Inhibition Effect of Some Cationic Surfactants on the Corrosion of Carbon Steel in Sulphuric Acid Solutions: Surface and Structural Properties

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The inhibition effect of three synthesized molecules of cationic surfactants namely, 2-(hexyloxy) -N, N, N-tris (2-hydroxyethyl) -2-oxoethanaminium chloride (compound I), 2-(dodecyloxy) -N, N, N-tris (2-hydroxyethyl) -2-oxoethanaminium chloride (compound II), and 2-(octadecyloxy) -N, N, N-tris (2-hydroxyethyl) -2-oxoethanaminium chloride (compound III) on the corrosion of carbon steel (Type L-52) in 0.5M\(\text{H}_2\text{SO}_4\) solution was investigated. The inhibition action of these surfactants was studied by weight loss, galvanostatic and potentiodynamic anodic polarization techniques. The percentage inhibition efficiency increases with increasing the inhibitor concentration and decreasing temperature. The adsorption of inhibitors on the steel surface obeys Langmuir adsorption isotherm. It was found that, the cationic surfactants compounds provides a good protection to steel against pitting corrosion in chloride containing solutions. Some surface properties has been determined and explained. The structural study proves that the degree of surfactants packing is more than 0.33 which indicated that the surfactants has rod or cylindrical shape.

Keywords: Carbon steel, corrosion inhibitors, surface activity, structural properties

1. INTRODUCTION

The corrosion of carbon steel in acidic solutions causes considerable costs. Acid solutions are widely used for removal of undesirable scale and rust in many industrial processes. The main problem of using carbon steel is its dissolution in acidic solution. The use of corrosion inhibitors is one of the most practical methods for protection of steel against corrosion in acidic solutions. The most well-known acid corrosion inhibitors are organic compounds such as those containing nitrogen, sulfur and
oxygen atoms and an aromatic ring [1-7]. The role of corrosion inhibitors may be displacing water from the metal surface, interaction with anodic or cathodic reaction sites to retard the oxidation and reduction corrosion reaction and prevent transportation of water and corrosive active species to the surface [8].

The use of surfactants compounds to inhibit the corrosion of carbon steel have many advantages, such as low toxicity, safe, easily adsorbed on the steel surface, low price, easy production, high inhibition efficiency [9-14]. The effect of the chemical structure of different surfactants molecules on their adsorption & micellization processes and thermodynamic properties was studied previously [15-20].

The aim of the present work is to study the inhibitive effect of three synthesized cationic surfactants toward the corrosion of carbon steel (Type L-52) in 0.5M H₂SO₄ solution using weight loss and galvanostatic polarization techniques. Moreover, the effect of temperature on the dissolution of carbon steel was studied and some activation thermodynamic parameters were calculated. Some surface activity and structural properties of the cationic surfactants compounds was determined and explained.

2. EXPERIMENTAL TECHNIQUES

2.1 Corrosion Measurements

Carbon steel of type (L-52) was used for this study has the chemical composition (wt%): C=0.26, Mn=1.35, P=0.04, S=0.05, Nb=0.005, V=0.02, Ti =0.03 and the remainder iron. Coupons steel with dimension 1 x 4 x 0.2 cm were used for weight loss measurements. For galvanostatic polarization studies a cylindrical rod embedded in araldite with exposed surface area 0.56 cm² was used. The electrodes were polished with different grades emery papers, degreased with acetone and rinsed by distilled water.

Weight loss measurements were carried out previously [21]. The percentage inhibition efficiency (IE) and a parameter (θ) which represents the part of the metal surface covered by the inhibitor molecules were calculated using the following equation:

\[
\% \text{IE} = \left[ 1 - \frac{W_{\text{add}}}{W_{\text{free}}} \right] 100
\]

\[
\theta = \left[ 1 - \frac{W_{\text{add}}}{W_{\text{free}}} \right]
\]

where \(W_{\text{free}}\) and \(W_{\text{add}}\) are the weight loss of C-steel coupons in free and inhibited acid solutions, respectively.

Galvanostatic polarization measurements were carried out using EG & G model 363 potentiostat/galvanostat corrosion measurement system. Three compartment cell with a saturated calomel reference electrode (SCE) and platinum foil auxiliary electrode was used. The percentage inhibition efficiency (IE) and a parameter (θ) which represents the part of the metal surface covered by
the inhibitor molecules were calculated from the corrosion current density values using the following equations.

\[
IE = \left[ 1 - \frac{I_{\text{add}}}{I_{\text{free}}} \right] 100
\]

(3)

\[
\theta = \left[ 1 - \frac{I_{\text{add}}}{I_{\text{free}}} \right]
\]

(4)

where, \( I_{\text{free}} \) and \( I_{\text{add}} \) are the corrosion current densities in absence and presence of inhibitors.

