solution the $i_{corr}$ value was 2550 μA cm$^{-2}$ (after 24 hours of immersion) whereas in the presence of the inhibitors $i_{corr}$ was 126 μA cm$^{-2}$ and 203 μA cm$^{-2}$ for 3N-12 (1 mM) and 3N-18 (0.01 mM), respectively. $R_p$ values were greater for inhibited solutions; being 126 Ω cm$^2$ and 161 Ω cm$^2$ for 3N-12 (1 mM) and 3N-18 (0.01 mM) respectively compared to the blank solution value of 13 Ω cm$^2$.

Inhibition efficiency was obtained from the following equation (1) [39]:

$$\text{IE} = \left(\frac{i_0 - i}{i_0}\right) \times 100\% \quad (1)$$

Where $i$ and $i_0$ are corrosion current density with and without the inhibitor respectively. The values of current corrosion density were calculated using the Stern-Geary equation (2) [21]:

$$i_{corr} = \frac{(b_a b_c/2.303(b_a+b_c))/R_p}{R_p} \quad (2)$$

From data in Table 1 it was observed that for 3N-12 IE increased with increasing concentration of the inhibitor and reaching the maximum around CMC value (1.06 mM [42]) and the behaviour was previously noticed in literature [44]. On increasing the inhibitor concentration above the CMC, IE values for 3N-12 are quite constant indicating that a stable layer of inhibitors is formed onto the stainless steel surface. Adding additional inhibitor molecules leads to micelles formation which does not change the current corrosion density [45]. This relationship was not observed for 3N-18. The maximum was reached at 0.01 mM (92%) whereas CMC is 0.076 mM. At concentrations higher than critical micellar concentration value, IE decreases. When CMC is discussed it is important to remember that it is not a single value but it is a range of concentrations which is represented by average. Moreover, gemini surfactants with 18 carbon atoms in a hydrophobic tail are more surface active than compounds with 12 carbon atoms which means they form micelles at lower concentrations and also adsorb onto interfaces at lower concentrations. Furthermore,
decreasing inhibition efficiency after reaching the CMC value may be attributed to a steric hindrance and repulsion due to the presence of long alkyl chains [7]. This response is similar to the mechanism of biological activity of cationic surfactants, which also relates to the adsorption onto a negatively charged cell membrane (with respect to the negatively charged metal surface). The biological activity of gemini compounds with C18 in alkyl chains is lower than for C12 due to reflexing of the alkyl chains [46,47].

As mentioned before, the highest inhibition efficiency for 3N-12 (95 %) was reached at 1 mM whereas for 3N-18 (92 %) at 0.01 mM. For compound with 18 carbon atoms in the alkyl chains a similar effect is reached at 100-times lower concentration than for compound with 12 carbon atoms. This is associated with micellization process. Elongating the alkyl chain decreases CMC values and that makes compounds active at lower concentrations [48].

3.3. Electrochemical impedance spectroscopy

Nyquist impedance diagrams (after 24 hours of immersion) for stainless steel in 3 M HCl solution without and with various concentrations of the synthesised gemini surfactants are represented in Figure 5. The plots presented exhibit a semicircular shape with a diameter reflecting corrosion resistance (larger diameter, higher corrosion resistance).

The experimental data was fitted to an equivalent circuit model (Figure 6) using the ZView2© programme. The proposed equivalent circuit consists of a solution resistance (Rs), a constant phase element (CPE-1), related to the capacitive behaviour of the inhibitor film formed on the surface of the metal, in parallel with a resistance (Rin) which is related to defects of the inhibitor film. The second constant phase element (CPE-2) in parallel with a charge transfer resistance (Rct) is related to the interface between the solution in the defects and the metal surface. Polarization resistance (RP) was calculated as the sum of Rs, Rin and Rct [49].

