The Synergistic Effect of NaHSO$_4$ and NaCl Salts on Corrosion Inhibition Performance of Two Gemini Cationic Surfactant Ionic Liquids

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Published: Jun 2020

Abstract
In this study, two imidazolium-based ionic liquid surfactants (TSIL and EFAIL) were first synthesized, and then investigated the synergistic effects of NaHSO$_4$ and NaCl salts on corrosion inhibition performance of TSIL and EFAIL inhibitors on low carbon steel samples in 1 M HCl solution. For this aim, the electrochemical techniques of potentiodynamic polarization and electrochemical impedance spectroscopy (EIS), surface morphology analyses, and quantum chemical calculations were employed. Results showed that adding salts to acidic solutions containing EFAIL and TSIL increased their inhibition efficiency. Furthermore, addition of NaHSO$_4$ to TSIL-containing solution could further increase the inhibition efficiency compared to other mixtures of the salts and the inhibitors. The DFT results also revealed that the energy gap of TSIL is lower than that of EFAIL, implying that TSIL has more chemical reactivity and less kinetic stability than EFAIL.

Keywords
Ionic liquid surfactant; EIS; polarization; acid corrosion; surface tension; density functional theory
1. INTRODUCTION

Because of having excellent mechanical properties of carbon steel, this metal is widely applied in many industries. The solutions of acidic are also employed in various industries for acid cleaning equipment, steel pickling process, leather processing, and acidization of oil[12], etc. The two popular acids consumed for this purpose are hydrochloric and sulfuric acids. These two acids are severely corrosive acid and they can cause severe dissolution of steel. So, slow resistance of steel against acidic environments is a very important problem.

In industry, various methods are used to protect steels against corrosion. The most excellent and convenient method of steel protection is use of inhibitor compounds in corrosive media[3–6]. To control, reduce, and prevent interactions between metal surface and corrosive environment, these compounds are added in corrosive environment[7–14]. The most excellent and efficient inhibitors are heterocycle compounds having π bonds and heteroatoms like sulfur, phosphorus, oxygen, and nitrogen in their structures[15–18]. On the other hand, most of inhibitor compounds are toxic and carcinogetic materials affecting the environment. Researchers have tried to find inhibitors with less toxicity and high compatibility with the environment. One of these compounds is ionic liquid (IL)[19,20]. Some IL compounds are known as nontoxic and environmentally friendly compounds for protection of the steel corrosion in acidic media. Ionic liquids have been introduced for the first time in 1914 by reporting the synthesis and physical properties of ethyl ammonium nitrate ionic liquid compound[21–24]. Ionic liquids are melted salts having asymmetric and huge organic cations as well as mineral anions. The melting point of the ionic liquid compounds is below 100 °C and is usually close to room temperature. Ionic liquids are a three-dimensional lattice of cations which are linked together by a subtle energy-balance between dispersion force, hydrogen bonds, and electrostatic interactions. These compounds have many excellent physicochemical properties, such as high electrical conductivity, low vapor pressure and volatility, wide liquidus range, high thermal stability, and no flammability hazard[25]. Because of these features, many compounds of ionic liquids are known as nontoxic and environmentally friendly compounds[22,26,27].

The synergistic effect of ionic liquids in the presence of other compounds has been considered to improve inhibition properties of the inhibitors and reduce costs[28]. There are some reports about studying synergistic effect between halide ions (such as Cl⁻, Br⁻, I⁻), and N-heterocyclic inhibitors for steel corrosion in acidic media. It has been demonstrated that the mixtures of o-phenanthroline/Cl⁻[29–31], pyrazole/halides[32], triazole derivative/Br⁻[33], and imidazoline derivative/I⁻[34] have been shown synergistic effects. It has been found that the addition of halide ions to the inhibitor-containing solutions can increase the inhibition effect of inhibitors. The order of inhibition effect of some halides is I⁻ > Br⁻ > Cl⁻. One reason mentioned for the most synergistic effect of I⁻ is its larger size (216 pm) and higher ability to polarize compared to other halides[34–36].