2.2 Synthesis of cationic surfactants

2-(hexyloxy) -N, N, N-tris (2-hydroxyethyl) -2-oxoethanaminium chloride (compound I), 2-(dodecyloxy) -N, N, N-tris (2-hydroxyethyl) -2-oxoethanaminium chloride (compound II), and 2-(octadecyloxy) -N, N, N-tris (2-hydroxyethyl) -2-oxoethanaminium chloride (compound III) were synthesized by esterification of the corresponding alcohols (hexyl, dodecyl octadecyl alcohols) with chloroacetic acid followed by quaternization with triethanolamine. Their chemical structures are identified using IR and 1H NMR, IR spectra revealed that the characteristic bands observed from OH stretching absorb strongly in the 3350 cm\(^{-1}\). The absorption of saturated aliphatic ester appears at frequencies 1725-1750 cm\(^{-1}\). The absorption of C-N stretching starts to appear at lower frequencies 1020-1200 cm\(^{-1}\). The characteristic absorption of C-H of CH\(_3\) stretching is a strong band in the 2918-2919 cm\(^{-1}\). C-H stretching range for CH\(_2\) is 2838-2851 cm\(^{-1}\). 1H NMR spectrum of the synthesized cationic surfactants revealed the following signals: singlet \( \sigma = 4.78 \) ppm (2H; CH\(_2\) in \( \text{CH}_2\text{N} \)), triplet \( \sigma = 3.79 \) ppm (2H; CH\(_2\) adjacent to OH in the fragment N-CH\(_2\)-CH\(_2\)-OH), triplet \( \sigma = 3.43 \) ppm (2H; CH\(_2\) adjacent to N in the fragment N-CH\(_2\)-CH\(_2\)-OH).

2.3 Surface tension measurements

Surface tension was measured using Du Nouy platinum ring (KRUSS TensiometerK100 for various concentrations of the synthesized surfactants; S\(_6\), S\(_{12}\), S\(_{18}\) at 25 °C). Water, doubly distilled from an all glass apparatus and having a surface tension of 72.8 mN m\(^{-1}\) at 25°C, was used to prepare all solutions. Values of the surface tension \( \gamma \) at 20°C for various concentrations of aqueous solutions of the synthesized cationic surfactants are calculated.

2.4 Structural properties

ACD/ChemSketch version (14.01,2013) was used to design chemical structures then geometrically optimized the HyperChem 8.0 program using PC with processor Core i7 (8 CPU 1.7 GHz). A unit cell of FCC crystal type (4 atoms) of Iron (Fe) was designed with parameters \( a = b = c = 3.61 \) Å and \( \alpha = \beta = \gamma = 90 \). Molar volume and alkyl chain length were determined. In every case, the
structures of n-alkyl derivatives and crystal lattice of carbon steel in as an individual structure were full geometry optimized. HyperChem 8.0.4 Windows Molecular Modeling system based on Molecular Mechanics force field MM+ (OPLS). Computations were started using Molecular Dynamics (MD) with an initially optimized individual structure of crystal lattice of Fe and linear alkane derivatives. Energy minima were calculated by MD at temperature to 300 K, and run time 1ps at step size 0.001. To compute dimension, structural parameters and the total energy of n-alkyl derivative, individual crystal lattice of Fe and the crystal lattice of Fe merged system, the straight hydrocarbon chains were situated close to the lattice surface. During MD, straight alkane could adhere along crystal lattice of Fe and the crystal lattice of Fe–alkane merged system was transferred through many local energetic minima, finally approaching the global minimum energy.

3. RESULTS AND DISCUSSION

3.1. Weight loss measurements

The effect of increasing concentration of cationic surfactants on the weight loss of carbon steel in 0.5M H₂SO₄ solution as corrosive medium was studied.

