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# ELECTROCHEMICAL FREQUENCY MODULATION ANALYSIS OF (3AR,6AR)-3A,6A-DI-P-TOLYLTETRAHYDROIMIDAZO[4,5-D]IMIDAZOLE-2,5(1H,3H)-DITHIONE AS A CORROSION INHIBITOR FOR CARBON STEEL IN 1M HCl MEDIUM

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| ABSTRACT | KEYWORDS |
|---|---|
| Anticorrosion properties, EFM intermodulation spectra, EFM charts, time-versus corrosion rate, corrosion current, corrosion resistance, anodic and cathodic Tafel constants of (3ar,6ar)-3a,6a-di-p-tolyltetrahydroimidazo[4,5-d] imidazole-2, 5 (1H,3H)- dithione inhibitor for carbon steel in a 1M HCl environment were investigated by using new electrochemical frequency modulation analysis method. The obtained results suggest that the inhibitor molecules influence the electrochemical cathodic and anodic half-reactions, forming an insoluble protective layer on the steel surface, and maximally neutralizing the carbon steel surface, and reduce the hydrogen- and chloride-free ions attacks. EFM results' accurate degrees were determined by causality factors. | EFM, intermodulation spectrum, Tafel constants, anticorrosion inhibitor, causality factor. |

## Introduction

The corrosion processes of steel materials are studied using many techniques [6-8], e.g., The traditional methods such as the potentiodynamic polarization, cyclic voltammetry, amperometry, linear polarization, chronoamperometry, electrochemical impedance spectroscopy, and polarization resistance. The conventional methods used a wide range of potential, which increases the measurement time; besides, most of them are destructive measurements, i.e., the steel surface will be damaged, and as a result, the measurements are not accurate, where the destructed steel surface impacts potential, current, frequency and current density changes. Additionally, the calculated current density by Tafel slopes is handy, not computed, resulting in that the hand action will not result in accurate results [9-12].

Recently, the electrochemical frequency modulation (EFM) is used for calculating the changes of the corrosion current density, potential, beta A (anodic Tafel constant), beta B (cathodic Tafel constant) and causality factors on the steel surface in corrosive environments. Additionally, it also shows transient changes in all of these electrochemical parameters. The EFM experiment is faster, more accurate and non-destructive. The EFM has some similarity to the conventional electrochemical impedance spectroscopy method; for example, it uses dual frequencies and waves perturbation signal around 10 mV amplitude. In EFM theory there are four types of' causality factors (2), (3), (4) and (6), and results are automatically comparing with causality factors' theoretically values. The EFM analysis shows how the electrochemical properties change in the active, mass transfer – controlled, and passive regions. The corrosion potential, corrosion current density, beta A (anodic Tafel constant), beta B (cathodic Tafel constant), and causality factors values are calculated by current peaks in intermodulation spectra. These current peaks are calculated by harmonic and intermodulation frequencies in the intermodulation spectra. The EFM uses minimal interference from the input signal. In brief, the EFM is a new technique and powerful method in corrosion science to investigate the electrochemical behaviour of the steel material surface [13-20].

In this article, the transient corrosion potential, corrosion current density, beta A (anodic Tafel constant), beta B (cathodic Tafel constant) values in the active, diffusion-controlled and passive regions on №2 carbon steel material surface were investigated in the absence and presence of a new corrosion inhibitor in 1M HCl acidic medium by the EFM tests. (3Ar,6ar)-3a,6a-di-p-tolyltetrahydroimidazo[4,5-d]imidazole-2,5(1H,3H)-dithione (totehyimimdi) was used as a new powerful corrosion inhibitor for №2 steel material surface, and its inhibition properties were invep to p electron trasfer (Rechemisorption)stigated by the EFM method. All obtained results were compared with the theoretical causality factors (2) and (3).