The inhibition synergistic effect of adenine and iodide ion (I⁻) in the H₂SO₄ solution has been studied[37]. In the study, it was found that the addition of iodide ions to solution containing adenine increase significantly inhibition efficiency value. Moreover, it was indicated that the inhibition mechanism in the presence of iodide ions occurs by electrostatic adsorption of protonated adenine on the surface charged via adsorption of iodide ions on low carbon steel surface.

In the other research work, the synergistic effect investigation of I⁻ ions and polyacrylamide (PA) on the pure iron corrosion in H₂SO₄ solution indicated that inhibition performance of the PA is increased in the presence of I⁻ ions, due to simultaneous adsorption of I⁻ ions and PA molecules on the surface of carbon steel sample[38].

In the present study, the synergistic effects of two salts containing ions of chloride (Cl⁻) and sulfate hydrogen (HSO₄⁻) on the inhibition properties of two surfactant inhibitors (TSIL and EFAIL) in HCl solutions has been studied. For this purpose, electrochemical techniques of electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization, surface morphology analyses, and as well as quantum chemical calculations were utilized.

2. METHODS

2.1. Materials and Solutions

Table 1 listed the chemical composition of the low carbon steel samples (20 mm × 40 mm × 1.5 mm) that were prepared by Esfahan Foolad Mobarakeh Company.
The TSIL and EFAIL inhibitors were synthesized as new corrosion inhibitors in our laboratory. The chemical structure and full name of these inhibitors is given in Figure 1. The synthesized inhibitor compounds were completely analyzed by $^1$H-NMR, $^{13}$C-NMR, and FT-IR, which the obtained results brought in S1.

The effects of NaHSO$_4$ and NaCl salts on inhibition properties of TSIL and TFAIL inhibitors were studied in acidic solution (1 M HCl). The salts and HCl solution were prepared from Merck Co. To prepare corrosive solution (1 M HCl), 37% HCl (Analytical grade) was added to double distilled water.

Then, 15 mg/L of the inhibitors as well as 0.001 M of NaHSO$_4$ and NaCl salts were added to the prepared corrosive solutions. Before the corrosion test, the low carbon steel samples were mechanically polished with different emery papers grades (400, 600, 800, and 1200). They were washed with acetone and distilled water. Finally, for the cleaning of rust products on metal surface, the samples were immersed in 5% v/v HCl solution for 2-3 s, then rinsed and dried.

### 2.2. Characterization of the Inhibition Performance

#### 2.2.1. Electrochemical Methods

The effects of NaHSO$_4$ and NaCl salts on inhibition properties of the TSIL and EFAIL inhibitors on the steel surface in acidic solution were investigated by potentiodynamic polarization and EIS techniques. For this purpose, an Ivium Vertex instrument (Ivium potentiostat/galvanostat) was used. The measurements were performed on a conventional three electrode cell, including working electrode (low carbon steel sample), reference electrode (Ag/AgCl/KCl), and counter electrode (graphite). Both experiments were carried out on 1 cm$^2$ of the samples and the rest of the samples were masked with a mixture of beeswax and colophony resin (3:1). The polarization measurements were performed at 1 mV/s scan rate (from -100 mV to +100 mV) at OCP (open circuit potential) condition. EIS was carried at OCP in the frequency scan of 10 kHz to 10 MHz.

#### 2.2.2. Surface Analyses of the Steel Samples

Panels of the low carbon steel were immersed to HCl solutions containing NaHSO$_4$ and NaCl salts as well as the EFAIL and TISL inhibitors. The surface morphology of the steel samples was characterized by SEM model AIS2100 after 1 h immersion in the corrosive solutions. The surface tension values were measured by Wilhelmy Technique on a KRUESS PROCESSOR TENSIOmeter K14 V3.07 at 25 °C temperature.