Table 1. Weight loss, IE and θ of surface active agents compounds for carbon steel corrosion in 0.5 H₂SO₄ solution.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Conc. (ppm)</th>
<th>Weight loss (mg dm⁻²)</th>
<th>% IE</th>
<th>θ</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>100</td>
<td>230</td>
<td>74.3</td>
<td>0.743</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>192</td>
<td>78.54</td>
<td>0.785</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>168</td>
<td>81.22</td>
<td>0.812</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>122</td>
<td>86.36</td>
<td>0.863</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>88</td>
<td>90.16</td>
<td>0.901</td>
</tr>
<tr>
<td>II</td>
<td>100</td>
<td>216</td>
<td>75.86</td>
<td>0.758</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>164</td>
<td>81.67</td>
<td>0.816</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>151</td>
<td>83.12</td>
<td>0.831</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>114</td>
<td>87.26</td>
<td>0.872</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>64</td>
<td>92.84</td>
<td>0.928</td>
</tr>
<tr>
<td>III</td>
<td>100</td>
<td>198</td>
<td>77.87</td>
<td>0.778</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>150</td>
<td>83.34</td>
<td>0.832</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>132</td>
<td>85.37</td>
<td>0.852</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>104</td>
<td>88.37</td>
<td>0.883</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>58</td>
<td>93.51</td>
<td>0.935</td>
</tr>
</tbody>
</table>

The values of percentage inhibition efficiency (IE) and surface coverage (θ) obtained from weight loss measurements are given in Table 2. It is clear that from Table 1 as the additives concentration is increased the weight loss decreases while the values of IE and θ increases due to the
increase of the number of adsorbed molecule at the steel surface. This indicate that the inhibiting effect of these additives. It is obvious that the values of IE increase with the inhibitor concentration, whereas decreases in the following order: Compound III > Compound II > Compound I. This behavior will be discussed later.

3.2. Adsorption isotherm:

The degree of surface coverage (θ) of carbon steel was calculated from equation (2). The values of θ for different concentrations of the studied compounds (I-III) at 30 °C have been used to explain the best isotherm to determine the adsorption process. The adsorption of the cationic surfactants compounds, on the surface of carbon steel electrode is regarded as substitutional adsorption process between surfactants compounds in the aqueous phase (Surf._aq) and the water molecules adsorbed on the carbon steel surface (H_2O)_{ads}

\[ \text{Surf}_{(aq)} + X(H_2O)_{ads} \rightleftharpoons \text{Surf}_{(ads)} + XH_2O_{(sol)} \] (5)

where \(X\) is the size ratio, that is the number of water molecules replaced by surfactants molecule. Attempts were made to fit θ values to various isotherms including Langumuir, Freundlich, Temkin and Frumkin isotherms. By far the best results are fitted by Langmuir adsorption isotherm. Langumuir adsorption isotherm could be represented using the following equation [22,23]:

![Figure 1. Langmuir adsorption isotherm](image-url)
\[
\frac{C}{\theta} = \frac{1}{K} + C
\]

(6)

where, \(K\) is the adsorptive equilibrium constant. Plotting \(\frac{C}{\theta}\) against \(C\) gave a straight line with unit slope value (Fig. 1) indicating the adsorption of cationic surfactants compounds on the steel surface follows Langmuir adsorption isotherm. From these results one can postulates that there is no interaction between the adsorbed molecules.

\[ K \]

Figure 2. Galvanostatic polarization curves of carbon steel in 0.5M H\(_2\)SO\(_4\) containing different concentrations of compound III (1) 0.00 (2) 100 (3) 200 (4) 300 (5) 400 (6) 500 ppm.

3.3. Galvanostatic polarization measurements:

Fig. 2 shows the anodic and cathodic polarization curves of carbon steel electrode in 0.5M H\(_2\)SO\(_4\) solution in absence and presence of varying concentrations of compound III as an example. Similar curves were obtained for the other two compounds (not shown). The values of cathodic (\(\beta_c\)) and anodic (\(\beta_a\)) Tafel constants were calculated from the linear region of the polarization curves. The corrosion current density (\(I_{corr}\)) was determined from the intersection of the linear parts of the anodic and cathodic curves with the stationary corrosion potential (\(E_{corr.}\)). Table 2 shows the effect the inhibitor concentrations on the corrosion kinetics parameters, such as \(\beta_a, \beta_c, E_{corr.}, I_{corr.}\), IE and \(\theta\).
Inspection of the data of Table 2 reveals that, the values of anodic \((\beta_a)\) and cathodic \((\beta_c)\) Tafel slopes are approximately constant suggesting the inhibiting action of these compounds acted by adsorption at the metal surface according to blocking adsorption mechanism. These compounds decrease the surface area available for anodic dissolution and cathodic hydrogen evolution reaction without affecting the reaction mechanism. This inhibitors can arranged mainly as mixed–type inhibitor. The values of \(E_{corr}\) change slowly to less negative values and the value of \(I_{corr}\). decrease and hence the values of IE’s increases .These data suggest that the inhibiting effect of these compounds. The values of IE's of the three tested compounds decrease in the following order:

compound III > compound II > compound I

Table 2. Corrosion parameter obtained from galvanostatic polarization measurements of carbon steel in 0.5M H₂SO₄ solution containing different concentrations of inhibitors at 30 °C