## 1. Material and methods

### 2.1 №2 steel samples

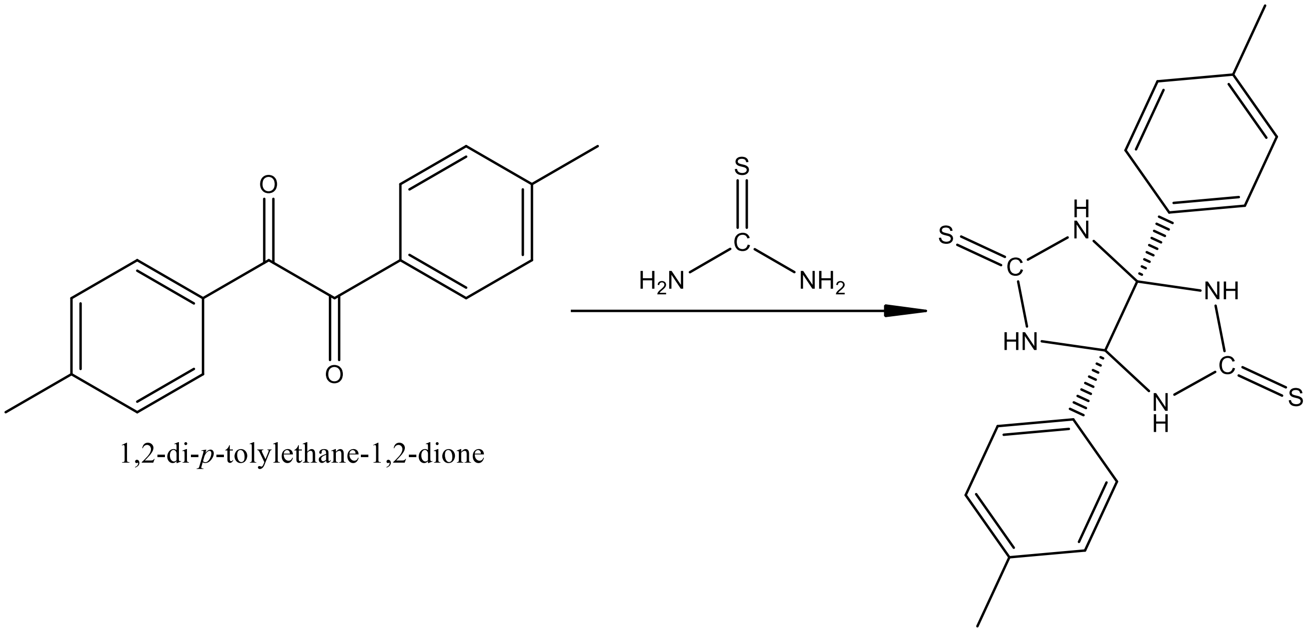
In this EFM experiment, it was used №2 steel material as a working electrode. №2 steel material is a member of the carbon steel family and mainly used in the chemical industry. In №2 steel material, Fe is mainly over 98%, and other elements percentages are the following:

Fe – 98,36; C – 0,2; Mn – 0,5; Si – 0,15; P – 0,04; S – 0,05; Cr – 0,3; Ni – 0,2; Cu – 0,2.

№2 steel material surface is cleaned and rub by SiC abrasive papers, then it is three times washed with distilled water, next ethanol, and isopropyl alcohol. Lastly, it is dried with acetone.

### 1.2. Synthesis of (3ar,6ar)-3a,6a-di-p-tolyltetrahydroimidazo[4,5-d]imidazole-2,5(1H,3H)-dithione

solvent. Then this mixture was sonicated by ultrasonic sound waves during 120 min at 55 °C temperature. After finish sonication processes, the tBuOH alcohol solvent is evaporated from the mixture, and next distilled water was added as a result white solid formed. This resulted in a white solid which is filtered from the mixture and washed by cold distilled water, dried to white powder called (3ar,6ar)-3a,6a-di-p-tolyltetrahydroimidazo[4,5-d]imidazole-2,5(1H,3H)-dithione [21]. The reaction schema is the following:



1,2-di-*p*-tolylethane-1,2-dione

(3a*r*,6a*r*)-3a,6a-di-*p*-tolyltetrahydroimidazo[4,5-*d*]imidazole-2,5(1*H*,3*H*)-dithione

### 2.3. Electrochemical frequency modulation measurement

EFM measurements experiments were conducted using Gamry Potentiostat (IFC1000-06177)/(PC5)Galvanostat/ZRA analyzer (Model G-300, Pstat model Interface 1000, USA), Instrument Version 3.25. The EFM experimental date was calculated by EFM 140-Electrochemical frequency modulation software and analyzed by Gamry Echem Analyst 6.22 software. The Experimental Framework version used is 6.22. In this research, it was used 10 mV amplitude potential perturbation signal, two 2 Hz, and 5 Hz sine waves. This frequency choice gives several advantages: two frequencies (harmonic, intermodulation) cannot impact each other; double layer capacity on steel surface impact slowly on frequency; the frequency requires low time for doing the EFM experiment. The base frequency was 0.1 Hz. All AFM experiments were conducted at room temperature (25 $^{0}$C). The №2 steel working electrode was immersed for 30 min before start the EFM experiments. During 30 min, the state-stable potential reaches the steady-state conditions. After this immersion time, the open circuit potential of №2 steel working electrode was calculated during 2 hours. The reason is that 20 hours is a stabilizing period for achieving a quasi-stationary amount for open circuit potential [22-26].

In EFM tests, the intermodulation spectra have harmonic and intermodulation current peaks. In the Echem Analyst software, the corrosion current, beta A (anodic Tafel constant), beta B (cathodic Tafel constant), corrosion rate, causality factors (2) and (3) values were calculated by large harmonic and intermodulation current peaks in intermodulation spectra.