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**Table 1. Elemental analysis of the low carbon steel**

<table>
<thead>
<tr>
<th>Elements</th>
<th>Cu</th>
<th>Mo</th>
<th>Cr</th>
<th>Ni</th>
<th>S</th>
<th>P</th>
<th>V</th>
<th>Mn</th>
<th>C</th>
<th>Si</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt.%</td>
<td>0.026</td>
<td>0.002</td>
<td>0.004</td>
<td>0.015</td>
<td>0.060</td>
<td>0.001</td>
<td>0.005</td>
<td>0.693</td>
<td>0.063</td>
<td>0.012</td>
<td>99.119</td>
</tr>
</tbody>
</table>

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**Figure 1. Molecular structure and full name of the TSIL and EFAIL inhibitors.**
By an OCA 15 plus type measuring system was measured the static contact angle of water on the metal surface. For this purpose, a small drop of the solutions was dripped on the surface of the samples. Then, after 10 s, the drop shape was recorded by a camera.

3. RESULTS AND DISCUSSION

3.1. Determination of Critical Micelle Concentration

The critical micelle concentration (CMC) is a well-known parameter for characterizing behavior of a surfactant in a specific solution. Both the nature of the aqueous environment and the chemical composition of the surfactant affect the CMC point. Therefore, the surface tension values of the solutions containing different concentrations of the EFAIL and TSIL inhibitors were measured [Figure 2].

According to Figure 2, for both the surfactants, the surface tension values decreased by the addition of their concentrations. The decrease in the surface tension can be attributed to the migration of the surfactant molecules from the solution to the surface and replacing water molecules at the surface. The CMC points can be obtained from the break points in the graphs. Therefore, the CMC values of 5 and 15 mg/L were obtained for the solutions containing the EFAIL and TSIL, respectively. These observations indicated that the EFAIL decreased the surface tension and CMC more than the TSIL. The only difference between the molecules of the EFAIL and TSIL is their anions (Cl\(^{-}\) in TSIL and HSO\(_4\)\(^{-}\) in EFAIL). Size of HSO\(_4\)\(^{-}\) ion is larger than Cl\(^{-}\) ion size. Therefore, HSO\(_4\)\(^{-}\) is less hydrated which plays a very important role in neutralizing surface charges on the micelle surface leading to lower CMC and the surface tension.

3.2. Electrochemical Studies

3.2.1. Measurements of Potentiodynamic Polarization

Polarization plots of low carbon steel immersed in 1 M HCl solutions comprising 15 mg/L of the TSIL and EFAIL inhibitors and 0.0001 M of NaCl and NaHSO\(_4\) salts are represented in Figure 3. The electrochemical parameters of corrosion potential (\(E_{\text{corr}}\)), corrosion current density (\(i_{\text{corr}}\)), and polarization resistance (\(R_p\)) obtained from polarization curves are represented in Tables 2 and 3.
According to Figure 3 (a) and (b), both anodic and cathodic reactions are blocked in the presence of the TSIL and EFAIL inhibitors. The shift of the $E_{\text{corr}}$ towards less negative values relates to the dominant blocking of anodic reaction compared with the cathodic reaction using the molecules of the two inhibitors.

It is clear from Tables 2 and 3 that the addition of the TSIL and EFAIL inhibitors to the acidic solution caused a decrease in corrosion current density as well as shift of corrosion potential to more positive values. This probably means that the steel surface behaves like a noble metal surface because of the adsorption of the inhibitor molecules and the formation of the protective layer on the surface of the metal, as well as reduction of the iron anodic dissolution due to the addition of the TSIL and EFAIL concentration, and finally protection of the metal surface from corrosion. Moreover, it can be seen that the EFAIL inhibited corrosion reaction much greater than the TSIL. The EFAIL decreased corrosion current density of the steel immersed in HCl solution much greater than the TSIL. This means that the type of surfactant anion is an effective and important factor on inhibition properties. The inhibitor with HSO$_4^-$ anion showed higher inhibition efficiency than the one with Cl$^-$. Both the size and charge of the anions are effective parameters on the inhibition properties of the surfactants. The values of inhibition efficiency were calculated by the following equation:

$$\text{IE}\% = \frac{(i - i_{\text{inh}})}{i} \times 100 \quad (1)$$

Where IE, i, and $i_{\text{inh}}$ represent the inhibition efficiency, corrosion current density in the absence and the presence of the inhibitor, respectively. The comparison of inhibition efficiency values for different samples is illustrated in Figure 4.