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Conc., ppm</th>
<th>(-E_{corr}) mV (SCE)</th>
<th>(I_{corr}) mA cm⁻²</th>
<th>(\beta_c) mVdec⁻¹</th>
<th>(\beta_a) mVdec⁻¹</th>
<th>% IE</th>
<th>(\theta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>-</td>
<td>482</td>
<td>1.482</td>
<td>294</td>
<td>92</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>I</td>
<td>100</td>
<td>499</td>
<td>0.364</td>
<td>297</td>
<td>96</td>
<td>75.44</td>
<td>0.754</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>502</td>
<td>0.306</td>
<td>308</td>
<td>102</td>
<td>79.35</td>
<td>0.793</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>512</td>
<td>0.257</td>
<td>312</td>
<td>109</td>
<td>82.66</td>
<td>0.827</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>516</td>
<td>0.195</td>
<td>324</td>
<td>118</td>
<td>86.84</td>
<td>0.868</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>524</td>
<td>0.124</td>
<td>338</td>
<td>124</td>
<td>91.63</td>
<td>0.916</td>
</tr>
<tr>
<td>II</td>
<td>100</td>
<td>502</td>
<td>0.342</td>
<td>308</td>
<td>102</td>
<td>76.92</td>
<td>0.769</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>508</td>
<td>0.252</td>
<td>318</td>
<td>114</td>
<td>82.99</td>
<td>0.830</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>512</td>
<td>0.236</td>
<td>328</td>
<td>124</td>
<td>84.07</td>
<td>0.841</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>518</td>
<td>0.166</td>
<td>322</td>
<td>132</td>
<td>88.79</td>
<td>0.888</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>526</td>
<td>0.112</td>
<td>338</td>
<td>148</td>
<td>92.44</td>
<td>0.924</td>
</tr>
<tr>
<td>III</td>
<td>100</td>
<td>512</td>
<td>0.321</td>
<td>316</td>
<td>106</td>
<td>78.34</td>
<td>0.783</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>516</td>
<td>0.226</td>
<td>322</td>
<td>118</td>
<td>84.75</td>
<td>0.847</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>520</td>
<td>0.206</td>
<td>336</td>
<td>130</td>
<td>86.09</td>
<td>0.861</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>522</td>
<td>0.148</td>
<td>342</td>
<td>142</td>
<td>90.01</td>
<td>0.900</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>528</td>
<td>0.102</td>
<td>352</td>
<td>152</td>
<td>93.11</td>
<td>0.931</td>
</tr>
</tbody>
</table>
3.4. Effect of temperature

The effect of rising temperature on the corrosion current density of carbon steel in free in 0.5M H₂SO₄ solution containing 500 ppm of three cationic surfactants molecules was tested in the temperature range of 30-60°C using galvanostatic polarization measurements. Similar curves to Fig.2 were obtained (not shown). The value of \(E_{\text{corr}}\), \(I_{\text{corr}}\) and \% IE are given in Table 3. It is clear from this table that, as the temperature increases, the values of corrosion current density increases and hence the inhibition efficiency of the additive decreases. This is due to the desorption is aided by increasing the temperature.