CPE was used to give a more accurate fit to the experimental results by taking into account the non ideal capacitive behaviour of the system [50]. The CPE of each semi-circle was used to derive the layer capacitance (Cl) using the following equation (3) [51]:

\[ C_l = \left( \frac{Q^* R^{1/n}}{R} \right) \]

Where \( n \) is the phase shift, (where \( n=1 \) for ideal capacitive behaviour) [52]. \( R \) is the \( R_{in} \) to obtain the capacitance of the solution and the inhibitor layer and \( R_{ct} \) to obtain the capacitance of the inhibitor layer and the metal. \( C_{l,1} \) is related to inhibitor layer capacitance and as \( R \) in
equation \( 3 \), \( R_n \) wa used. Whereas \( C_{\text{I-2}} \) is related to double layer capacitance and \( R \) in equation 3 was represented by \( R_{\text{ct}} \).

Inhibition efficiency (IE) was calculated using charge transfer resistance values according to the following equation (4) [53]:

\[
\text{IE\%} = \left( \frac{(R_p-R_p^0)}{R_p} \right) \times 100
\]

Where \( R_p \) and \( R_p^0 \) are the charge transfer resistance values with and without inhibitors for stainless steel in 3 M HCl, respectively.

Corrosion rate was calculated using following equation (5) [54]:

\[
\text{Corrosion rate} = i_{\text{corr}} \times A_w \times 10 \times 3.15 \times 10^7 \times nF d
\]

Where \( i_{\text{corr}} \) is the current density [A cm\(^{-2}\)], \( A_w = 56 \text{ g mol}^{-1} \) for iron, \( F \) - Faraday’s constant (96500 C mol\(^{-1}\)), \( n=2 \), \( d \) - density of stainless steel (7.93 g cm\(^{-3}\)), \( 3.15 \times 10^7 \) - one year in seconds and 10 is a conversion factor to obtain the results in mm [54]. The current density was calculated from equation (2).

The impedance parameters obtained by fitting the EIS data to the equivalent circuit, the inhibition efficiency (IE) and corrosion rate (CR) are presents in Table 2.

\( R_p \) values increase with increasing inhibitor concentration and reach the highest values around CMC. The rise in the resistance values indicates a reduction of the stainless steel corrosion rate. The double layer capacitance values decrease in the presence of the tested inhibitors from 4890 to 200 and 268 \( \mu \text{F/cm}^2 \) for 3N-12 and 3N-18, respectively. In the case of the capacitance of the inhibitor layer it can be observed that it decreases with the increase of the inhibitor concentration in the case of the 3N-12. This could be indicating an increase in the thickness of the film as more molecules are joining to the film. Regarding the 3N-18, it can be observed a decrease before the CMC value and how at higher concentrations the capacitance increases again, probably due to the film getting thinner or the interfacial area increased as defects due to the interaction between molecules are formed. The decrease in the capacitance values may also be related to the replacement of the water molecules by the inhibitor molecules according to the following equation (6) [22]:

\[
\text{Inh}_{(\text{sol})} + xH_2O_{(\text{ads})} \rightarrow \text{Inh}_{(\text{ads})} + xH_2O_{(\text{sol})}
\]

Where \( \text{Inh}_{(\text{sol})}/ \text{Inh}_{(\text{ads})} \) are inhibitor molecules in the aqueous phase/adsorbed at the metal surface, \( H_2O_{(\text{ads})}/H_2O_{(\text{sol})} \) are water molecules adsorbed at the metal /in the aqueous phase and x is the molar ratio, the number of water molecules replaced by one inhibitor molecule.
Decrease $C_l$ values result from a decrease of the local dielectric constant and/or increase in the electrical double layer thickness, suggesting the inhibitors act by adsorption at the metal/solution interface \([55,56]\) In the case of 3N-18, at concentration above CMC value (C=1 mM) $C_l$ values increased due to thinning of the protective film.

Figure 7 presents the evolution of the corrosion resistance with immersion time for the tested gemini surfactants.