## 2. Results and discussion

The EFM investigating method is new and more sensitive than historical methods in corrosion science. It gives several advantages for corrosion research. Firstly, using harmonic and intermodulation frequencies in the EFM experiment makes the electrochemical calculation more clearly and require low interference, and gives additional benefits with contras to historical methods. Secondly, the EFM experiments use two 2 and 5 Hz sinusoidal waves around 10 mV perturbation signal amplitude, meaning that this low amplitude minimal destroy working electrode and Gamry electrochemical instrument parts. Thirdly, causality factors (2) and (3) can show an accurate degree of obtained results. Lastly, the EFM technique can indicate that change of oxygen, hydrogen, carbon dioxygen, and corrosive gas on the steel surface, and supplementary hydrodynamic condition [22-26].

The EFM uses two sine waves that forward into the electrochemical cell. The Current response includes only input frequency in historical methods. But the current response includes complex frequencies: summary, different, and vary of the two inputs (1 and 5 Hz) frequencies in the EFM method. In contrast to historical corrosion research methods like PDP, LP, CV, EIS, and gravimetric, the electrochemical frequency modulation method is more sensitive and gives some benefits for corrosion research. For instance, the EFM experiments show that addition kinetic properties: intermodulation spectrum, Fourier Transform of the time series data in time versus current graph, and time versus corrosion rate/Icorr, causality factors (2 and 3), polarization resistance, beta A (anodic Tafel constant) and beta C (cathodic Tafel constant).

In the EFM analysis, the calculation of Icorr, beta A (anodic Tafel constant), beta C (cathodic Tafel constant) depends on corrosion mechanism types on the steel surface. Three types of corrosion mechanisms occur on the steel surface: activation, diffusion, and passive.

In the mechanism of the activation control corrosion process, the steel surface dissolute in a corrosive environment. In the steel dissolute electrochemical reaction, the beta A (anodic Tafel constant) is lower than beta C (cathodic Tafel constant). In this type of corrosion mechanism, Icorr, beta A (anodic Tafel constant), beta C (cathodic Tafel constant) are calculated by the following equations [22-26]:

$$\mathrm{I_{corr}} = \frac{(\mathrm{I}_{\omega_1 \cdot \omega_2})^2}{2\sqrt{8\mathrm{I}_{\omega_1 \cdot \omega_2}\,\mathrm{I}_{2\omega_2 \pm \omega_1} - 3(\mathrm{I}_{\omega_1 \cdot \omega_2})^2}} \qquad (1)$$

$$\text{Beta A} = \frac{\mathrm{I}_{\omega_1 \cdot \omega_2}\mathrm{U}^{\square}}{\mathrm{I}_{\omega_2 \pm \omega_1} + \sqrt{8\mathrm{I}_{\omega_1 \cdot \omega_2}\,\mathrm{I}_{2\omega_2 \pm \omega_1} - 3(\mathrm{I}_{\omega_1 \cdot \omega_2})^2}} \qquad (2)$$

$$\text{Beta C} = \frac{\mathrm{I}_{\omega_1 \cdot \omega_2}\mathrm{U}^{\square}}{-\mathrm{I}_{\omega_2 \pm \omega_1} + \sqrt{8\mathrm{I}_{\omega_1 \cdot \omega_2}\,\mathrm{I}_{2\omega_2 \pm \omega_1} - 3(\mathrm{I}_{\omega_1 \cdot \omega_2})^2}} \qquad (3)$$

In the mechanism of diffusion control corrosion process on the steel electrode surface, the corrosion reaction products are moved from the steel electrode surface, and the reaction center will be activated. So the beta C is infinity (beta C $\rightarrow \infty$), and the cathodic reaction is controlled by $H_2$ gas diffusion in this diffusion mechanism, the cathodic reaction is the following:

$$Fe + H^+ \leftrightarrow FeH^+_{(ads)}$$

$$FeH^+_{(ads)} + e^- \leftrightarrow FeH_{(ads)}$$

$$FeH_{(ads)} + H^+ + e^- \leftrightarrow Fe + H_2$$

The EFM experiment can show how hydrogen gas diffusion can influence on the cathodic half-reaction on the steel surface.

In this type of corrosion mechanism Icorr and beta A (anodic Tafel constant) is calculated by the following equations [22-26]:

$$\mathrm{I_{corr}} = \frac{(\mathrm{I}_{\omega_1 \cdot \omega_2})^2}{2\mathrm{I}_{\omega_2 \pm \omega_1}} \qquad (4)$$

$$\text{Beta A} = \frac{I_{\omega_1 \cdot \omega_2} U^{\square}}{2I_{\omega_2 \pm \omega_1}} \qquad (5)$$

Where U is amplitude, $I_{2\omega_1}$ and $I_{2\omega_2}$ are current peaks at harmonic frequencies of $2\omega_1$ and $2\omega_2$, $I_{\omega_1}$ and $I_{\omega_2}$ are intermodulation current peaks at harmonic frequencies of $\omega_1$ and $\omega_2$, $I_{\omega_2 \pm \omega_1}$ is intermodulation current peaks at angular frequencies of $\omega_2 \pm \omega_1$.