<table>
<thead>
<tr>
<th>Temperature °C.</th>
<th>(-E_{\text{corr}}) mV (SCE)</th>
<th>(I_{\text{corr}}) mA cm(^{-2})</th>
<th>% IE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5M H₂SO₄</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>482</td>
<td>1.482</td>
<td>-</td>
</tr>
<tr>
<td>40</td>
<td>495</td>
<td>1.503</td>
<td>-</td>
</tr>
<tr>
<td>50</td>
<td>500</td>
<td>1.535</td>
<td>-</td>
</tr>
<tr>
<td>60</td>
<td>502</td>
<td>1.664</td>
<td>-</td>
</tr>
<tr>
<td>0.5M H₂SO₄+500ppm of inh.I</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>524</td>
<td>0.124</td>
<td>91.63</td>
</tr>
<tr>
<td>40</td>
<td>529</td>
<td>0.152</td>
<td>89.88</td>
</tr>
<tr>
<td>50</td>
<td>534</td>
<td>0.182</td>
<td>88.14</td>
</tr>
<tr>
<td>60</td>
<td>538</td>
<td>0.212</td>
<td>87.25</td>
</tr>
<tr>
<td>0.5M H₂SO₄+500ppm of inh.II</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>526</td>
<td>0.112</td>
<td>92.44</td>
</tr>
<tr>
<td>40</td>
<td>530</td>
<td>0.140</td>
<td>90.68</td>
</tr>
<tr>
<td>50</td>
<td>532</td>
<td>0.166</td>
<td>89.18</td>
</tr>
<tr>
<td>60</td>
<td>536</td>
<td>0.185</td>
<td>88.88</td>
</tr>
<tr>
<td>0.5M H₂SO₄+500ppm of inh.III</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>528</td>
<td>0.102</td>
<td>93.11</td>
</tr>
<tr>
<td>40</td>
<td>532</td>
<td>0.112</td>
<td>92.54</td>
</tr>
<tr>
<td>50</td>
<td>537</td>
<td>0.153</td>
<td>90.03</td>
</tr>
<tr>
<td>60</td>
<td>538</td>
<td>0.172</td>
<td>89.66</td>
</tr>
</tbody>
</table>
Figure 3. Relation between log $R_{\text{corr}}$ and the reciprocal of the absolute temperature of carbon steel electrode in (a) free 0.5M H$_2$SO$_4$ solution (b) in 0.5M H$_2$SO$_4$ solution presence of different compounds

This behavior proves that the adsorption of inhibitors on C-steel surface occurs through physical adsorption.

The values of activation energy was calculated using Arrehenius equation [24,25]

$$\log R_{\text{corr}} = \log A - \frac{E_a}{2.303 RT}$$  \hspace{1cm} (7)

where, $R_{\text{corr}}$ is the rate of metal dissolution reaction and is related directly to the corrosion current density $I_{\text{corr}}$ and hence replacement $R_{\text{corr}}$ by $I_{\text{corr}}$ [26], $A$ is Arrehenius constant, $R$ is the gas constant and $T$ is the absolute temperature.

Fig. (3) represents the relation between the logarithmic of the concentration of inhibitors and the reciprocal of temperature ($\log R_{\text{corr}}$ vs $1/T$ ) for free 0.5M H$_2$SO$_4$ solution and inhibited solution containing 500 ppm of the studied compounds. From the slope of the straight lines

The values of $E_a$ was calculated and equal to to 21.06 KJ mol$^{-1}$ in 0.5M H$_2$SO$_4$ and equal to 28.72,34.46 and 38.29KJ mol$^{-1}$ in presence of compound I, II and III, respectively

The higher values of Ea in the presence of inhibitors compared to the blank solution indicates that the inhibitors will be effective at low temperatures but the efficiencies will diminished at higher temperatures. The increase of the activation energy in the presence of inhibitors is attributed to an appreciable decease in the adsorption process of the inhibitors on the metal surface with increase of
temperature and a corresponding increase in the reaction rate because of the greater area of the metal that is exposed to the acid.

The enthalpy of activation ($\Delta H^*$) and the entropy of activation ($\Delta S^*$) and for dissolution of carbon steel in 0.5M H$_2$SO$_4$ solution containing 500 ppm of each used compound were calculated by applying the transition state equation [24,25].

$$R_{corr} = \frac{RT}{Nh} \exp \left( \frac{\Delta S^*}{R} \right) \exp \left( -\frac{\Delta H^*}{RT} \right)$$

(8)

where $N$ is Avogadro's number, $h$ is Planck's constant. Plotting $\log \left( \frac{R_{corr}}{T} \right)$ vs $\left( \frac{1}{T} \right)$ (Fig.4) should gave straight line with a slope of $\left( -\frac{\Delta H^*}{2.303 R} \right)$ and an intercept $[\log \left( \frac{R}{Nh} - \frac{\Delta S^*}{2.303R} \right)]$. The values of $\Delta H^*$ obtained from the slope of the straight line and equal 10.25 KJ mol$^{-1}$ in 0.5M H$_2$SO$_4$ and equal 13.18, 17.21 and 19.22 KJ mol$^{-1}$ in presence of compound I, II and III, respectively.

Figure 4. Arrhenius plots of $\log \left( \frac{R_{corr}}{T} \right)$ and the reciprocal of the absolute temperature of carbon steel electrode in (a)free 0.5M H$_2$SO$_4$ solution (b) in 0.5M H$_2$SO$_4$ solution presence of different compounds.