Initially, after 1h it is suggested that there is not full coverage of the surface by the 3N-12 molecules, the highest concentration of the inhibitor is providing the highest degree of protection, due to the quicker diffusion to the surface and the highest value of $R_p$. With continued immersion (up to 24 hours), the decrease of charge transfer resistance slows down and becomes more constant for both, 1mM and 2 mM solutions than for that of the other concentrations. However, for 3N-18, the concentration higher than CMC values is reducing the protectiveness of the metal from the beginning of the immersion (the highest charge transfer resistance was observed for 0.01 mM solution). Therefore, in the case of the 3N-18 inhibitor, the effect of the steric hindrance and repulsion due to the presence of long alkyl chains is observed from the beginning of the immersion.

The inhibition efficiency of the gemini surfactants obtained from the EIS measurements is in good agreement with the values obtained from the polarisation measurements.

3.4. Adsorption isotherm

The first step of corrosion inhibition is the adsorption of the inhibitor molecules at the metal/solution interface \([22]\). On this basis the data (IE) obtained from the EIS measurements have been converted to surface coverage and then fitted to different theoretical adsorption isotherms \([57]\). The surface coverage ($\theta$) was calculated from equation (7) \([58]\):

$$\theta = \text{IE}\%/100 \quad (7)$$

Analysis of the results suggests the Langmuir adsorption isotherm equation (8) provides the best fitting ($R^2$ close to 1) for the results obtained with the inhibitors \([57,59]\).

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (8)$$

Where C is the inhibitor concentration [mol/dm$^3$] and $K_{ads}$ is the adsorptive equilibrium constant.

A plot of $C/\theta$ vs C is presented in Figure 8. A linear regression was used and intercepts were determined by extrapolation. Each intercept was equal to the reciprocal of the adsorptive
equilibrium constant \((K_{ads})\) [22] and this parameter was used to determine the Gibbs free energy \(\Delta G_{ads}\) based upon equation (9) [29,30]:

\[
\Delta G_{ads} = -RT \ln(55.5K_{ads})
\]  

(9)

Where \(R\) is the gas constant \(8.314 \text{ J mol}^{-1} \text{ K}^{-1}\), \(T\) is temperature (K) and the value 55.5 is the molar concentration of water. The values of \(K_{ads}\) and \(\Delta G_{ads}\) are reported in Table 3.

The calculated \(\Delta G_{ads}\) values are negative indicating the adsorption process is spontaneous and the range of values, between -34.49 and -48.17 kJ/mol, reveal that the process involves both physisorption and chemisorption for 3N-12 and chemisorption for 3N-18. \(\Delta G_{ads} > -20 \text{ kJ/mol}\) indicates pure physisorption, the electrostatic interaction between charged inhibitor molecules and charged metal surface whereas \(\Delta G_{ads} < -40 \text{ kJ/mol}\) involves chemisorption [45].

It can be observed that the fitting in the case of the long chain inhibitor, 3N-18, is not showing perfect linearity to the Langmuir isotherm as a consequence of interactions between molecules, such as steric hindrance and the repulsion of long alkyl chains [60] which was also the reason of taking out the last point in the graph (0.1 mM) from the fitting. Langmuir isotherms are based on certain assumptions such as monolayer adsorption and identical molecules without any lateral interaction. However, the Langmuir isotherm is the one with the best fitting to the experimental data and, as far as the system is following a Langmuir trend, helps to provide some insights in the way the molecules are adsorbed on the metal surface.

3.5. Surface morphology

To confirm the inhibition effect of the gemini surfactants, recorded from the electrochemical tests, on AISI 304 stainless steel, SEM micrographs were obtained from surfaces exposed to 3 M HCl and surfaces exposed to 3 M HCl in the presence of 3N-12 (1 mM) and 3N-18 (0.01 mM) (Figure 9a-d). Here it can be seen that the surface of the metal prior to immersion in the 3 M HCl solution is free from any detectable defects (Figure 9a). Figure 9b represents the stainless steel in uninhibited solution of 3 M HCl, which shows a heavily corroded surface with the presence of pits. The stainless steel surface was smoother, showing less damage, in the presence of both inhibitors (Figure 9c and d), indicating that tested gemini surfactants reduce the corrosion rate of stainless steel in 3 M HCl. This is considered to be due to the formation of a protective layer on the metal surface, SEM observation of the sample surfaces after exposure to the different solutions with inhibitors, shows limited attack of the surface and is in agreement with the electrochemical results.
The roughness ($R_a$) of the stainless steel surface was determined (Table 4) from the VK Analyzer based on micrographs taken using confocal laser scanning microscopy. The inhibited steel surface is smoother than the uninhibited surface indicating that the presence of a protective layer of adsorbed molecules reduces corrosion attack and in turn, the rate of corrosion of stainless steel in 3 M HCl.