Figure 4 shows that adding 0.0001 M NaCl and NaHSO$_4$ salts into the HCl solutions containing the inhibitors increased the inhibition efficiency values. The addition of the salts to the HCl solution inhibited both anodic and cathodic reactions. This means that Cl$^-$ and HSO$_4^-$ ions had a synergistic effect on the inhibition properties of the inhibitors. Figure 4 indicate that addition of NaHSO$_4$ salt in the acidic solution increase the inhibition efficiency more than NaCl salt. Moreover, Figure 4 data exhibited that the addition of the two salts to the solution containing the TSIL inhibitor has more increase in the inhibition efficiency values compared with the EFAIL inhibitor.

### 3.2.2. EIS Measurements

Electrochemical impedance spectroscopy was also utilized to reveal the synergistic effects of addition of NaHSO$_4$ and NaCl salts to the acidic solutions containing TSIL and EFAIL inhibitors at 25 °C. The obtained impedance data are shown as Nyquist and Bode plots in Figures 5 and 6.

The Nyquist plots are not ideal and perfect semicircles due to probably inhomogeneity and roughness of the surface of the samples. Generally, in the evaluation of the Nyquist diagrams, the actual impedance difference at the lower and higher frequencies created the charge transfer. In the present Nyquist diagrams, the semicircles with alone one time constant were obtained, indicating that the charge transfer process dominated...
the steel corrosion process into the studied corrosive media. Therefore, the expansion of the semicircles indicates a tendency for increasing the charge transfer resistance as the concentration of the inhibitors and salts increases\(^{[43]}\). The addition of the TSIL does not significantly alter the shape of the Nyquist plots, but the form of semicircles be changed in the presence of EFAIL. This may indicate the constitution of a strong adsorption layer upon the surface of the metal. The equivalent circuits presented in Figure 5 are utilized to extract some electrochemical parameters from impedance data. For more accurate fit of impedance data, CPE (Constant Phase Element) parameter be applied in lieu of double layer capacitance (Cdl). The CPE parameter is obtained from \(Y_0\) and \(n\) parameters. These parameters are the magnitude and exponent of CPE, respectively. The \(n\) parameter shows the roughness or heterogeneity of the electrode surface.

The corrosion inhibition efficiency (IE\%) and capacitance (C) were calculated by using the following formulas\(^{[44–46]}\):

\[
\text{IE}\% = \left( \frac{R_p - R_{p(\text{inh})}}{R_p} \right) \times 100
\]

\[
C = \left( Y_0 R_{p(\text{inh})} \right)^{1-n} \quad \text{(2)}
\]

Where \(R_p\) and \(R_{p(\text{inh})}\) represent the polarization resistance without and with the inhibitors, respectively. The
According to Tables 4 and 5, addition of TSIL and EFAIL inhibitors to the acidic solution lead to an increase in $R_p$ and decrease in $C$. This means that water molecules are replaced with the molecules of EFAIL and TSIL on the metal surface. The inhibitor layer adsorbed on the metal surface has dielectric constant value lower than water molecules. This finding demonstrates formation of a protective inhibitor layer on the metal surface in HCl solutions containing TSIL and EFAIL. The obtained results show higher inhibition efficiency of EFAIL than TSIL. Tables 4 and 5 show that the addition of 0.0001 M of NaCl and NaHSO$_4$ salts to the acidic solutions containing 15 mg/L of EFAIL and TSIL inhibitors, increases the inhibition efficiency values. In the presence of NaCl and NaHSO$_4$ salts, the $R_p$ value is increased, while $C$ value is decreased. This observation can also show the synergistic effects of salts on increasing the inhibition action of the inhibitors. It is also obvious from the results shown in Tables 4 and 5 that NaHSO$_4$ salt shows higher synergistic effect than NaCl, and NaHSO$_4$ salt shows more increase in the inhibition efficiency value.