The last corrosion mechanism called passive. In this corrosion process, the anodic half-reaction is passived and is controlled by forming a passive layer on the steel surface. Anodic half-reaction process is the following:

$$Fe + Cl^{-} \leftrightarrow FeCl^{-}_{(ads)}$$

$$FeCl^{-}_{(ads)} \leftrightarrow FeCl_{(ads)} + e^{-}$$

$$FeCl_{(ads)} \leftrightarrow FeCl^{+}_{(ads)} + e^{-}$$

$$FeCl^{+}_{(ads)} + Cl^{-} \leftrightarrow FeCl_{2(ads)}$$

$FeCl_2$ salts formed and adsorbed on the steel surface, which passived anodic reaction. When the anodic half-reaction fully passivated, beta A is infinity ($\text{beta A} \to \infty$), Icorr and beta C (cathodic Tafel constant) is calculated by following equations [22-26]:

$$I_{corr} = \frac{(I_{\omega_1 \cdot \omega_2})^2}{2I_{\omega_2 \pm \omega_1}} \qquad (6)$$

$$\text{Beta C} = \frac{I_{\omega_1 \cdot \omega_2} U^{\square}}{2I_{\omega_2 \pm \omega_1}} \qquad (7)$$

In the EFM experiment, two connections are important to clarify the EFM results' accurate degree. Firstly connection is between input frequency perturbation and response signal. The second connection is between current on the harmonic frequency and current on intermodulation frequency. This two connection is called causality factor. In EFM theory, there are 4 types' causality factors (2, 3, 4, and 6). In this EFM analysis, it was used (2) and (3) causality factors, they are calculated by following equations [22-26]:

$$\text{Causality factor (2)} = \frac{I_{\omega_1 \pm \omega_2}}{I_{2\omega_1}} = 2 \qquad (8)$$

$$\text{Causality factor (3)} = \frac{I_{2\omega_1 \pm \omega_2}}{I_{3\omega_1}} = 3 \qquad (9)$$

In the EFM experiment, the inhibition efficiency is calculated by the following equation:

$$\%IE_{EFM} = \frac{I^{0}_{corr} - I^{inh}_{corr}}{I^{0}_{corr}} \times 100 \qquad (10)$$

Where, $I^{0}_{corr}$ is corrosion current in inhibitor absence medium, $I^{inh}_{corr}$ is corrosion current in inhibitor presence medium and $\%IE_{EFM}$ is inhibition efficiency.