4. Conclusion

The studied gemini surfactants with 3-azamethyl pentamethylene spacer are good inhibitors, exhibiting efficiencies above 90%, when added to the 3 M HCl at a concentration level around the CMC. Elongating the alkyl chain from C12 to C18 increases the inhibition efficiency for lower concentrations. 3N-18 reached a similar level of inhibition at surfactant concentrations 100-times lower than 3N-12. The Langmuir isotherm was used to model the adsorption of the inhibitors and the parameters indicated that both chemisorption and physisorption took place. In the presence of the inhibitors, the open circuit potential of the stainless steel shifts towards more positive values, than that of the blank sample, suggesting the formation of protective layer on the stainless steel surface. The studied surfactants act as mixed-type inhibitors by affecting both cathodic and anodic sites without changing the corrosion mechanism, but reducing the active surface.

5. Acknowledgement

This work has been supported by the National Centre for Research and Development (Poland; TANGO1/266340/NCBR/2015).

The authors would also like to thank the School of Materials, University of Manchester for providing research facilities.

6. References


FIGURES AND TABLES

Figure 1. Structure of the N-substituted gemini surfactants.

\[ \text{3N-12} \ (R = C_{12}H_{25}) \]
\[ \text{3N-18} \ (R = C_{18}H_{37}) \]
Figure 2. Open circuit potential-time curves for stainless steel electrode immersed in 3M HCl in the absence and presence of synthesised cationic surfactants.
Figure 3. Tafel plots for stainless steel in 3M HCl and 3M HCl with different concentrations of 3N-12.
Figure 4. Tafel plots for stainless steel in 3M HCl and 3M HCl with different concentrations of 3N-18.
Figure 5. Nyquist plots for stainless steel in 3M HCl in the presence and absence of selected inhibitors (at their most effective concentrations).
Figure 6. The equivalent circuit for the studied system.
Figure 7. The evolution of charge transfer resistance with the time plots for tested gemini surfactants.
Figure 8. Langmuir isotherm adsorption model of 3N-12 and 3N-18 for stainless steel in 3M HCl.
Figure 9. SEM images of stainless steel surface: a) before immersion; b) after immersion in 3M HCl; c) after immersion in 3M HCl with 3N-12 (1mM); d) after immersion in 3M HCl with 3N-18 (0.01mM).
Table 1. Electrochemical polarisation parameters and inhibition efficiency (IE) for stainless steel in 3M HCl in the absence and presence of different concentrations of inhibitors at room temperature.