The results of phase angle at 10 kHz and impedance at 10 mHz obtained from Bode plots are presented in Figure 7.

According to Figure 7, impedance at 10 mHz is increased in the presence of the inhibitors. Moreover, the addition of salts caused a further increase in corrosion inhibition efficiency of the inhibitors. The synergistic effects of salts were again found from the results obtained from Bode plots. At 10 kHz, the phase angle is a parameter that indicates capacitor of inhibition layer absorbed on the metal surface[^47].

As can be seen in Figure 7, the angles of contact were compared between samples immersed in acidic medium containing TSIL and EFAIL and samples immersed in an inhibitor-free solution. It was found that the contact angle at 10 kHz in the acidic medium containing inhibitor was much more negative than the blank medium. The most negative phase angle values were obtained in the presence of both inhibitors and salts. This means that the addition of salts caused more negative phase angle values. The phase angle is negative, and so electrochemical behavior becomes more capacitive. The inhibitor molecules adsorbed on the metal surface show high charge transfer resistance indicating low current tendency to pass through double-layer capacitance. It can again be seen that NaHSO$_4$ had more effect on phase angle than NaCl.
3.3. Surface Morphology Studies

3.3.1. SEM

Figure 7 represents the SEM micrographs of samples after 1h immersion in the acidic solutions containing the EFAIL and TSIL inhibitors in the presence and absence of salts.

Figure 8 (a) illustrates that the steel surface exposed to HCl solution without the inhibitor was strongly damaged via chloride anion, and the extreme carbon steel dissolution was observed. It can be seen that wide and deep holes formed on this sample and porosity of the metal surface increased considerably. But by addition of the inhibitors (TSIL and EFAIL) to the acidic solution has been reduced damage of the surface as well as surface porosity, and the surface morphology of the carbon steel sample obtains a significant improvement. Figure 8 makes it clear that the damage of the surface reduced further by the addition of salts. For the steel immersed in an acidic solution containing the EFAIL was seen a surface of smoother with porosity and degradation of lower than TSIL. Moreover, addition of the NaHSO$_4$ caused the lowest surface damage and porosity, indicating that the inhibition effect of the inhibitors was enhanced in the presence of this salt more than NaCl. Accordingly, the SEM results are well in accordance with the other obtained results.

3.3.2. Measurements of the Contact Angle

The measurement of the contact angle with water droplet was done on the steel surface exposed to solutions of 1 M HCl in the presence and absence of the inhibitors. The result of measurement of the contact angle is illustrated in Figure 9.

As depicted in Figure 9, the water contact angle on the fresh bare steel is about 106°. The contact angle was significantly reduced for the sample exposed to HCl solution without inhibitor. This is probably because of the severe corrosion of the metal in HCl solution, and so corrosion product remaining on the steel surface increases the roughness of the surface. It is clear in Figure 9 that the addition of inhibitors caused a lower decrease in contact angle. It demonstrates the adsorption of the inhibitor molecules on the metal surface, which protected the surface against corrosion. As a result, surface roughness did not increase significantly due to the lower production of corrosion products on the metal surface. The decreasing contact angle on the sample exposed to the HCl solution containing EFAIL was noticeably lower than the one immersed in the solution with TSIL. This observation demonstrates that EFAIL prevented metal surface from corrosion more efficiently than TSIL. The EFAIL layer adsorbed on the metal surface also makes it more hydrophobic compared to a blank sample.