The values of $\Delta H^*$ are different for studied compounds which mean that their structure affect the strength of its adsorption on the metal surface. The positive values of $\Delta H^*$ reflects the endothermic nature of steel dissolution The values of $\Delta S^*$ calculated from the intercept of the straight line were found to 293.22 J mol$^{-1}$ k$^{-1}$ in 0.5M H$_2$SO$_4$ and 308.15, 312.88 and 314.82 J mol$^{-1}$ K$^{-1}$ for compound I, II and III, respectively.

The negative values of $\Delta S^*$ in the absence and presence of the inhibitors implies the surfactants molecules freely moving in the bulk solution were adsorbed in an orderly fashion onto the carbon steel. This implies the activated complex is the rate determining step and represents association rather than
dissolution step. It is also reveals that an increase in the order takes place in going from reactants to the activated complex.

3.5. Inhibition of pitting corrosion

Fig. (5) represents the effect of increasing concentrations of compound III on the potentiodynamic anodic polarization curves of carbon steel electrode in 0.5M H₂SO₄ +0.1MNaCl (as pitting corrosion agent) at a scan rate 1mV/sec. as an example of the studied surfactants molecules. Similar curves were obtained for the other two molecules (not shown). Inspection of this figure, there is no any anodic oxidation peak or any active-passive transition are observed in the anodic scan. The potential was swept from negative potential toward anodic direction up to the pitting potential (E_{pitt}). The pitting potential was taken as the potential at which the current following along the passive film increases suddenly to higher values, denoting the destruction of passive film and initiation of visible pits. The increasing of concentration of additives shifted E_{pitt} to more positive (noble) direction. This indicates that the inhibitive action of this compounds for pitting corrosion.

Fig. (6) represents the relationship between E_{pitt} and logarithmic of the molar concentrations of inhibitors. It is clear from this figure, as the concentration of additives increases, the pitting potential shifted to more positive values accordance with the following equation:

\[ E_{pitt} = a + b \log C_{inh.} \quad (9) \]

Figure 5. Potentiodynamic anodic polarization curves of carbon steel in 0.5M H₂SO₄ solution + 0.5M NaCl containing different concentrations of compound III (1) 0.00 (2) 100 (3) 200 (4) 300 (5) 400 (6) 500 ppm at a scan rate 1mV/sec⁻¹.
where, $a$ and $b$ are constants depending on the type of additives and the nature of the electrode.

At one and the same inhibitor concentrations, the shift of pitting potential in the positive (noble) direction decreases in the following order:

$$\text{compound III} > \text{compound II} > \text{compound I}$$

**Figure 6.** Relation between the logarithmic concentration of inhibitors and pitting potential

It is obvious that, the order of inhibition efficiency is the same from the different techniques but yielded different absolute values, probably due to the different experimental conditions.

### 3.6. Surface and thermodynamic properties.

Due to the insolubility of hydrophobic chain in water causes the molecules first adsorb at the liquid/air interface of the solution, until the surface of the solution is completely occupied. Since the surface tension ($\gamma$) of water is higher than that of the hydrocarbon, accumulation of the surfactants at the interface results in a decrease in the surface tension, but above $2 \times 10^{-3}$ M the surface tension becomes almost constant. Then, the excess Amphiphilic molecules spontaneously tend to self-aggregate in the bulk forming micelles into a variety of structures. The occurrence of a CMC is the result of two competing factors. Transferee of the hydrocarbon chain out of water into the oil-like interior of the micelle drives micellization. Repulsion between head groups as they close together opposes it. Fig.7 represents the plots of surface tension ($\gamma$) and the logarithmic concentration of
surfactants compounds. The critical micelle concentration (CMC) values were obtained from the break point in Fig 7 and given in Table (4). The values of CMC decreases with increasing the chain length.

3.7. Maximum Surface Excess ($\Gamma_{\text{max}}$).

The surface tension data are used to calculate the maximum surface excess concentration of surfactant at the air/interface ($\Gamma_{\text{max}}$) by applying Gibb's equation:

$$\Gamma_{\text{max}} = \frac{-1}{2.303nRT} \left[ \frac{d\gamma}{d \ln C} \right]$$  \hspace{1cm} (10)

Figure 7. Variations of surface tension of 2- (alkyloxy)- N,N,N-tris (2hydroxyethyl) - 2-oxoethanaminium chloride S6-18 vs different concentrations at 27°C

where, $\Gamma_{\text{max}}$ is called surface excess, $d\gamma$ is the equilibrium surface tension (mM/m) at the surfactant concentration. The parameters $R$ and $T$ have their usual meaning. And $n$ is constant depends upon the individual ions comprising the surfactants, $n$= 2 for ionic surfactants.