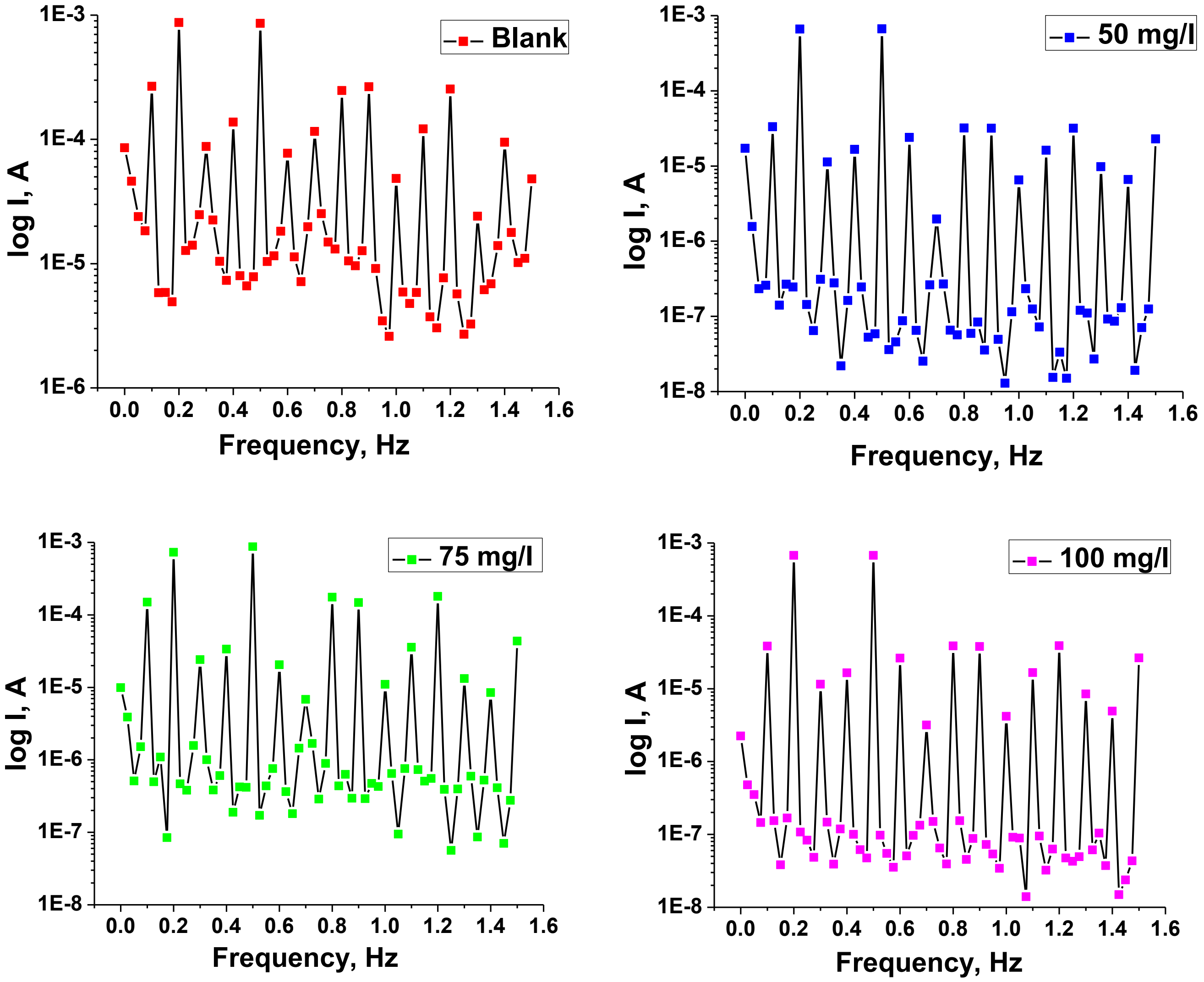


Fig.1. EFM intermodulation spectrums for №2 steel in 1M HCl medium in absence and presence of (3ar,6ar)-3a,6a-di-p-tolyltetrahydroimidazo[4,5-d]imidazole-2,5(1H,3H)-dithione inhibitor at various concentration (25 $^0$C)

The EFM intermodulation spectrums for №2 steel in 1M HCl medium in the absence and presence of (3ar,6ar)-3a,6a-di-p-tolyltetrahydroimidazo[4,5-d]imidazole-2,5(1H,3H)-dithione inhibitor at various concentration were presented in Fig.1. All EFM tests were carried out at room temperature (25 $^0$C). The current peaks in these intermodulation spectrums are responded on calculate corrosion current. It is clear from these spectrums the current fluctuated around 125-170 µA for №2 steel in without inhibitor medium. Because the 1M HCl corrosion environment is very strong for the steel surface, and hydrogen and chlorine ions affect the growth of intermodulation spectrum peaks. In contrast to the inhibited medium, the current peaks fluctuated around 10-15 µA for №2 steel. The reason is that the inhibitor molecules impact the anodic and cathodic electrochemical half-reaction on the metal surface, meaning that inhibitor molecules influence metal surface current-connection abilities and intermodulation spectrum.

The EFM charts for №2 steel in 1M HCl medium in absence and presence of (3ar,6ar)-3a,6a-di-p-tolyltetrahydroimidazo[4,5-d]imidazole-2,5(1H,3H)-dithione inhibitor at various concentration firstly measured and discussed in this research paper, results are presented in Fig.2. It is reported from Fig.2 the current fluctuated between +1mA and -1mA areas during a given time in 1M HCl environment, suggest that corrosion processes are faster and many free ions are formed on the steel surface, and large number free ions on the steel surface impact the increase of corrosion current force. When (3ar,6ar)-3a,6a-di-p-tolyltetrahydroimidazo[4,5-d]imidazole-2,5(1H,3H)-dithione inhibitor adds to the corroded environment, the current fluctuated between +140µA and -131 µA during a given period, suggest that inhibitor molecules formed thin layer and dramatically reduce free ions number on the steel surface. Time-versus current depends on inhibitor concentration, which means that at large inhibitor concentration, time-versus current occurs in lower areas.