3.4. Calculation of Quantum Chemical Parameters

Based on many previous published researches, the molecular electronic structure and molecular geometry structure are related to the inhibition performance of the inhibitor compounds$^{[48-50]}$. Therefore, the density functional theory (DFT) calculations were used to compare the effects of NaHSO$_4$ and NaCl salts on the inhibition performance of the TSIL and EFAIL. Full geometry optimizations of the TSIL and EFAIL molecules were performed without any symmetry constraints with B3LYP exchange-correlation functional theory$^{[51-53]}$.

<table>
<thead>
<tr>
<th>Concentration (mg/L)</th>
<th>$R_{ct}$ (Ω.cm$^2$)</th>
<th>$n$</th>
<th>$Y_{0}$ (µS/Ω.cm$^2$)</th>
<th>$C$ (µF/cm$^2$)</th>
<th>IE%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>112</td>
<td>0.89</td>
<td>38.5</td>
<td>19.6</td>
<td>-</td>
</tr>
<tr>
<td>15 mg/L</td>
<td>197</td>
<td>0.86</td>
<td>26.49</td>
<td>11.2</td>
<td>43</td>
</tr>
<tr>
<td>15 mg/L TSIL + 0.001 M NaHSO$_4$</td>
<td>463</td>
<td>0.78</td>
<td>8.71</td>
<td>4.7</td>
<td>75</td>
</tr>
<tr>
<td>15 mg/L TSIL + 0.001 M NaCl</td>
<td>329</td>
<td>0.78</td>
<td>9.51</td>
<td>4.1</td>
<td>66</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Concentration (mg/L)</th>
<th>$R_{ct}$ (Ω.cm$^2$)</th>
<th>$n$</th>
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</tr>
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</table>
Along with this method, the standard basis set of 6-31+G* Pople was used in Gaussian 98 package\textsuperscript{[54]}. Harmonic vibrational frequencies were also evaluated to the determination of the minimum stationary points as a demonstration of the equilibrium structures. As such, the energies of the highest occupied molecular orbital (E\textsubscript{HOMO}) and the lowest unoccupied molecular orbital (E\textsubscript{LUMO}), and as well as the energy gap (ΔE = E\textsubscript{LUMO} - E\textsubscript{HOMO}) were calculated for obtaining the optimized structures. To gain a better understanding of the inhibition mechanism of the TSIL and EFAIL inhibitors, the required quantum chemical parameters were calculated. Figure 10 shows the optimized geometric structures and electron density distributions of LUMO and highest occupied molecular orbital (HOMO) orbitals of the TSIL and EFAIL inhibitor molecules, as well as imidazolium-based cation (Im) of the two inhibitors. The values of parameters calculated using quantum chemical calculations are reported in Table 6. The molecular orbital theory of Frontier is mostly dependent on tendencies to donate or accept electrons. Therefore, high energy level of HOMO orbitals indicates strong ability of the molecule for donating electrons to good acceptor molecules with empty molecular orbital and low LUMO energy level. The high HOMO energy level of an inhibitor molecule indicates existence of a strong interaction of the molecule and the metal surface. As clearly observed in Table 6, the HOMO molecular orbital energy level of the imidazolium-based cation in the absence of NaHSO\textsubscript{4} and NaCl salts is lower than the TSIL and EFAIL.

Figure 5. Nyquist diagrams of the steel samples immersed in 1 M HCl solutions (a) containing EFAIL and (b) TSIL in the presence and absence of NaHSO\textsubscript{4} and NaCl salts after 1 h immersion.
inhibitors, indicating that the inhibition efficiency of the Im cation is intensified in the presence of NaHSO₄ and NaCl salts. According to the values provided in Table 6, the HOMO energy level of TSIL is −5.565 eV, which reveals the better inhibition efficiency of the TSIL inhibitor molecules compared to the EFAIL molecules. On the other hand, the HOMO energy level of the EFAIL molecule is obtained −6.535 eV value due to the presence of HSO₄⁻ ions in its structure. Furthermore, the energy gap (∆E\textsubscript{HOMO-LUMO}) is a key factor for chemical reactivity of the inhibitor molecules.