A substance which lowers the surface energy is thus present in excess at or near the surface, i.e., when the surface tension decreases with increasing activity of surfactant, $\Gamma_{\text{max}}$ is positive.
The values of calculated $\Gamma_{\text{max}}$ are represented in Table 4. Increasing the hydrophobic character in the denoted homologous series of the cationic surfactants let $\Gamma_{\text{max}}$ attain at lower concentration.

3.8. Standard Free energy of Micellization

The standard free energy of micellization, $\Delta G^o_{\text{mic}}$ for synthesized surfactants are calculated at temperature used 25 $^\circ$C by using the relationship:

$$\Delta G^o_{\text{mic}} = -RT \ln \text{CMC}$$

Obviously, the standard free energies of micellization (Table 4) for 2-(alkyloxy) -N, N, N-tris (2-hydroxyethyl) -2-oxoethanaminium chloride

Compounds I, II and III homologues are always negative values, indicating that the micellization is a spontaneous process. The free energy change $\Delta G^o$ involved in the transfer of a methylene group from an aqueous environment to the interior of the micelle is negative, thus forming micellization, which account for the fact that CMC decreases with increasing in the length of the hydrophobic group i.e., introduction of additional methylene group into hydrophobic part favors the micellization.

3.9. Standard free energy of adsorption.

$\Delta G^o_{\text{ad}}$ values were calculated using the relationship:

$$\Delta G^o_{\text{ad}} = \Delta G^o_{\text{mic}} - \Delta \text{CMC} A_{\text{min}}$$

Table 4 lists the standard free energies of adsorption ($\Delta G^o_{\text{ad}}$) for the synthesized surfactants.

Here, the standard state for the surface phase is defined as a surface filled with a monolayer of surface - active agent, in the present case, equation (12) becomes

$$\Delta G^o_{\text{ad}} = \Delta G^o_{\text{mic}} - (6.023 \times 10^{-1} \Delta \text{cmc} A_{\text{min}})$$

According to the data in Table 4, $\Delta G^o_{\text{ad}}$ of the cationic surfactants are often slightly higher than $\Delta G^o_{\text{mic}}$. This indicates that the surfactant molecules tend to adsorb at the planar aqueous solution/air interface compared rather than micelle formation.

Table 4. Critical micelle concentration CMC, Maximum surface excess $\Gamma_{\text{max}}$ and Minimum surface area $A_{\text{min}}$. Standard free energy of micellization and adsorption of the solutions of the synthesized surfactants

<table>
<thead>
<tr>
<th>Cationic Surfactants</th>
<th>CMC $\times 10^{-3}$</th>
<th>$\Gamma_{\text{max}} 10^{-10}$ mol/cm$^2$</th>
<th>$\Delta G^o_{\text{mic}}$</th>
<th>$\Delta G^o_{\text{ad}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound I</td>
<td>4.0</td>
<td>4.01</td>
<td>-13.66</td>
<td>-13.68</td>
</tr>
<tr>
<td>Compound II</td>
<td>3.0</td>
<td>3.75</td>
<td>-14.38</td>
<td>-14.40</td>
</tr>
<tr>
<td>Compound III</td>
<td>2.2</td>
<td>3.20</td>
<td>-15.38</td>
<td>-15.40</td>
</tr>
</tbody>
</table>
3.10. Structural properties and degree of packing of surfactants

Energy of adsorption can be defined as follows[27]:

$$\Delta E (\text{kJ/mol}) = [(E_{R-x} + E_{\text{Fe}}) - E_{R-x+\text{Fe}}]$$  (14)

where $E_{R-x}$ is the total energy of n-alkyl chain derivatives, $E_{\text{Fe}}$ is the total energy of crystal lattice of Iron and $E_{R-x+\text{Fe}}$ is the total energy of the two merged molecules.