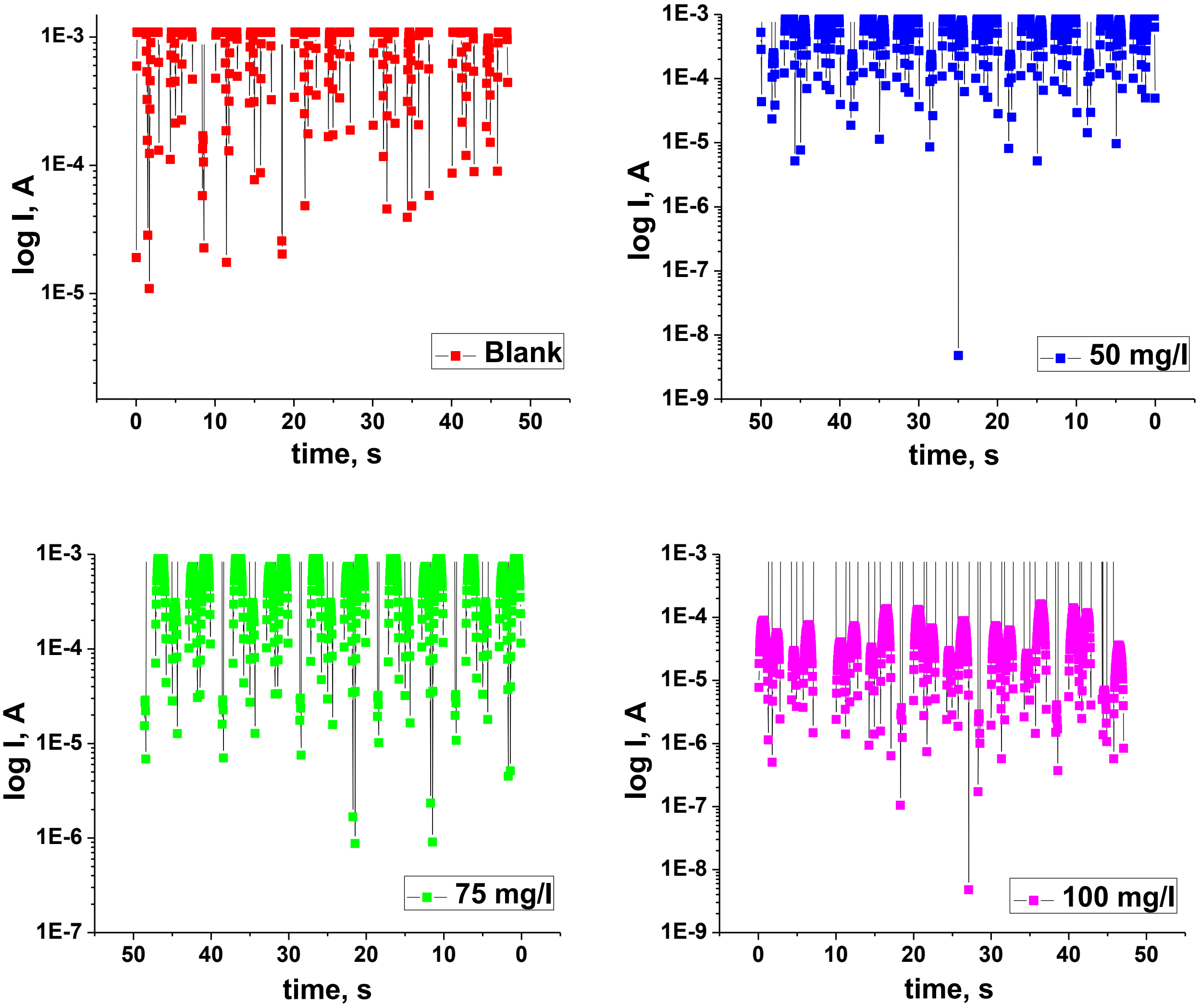


Fig.2. EFM charts for №2 steel in 1M HCl medium in absence and presence of (3ar,6ar)-3a,6a-di-p-tolyltetrahydroimidazo[4,5-d]imidazole-2,5(1H,3H)-dithione inhibitor at various concentration (25 $^{0}$C).

EFM analysis results for №2 steel in 1M HCl medium in the absence and presence of (3ar,6ar)-3a,6a-di-p-tolyltetrahydroimidazo[4,5-d]imidazole-2,5(1H,3H)-dithione inhibitor at various concentration were investigated and presented in Table 1. EFM experiments were performed in the activation, diffusion, and passivation corrosion mechanisms.

In the activation corrosion mechanism, the corrosion current and corrosion rates were 282.2 µA and 129 mpy respectively in 1M HCl medium, which means that the carbon steel electrode dissolute in 1M HCl medium and Fe$^{+2}$, Fe$^{+3}$ ions were formed. These ions impact the growth of corrosion current and corrosion rates. When (3ar,6ar)-3a,6a-di-p-tolyltetrahydroimidazo[4,5-d]imidazole-2,5(1H,3H)-dithione inhibitor molecules add to corrosion medium, they dramatically reduced Fe$^{+2}$ and Fe$^{+3}$ ions number by forming Fe-inhibitor complex and adsorbing on the steel surface as a consequence the corrosion current and corrosion rate dramatically reduced. This action depends on inhibitor concentration.