<table>
<thead>
<tr>
<th>Concentration of the surfactant [mM]</th>
<th>$E$ vs SCE [mV]</th>
<th>$b_a$ [mV]</th>
<th>$b_c$ [mV]</th>
<th>$R_p$ [Ω cm$^2$]</th>
<th>$i_{corr}$ [μA cm$^{-2}$]</th>
<th>IE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>-354.9</td>
<td>128</td>
<td>177</td>
<td>12.7</td>
<td>2550.0</td>
<td>-</td>
</tr>
<tr>
<td>3N-12</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>-324.5</td>
<td>136</td>
<td>114</td>
<td>27.8</td>
<td>969.6</td>
<td>62</td>
</tr>
<tr>
<td>0.5</td>
<td>-327.1</td>
<td>135</td>
<td>135</td>
<td>87.7</td>
<td>334.6</td>
<td>87</td>
</tr>
<tr>
<td>1</td>
<td>-329.4</td>
<td>152</td>
<td>121</td>
<td>126.4</td>
<td>316.0</td>
<td>95</td>
</tr>
<tr>
<td>2</td>
<td>-328.2</td>
<td>194</td>
<td>133</td>
<td>225.6</td>
<td>152.1</td>
<td>94</td>
</tr>
<tr>
<td>3N-18</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.005</td>
<td>-355.4</td>
<td>152</td>
<td>118</td>
<td>23.3</td>
<td>1238.0</td>
<td>50</td>
</tr>
<tr>
<td>0.01</td>
<td>-313.5</td>
<td>165</td>
<td>138</td>
<td>161.1</td>
<td>202.7</td>
<td>92</td>
</tr>
<tr>
<td>0.05</td>
<td>-330.2</td>
<td>181</td>
<td>118</td>
<td>41.3</td>
<td>751.6</td>
<td>70</td>
</tr>
<tr>
<td>0.1</td>
<td>-349.7</td>
<td>164</td>
<td>110</td>
<td>17.05</td>
<td>1687.8</td>
<td>36</td>
</tr>
</tbody>
</table>
Table 2. EIS parameters for corrosion of stainless steel in 3M HCl in absence and presence of different concentrations of the selected surfactants (after 24 hours).

<table>
<thead>
<tr>
<th>Concentration of surfactant [mM]</th>
<th>$R_p$ [Ωcm$^2$]</th>
<th>$C_{h1}$ [μF/cm$^2$]</th>
<th>$C_{h2}$ [μF/cm$^2$]</th>
<th>CR [mm/year]</th>
<th>IE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3M HCl</td>
<td>0</td>
<td>18.86</td>
<td>4890</td>
<td>19.74</td>
<td>-</td>
</tr>
<tr>
<td>3N-12</td>
<td>0.1</td>
<td>48.28</td>
<td>1462</td>
<td>812</td>
<td>6.44</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>138.16</td>
<td>810</td>
<td>278</td>
<td>2.45</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>349.38</td>
<td>570</td>
<td>297</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>301.87</td>
<td>531</td>
<td>200</td>
<td>1.31</td>
</tr>
<tr>
<td>3N-18</td>
<td>0.005</td>
<td>37.72</td>
<td>1894</td>
<td>1586</td>
<td>8.82</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>211.42</td>
<td>403</td>
<td>268</td>
<td>1.78</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>65.69</td>
<td>766</td>
<td>649</td>
<td>5.45</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>25.92</td>
<td>2397</td>
<td>2261</td>
<td>12.73</td>
</tr>
</tbody>
</table>
Table 3. Thermodynamic parameters of adsorption on stainless steel surface in 3M HCl containing different concentrations of the corrosion inhibitors.

<table>
<thead>
<tr>
<th></th>
<th>$R^2$</th>
<th>slope</th>
<th>$K_{ads}$ [M$^{-1}$] x 10$^3$</th>
<th>$\Delta G_{ads}$ [kJ mol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3N-12</td>
<td>0.9994</td>
<td>1.0307</td>
<td>20</td>
<td>-34.49</td>
</tr>
<tr>
<td>3N-18</td>
<td>0.9924</td>
<td>1.3976</td>
<td>5000</td>
<td>-48.17</td>
</tr>
</tbody>
</table>
Table 4. The roughness of the stainless steel samples before and after (24 hours) immersion in 3 M HCl without and with tested corrosion inhibitors (the most efficient concentration).

<table>
<thead>
<tr>
<th></th>
<th>Before immersion</th>
<th>HCl 3 M</th>
<th>3N-12 1 mM</th>
<th>3N-18 0.01 mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_a$ [μm]</td>
<td>2</td>
<td>5</td>
<td>2</td>
<td>4</td>
</tr>
</tbody>
</table>
Graphical abstract
Highlights

- Gemini surfactants with 3-azamethylpentamethylene spacer were studied as corrosion inhibitors
- Inhibition efficiency was investigated using electrochemical methods
- Adsorption follows a Langmuir adsorption isotherm model