Whatever the ∆E\textsubscript{HOMO-LUMO} value of molecules of an inhibitor be smaller, the inhibitory efficiency of the molecules has higher level. The obtained results show that the energy gap of the TSIL molecule is lower than

Figure 6. Bode plots of the steel samples immersed in 1 M HCl solutions (a) containing TSIL and (b) EFAIL in the presence and absence of NaHSO4 and NaCl salts after 1 h immersion.
that of EFAIL molecule, implying that the TSIL has more chemical reactivity and less kinetic stability than EFAIL.

3.5. Inhibition Mechanism of Surfactants in the Presence and Absence of Salts

When the steel is placed in a hydrochloric acid solution, its surface becomes positively charged. Therefore, Cl$^-$ or HSO$_4^-$ ions tend to be adsorbed on the positively charged sites changing the surface charge into negative charge. In the next step, the EFAIL and TSIL molecules can interact with metal surface, and so forms monomolecular layers on the surface.

The inhibitor molecules could also reduce the hydrogen evolution reaction of H$^+$ ions at cathodic regions on the metal surface. Adding salt causes several effects, one of which may be decrease in CMC and surface tension. This effect could be attributed to compressing the electrical double layer surrounding micelles, which decreases the electrostatic repulsion between the polar heads of compounds. Therefore, the CMC occurs at a lower concentration in comparison with solutions without salts. In other words, the effect of salts in the solution can

Figure 7. Values of (a) phase angle at 10 mHz and (b) impedance at 10 kHz of the steel samples in 1 M HCl solutions containing (a) TSIL and (b) EFAIL in the presence and absence of NaHSO4 and NaCl salts after 1 h immersion.
be attributed to a change in the ionic force of the solution and also an effect on the ionic force of the EFAIL and TSIL. Since the anion of salt decreases the solubility of the inhibitor molecules, the EFAIL or TSIL molecules prefer to form micelles at lower concentrations. It has been shown that adding NaHSO\(_4\) to the inhibitor-containing solution causes a more effect on its inhibition performance enhancement. HSO\(_4^-\) ion is larger than Cl\(^-\) one. Therefore, the HSO\(_4^-\) salt has less hydration that it can be highly effective at neutralizing surface charges of micelle\(^{[47]}\).

4. CONCLUSIONS

The aim of this study is to elucidate the corrosion behaviour of low carbon steel samples in the 1 M HCl solution containing mixtures of TSIL and EFAIL inhibitors and NaHSO\(_4\) and NaCl salts, as well as investigation of inhibition mechanism of these compounds using the experimental and theoretical approaches. The main results are summarized below.

Figure 8. SEM micrographs of the steel samples immersed in 1 M HCl solutions (a) without inhibitor, and with (b) 15 mg/L EFAIL + 0.001 M NaHSO\(_4\), (c) 15 mg/L EFAIL + 0.001 M NaCl, (d) 15 mg/L TSIL + 0.001 M NaHSO\(_4\), and (e) 15 mg/L TSIL + 0.001 M NaCl, after 1 h immersion.
The electrochemical results showed that the addition of TSIL and EFAIL inhibitors to the HCl solution caused decrease in the corrosion current density and displacement of corrosion potential towards less negative values. It was shown that the EFAIL inhibitor with HSO$_4^-$ ions could inhibit corrosion rate significantly as compared to the TSIL inhibitor with Cl$^-$ ions.

Addition of salts to 1 M HCl solutions containing TSIL and EFAIL inhibitors could inhibit further corrosion of the steel sample surface. In addition, NaHSO$_4$ salt showed better synergistic effect than NaCl salt in the presence of the two TSIL and EFAIL inhibitors, separately.
The metal surface degradation was obviously decreased in the presence of the inhibitors, especially when the mixture of each inhibitors and salts was used.

The neutralization of micelle surface charges via HSO\textsuperscript{-}4 ions with them larger size and less hydration is more than relatively small Cl\textsuperscript{-} ions with more hydration.

REFERENCES