On the other hand, the corrosion processes were strong, acting in diffusion and passivation corrosion mechanisms. The corrosion current and corrosion rate were recorded 3678 µA and 1681 mpy relatively in 1M HCl medium because $H_2$ gas is formed on the cathodic site, which destroys the steel surface. In addition, the forming $FeCl_2$ and $FeCl_3$ salts layer on the steel surface was good soluble in acid medium and good adsorbent for $H^+$ and $Cl^-$ ions. In contrast, the corrosion current and corrosion rates were 295 µA and 134.8 mpy respectively in inhibited medium, suggest that inhibitor adsorbed and formed a protective layer on the steel surface. This protective layer significantly reduced $H^+$ and $Cl^-$ ions adsorption on the steel surface, resulting that corrosion processes reduced on both cathodic and anodic sites.

(3Ar,6ar)-3a,6a-di-p-tolyltetrahydroimidazo[4,5-d]imidazole-2,5(1H,3H)-dithione inhibitor EFM efficiency is over 80% at optimum concentration (100 mg/l), shows that (3ar,6ar)-3a,6a-di-p-tolyltetrahydroimidazo[4,5-d]imidazole-2,5(1H,3H)-dithione is good protective agents for steel surface in acid medium and maybe use in chemical industry for protect carbon steel materials from acid corrosion.

EFM results' accurate degree in the activation, diffusion, and passivation corrosion mechanisms were determined by the causality factor, indicating that the EFM results were more trustable.

Table 1. EFM analysis results for №2 steel in 1M HCl medium in absence and presence of (3ar,6ar)-3a,6a-di-p-tolyltetrahydroimidazo[4,5-d]imidazole-2,5(1H,3H)-dithione inhibitor at various concentration ($25\ ^{0}C$).

| Inhibitor concentration, mg/l | Icorr, µA | Beta A, mV/decade | Beta C, mV/decade | CR, mpy | Causality factor (2) | Causality factor (3) | %IE$_{EFM}$ |
|---|---|---|---|---|---|---|---|
| Activate control corrosion mechanism | | | | | | | |
| Blank | 282.2 | 19.73 | 23.01 | 129 | 1.95 | 2.96 | - |
| 50 | 81 | 81.55 | 105.25 | 37.02 | 1.75 | 2.81 | 71.30 |
| 75 | 69.19 | 65.87 | 82.21 | 31.63 | 1.93 | 2.95 | 75.48 |
| 100 | 51.91 | 54.96 | 78.43 | 23.72 | 2.03 | 3.02 | 81.60 |
| Diffusion control corrosion mechanism | | | | | | | |
| Blank | 3678 | 138.5 | - | 1681 | 1.93 | 2.97 | - |
| 50 | 656.52 | 232.8 | - | 300.05 | 1.71 | 2.83 | 82.15 |
| 75 | 488.80 | 208.9 | - | 223.40 | 1.90 | 2.96 | 86.71 |
| 100 | 295 | 183.7 | - | 134.8 | 2.05 | 3.05 | 91.98 |
| Passive control corrosion mechanism | | | | | | | |
| Blank | 3678 | - | 138.5 | 1681 | 1.93 | 2.97 | - |
| 50 | 656.52 | - | 232.8 | 300.05 | 1.71 | 2.83 | 82.15 |
| 75 | 488.80 | - | 208.9 | 223.40 | 1.90 | 2.96 | 86.71 |
| 100 | 295 | - | 183.7 | 134.8 | 2.05 | 3.05 | 91.98 |