The packing parameters "P"[28] for the optimal aggregation shape of the amphiphiles are determined from Molecular parameters, hydrophobic volume, chain length, and head group area.

$$P = \frac{V_o}{a_o l_o}$$  (15)

where, $V_o$ and $l_o$ are the molar volume and hydrophobic tail length respectively $a_o$ equilibrium area per molecule at the aggregate interface

The values of molar Volume ($V_o$), alkyl chain length ($l_o$), Minimum surface area ($A_{\text{min}}$), critical packing factor (P) for the synthesized molecules and Energy of adsorption of surfactants on the crystal lattice of steel $E_{\text{ads}}$, are given in Table 5. It is obvious that the values $V_o$ and $l_o$ increases with increasing the chain length but the values of $p$ and $E_{\text{ads}}$ decreases.

For the synthesized series, the calculated critical packing factor were found to be $P > 0.33$. It indicated that the cylindrical micelles are the predominant shape for the synthesized amphiphiles

Table 5. Molar volume $V_o$, alkyl chain length $l_o$, Minimum surface Area $A_{\text{min}}$ and critical packing factor $P$ for the synthesized molecules and Energy of adsorption of surfactants on the crystal lattice of Iron $E_{\text{ads}}$.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$V_o$ nm$^3$</th>
<th>$l_o$ nm</th>
<th>$A_{\text{min}}$ nm$^2$</th>
<th>$P$</th>
<th>$E_{\text{ads}}$ kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound I</td>
<td>0.291</td>
<td>0.90</td>
<td>0.66</td>
<td>0.48</td>
<td>47.66</td>
</tr>
<tr>
<td>Compound II</td>
<td>0.377</td>
<td>1.65</td>
<td>0.66</td>
<td>0.36</td>
<td>42.75</td>
</tr>
<tr>
<td>Compound III</td>
<td>0.478</td>
<td>2.39</td>
<td>0.66</td>
<td>0.31</td>
<td>37.55</td>
</tr>
</tbody>
</table>

For the synthesized series, the calculated critical packing factor were found to be $P > 0.33$. It indicated that the cylindrical micelles are the predominant shape for the synthesized amphiphiles

Figure 8. Shows adsorption of one molecule of surfactants on a unit cell of steel
3.11. The Relation between the Inhibition Efficiency and Surface Properties of the Synthesized Cationic Surfactants

Most of organic corrosion inhibitors are adsorbed on the metal solution interface by displacing water molecules from the surface and forming a compact barrier film. The ability of cationic surfactants to adsorb on the steel surface is directly related to its ability to aggregate and form micelles. There is equilibrium between the singly adsorbed surfactants molecules. The equilibrium occurred at the concentration of complete surface saturation. The micelle formation is the most vital point of view in the surfactant because it is the most effective geometrical arrangement of the molecule at the desired concentration [29].

The values of inhibition efficiency of the three tested compounds and the shift of pitting potential in the positive direction decreases in the following order: compound III > compound II > compound I

This behavior are constituent with increasing the number of carbon chain. The surfactant molecules with long hydrocarbon chain tend to be curled up in water to minimize the area of contact between the hydrophobic hydrocarbon chain and the water molecule[30]. The increase resistance to corrosion could be attributed to a gradual decrease with concentration of the interfacial tension which leads to a decrease in the bulk concentration of the inhibitor and its increase at the electrode surface.

The order of inhibition efficiency of the cationic surfactants using different techniques are in a good agreements with the results obtained from surface and structural properties of cationic surfactants in tables 4 and 5. The values of \( \Gamma_{\text{max}} \), CMC and \( E_{\text{ads}} \) of the cationic surfactants decreases with increasing of the carbon chain length which could be due to the hydrophobic effect of carbon chain. It is seems that the cationic surfactants favor adsorption rather than micellization. The values of \( \Delta G^{\circ}_{\text{ad}} \) are more slightly negative compared with the values of \( \Delta G^{\circ}_{\text{mic}} \). This indicates that the strong adsorption of the surfactants compounds.

4. CONCLUSIONS

1- The synthesized cationic surfactant are efficient inhibitors for corrosion of carbon steel in 0.5MH\(_2\)SO\(_4\) solution.
2- The inhibition efficiency increases with increase in the concentration of these inhibitors but decreases with an increase in temperature.
3- The inhibition action is due to the adsorption of cationic surfactants on the carbon steel surface.
4- The adsorption process obeys Langmuir isotherm.
5- Cationic surfactants molecules provide a good resistance to pitting corrosion in chloride containing solutions.
6- The values of \( \Gamma_{\text{max}} \), CMC and \( E_{\text{ads}} \) of the cationic surfactants decreases with increasing of the carbon chain length due to the hydrophobic effect of carbon chain.
7- The structural study proves that the degree of surfactants packing is more than 0.33 which indicated that the surfactants has rod or cylindrical shape.

References


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