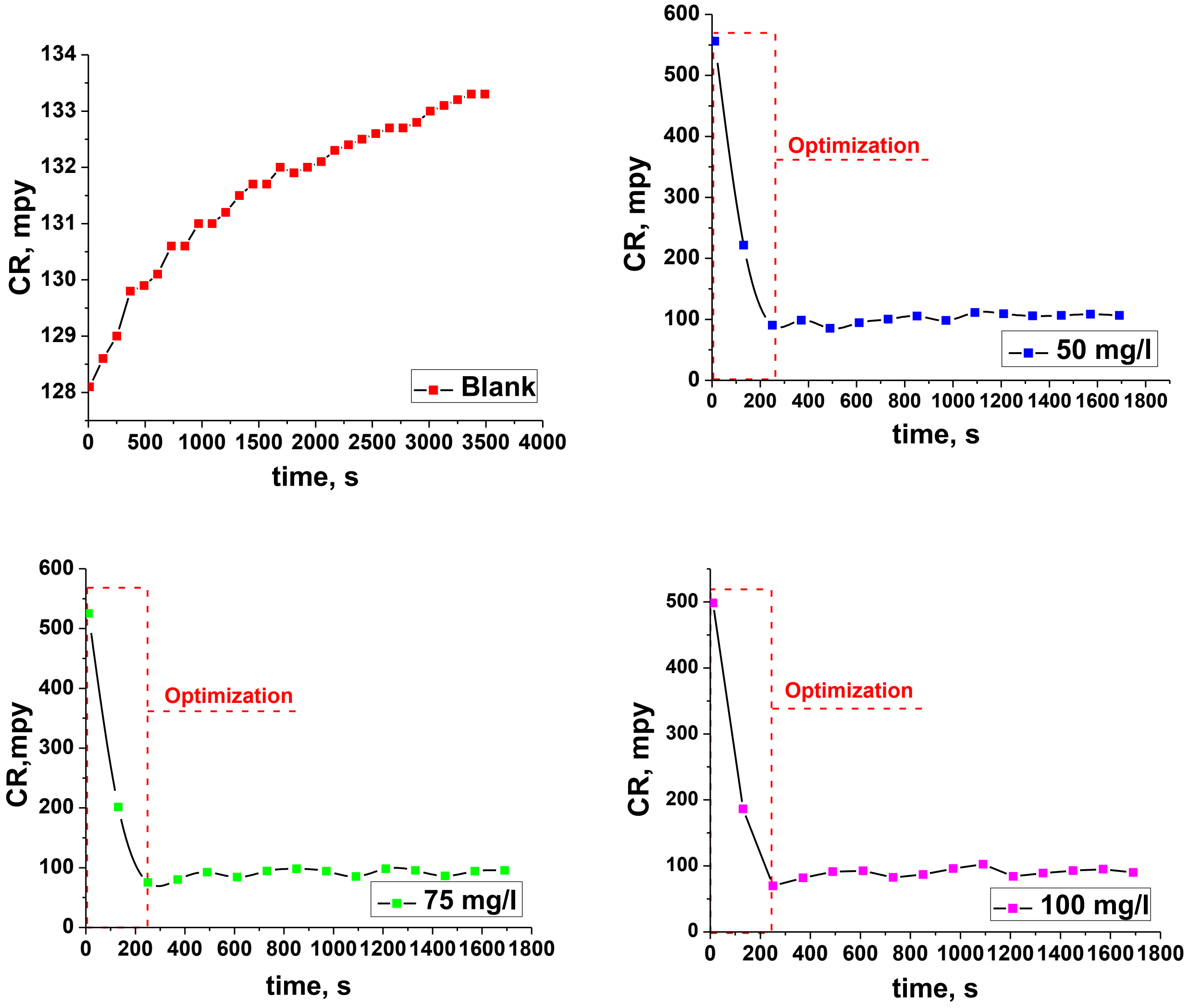


Fig.3. Time-versus corrosion rate for №2 steel in 1M HCl medium in absence and presence of (3ar,6ar)-3a,6a-di-p-tolyltetrahydroimidazo[4,5-d]imidazole-2,5(1H,3H)-dithione inhibitor at various concentration (25 $^0$C).

Time-versus corrosion rate for №2 steel in 1M HCl medium in absence and presence of (3ar,6ar)-3a,6a-di-p-tolyltetrahydroimidazo[4,5-d]imidazole-2,5(1H,3H)-dithione inhibitor at various concentration were investigated and presented in Fig.3. It was shown from these graphs that, the corrosion rate significantly increased from 128 to 133.5 mpy during a given period in 1M HCl environment, suggest that corrosion processes are faster and growth on the steel surface.

On the other hand, the corrosion rate in an inhibited environment dramatically went down during optimization time, which is around 250 s. In the optimization time the decrease of corrosion rate depends on inhibitor concentration. For example, the corrosion rate is maintained around 50-60 mpy at 100 mg/l inhibitor concentration. Optimization processes require several anti-corrosion activities: firstly, the inhibitor molecules connect with iron ions and form an iron-inhibitor-complex in the corrosion medium; secondly, this forms complex adsorb on the steel surface and neutralize steel surface free ions. After optimization time, the corrosion rate for inhibited medium stabilizes around low point, suggests that inhibitor molecules form a protective layer on the steel surface, which they are more stable and dissolute in 1M HCl corrosive medium. So A inhibitor is a more effective inhibitor, and maximally protects the steel surface from corrosive attacks.

Time-versus corrosion current for №2 steel in 1M HCl medium in absence and presence of (3ar,6ar)-3a,6a-di-p-tolyltetrahydroimidazo[4,5-d]imidazole-2,5(1H,3H)-dithione inhibitor at various concentration was investigated, resulted in Fig.4. Corrosion current dramatically rocked from 280 µA to 310 µA during a given period in inhibitor absence environment. However, it dramatically reduced to around 50-60 µA and stabilized in the inhibited environment. This change depends on inhibitor concentration. The corrosion current change difference between uninhibited and inhibited medium is around 250 µA, stating that the inhibitor molecule is a mixed type of inhibitor and impacts on both cathodic and anodic processes on the steel surface.

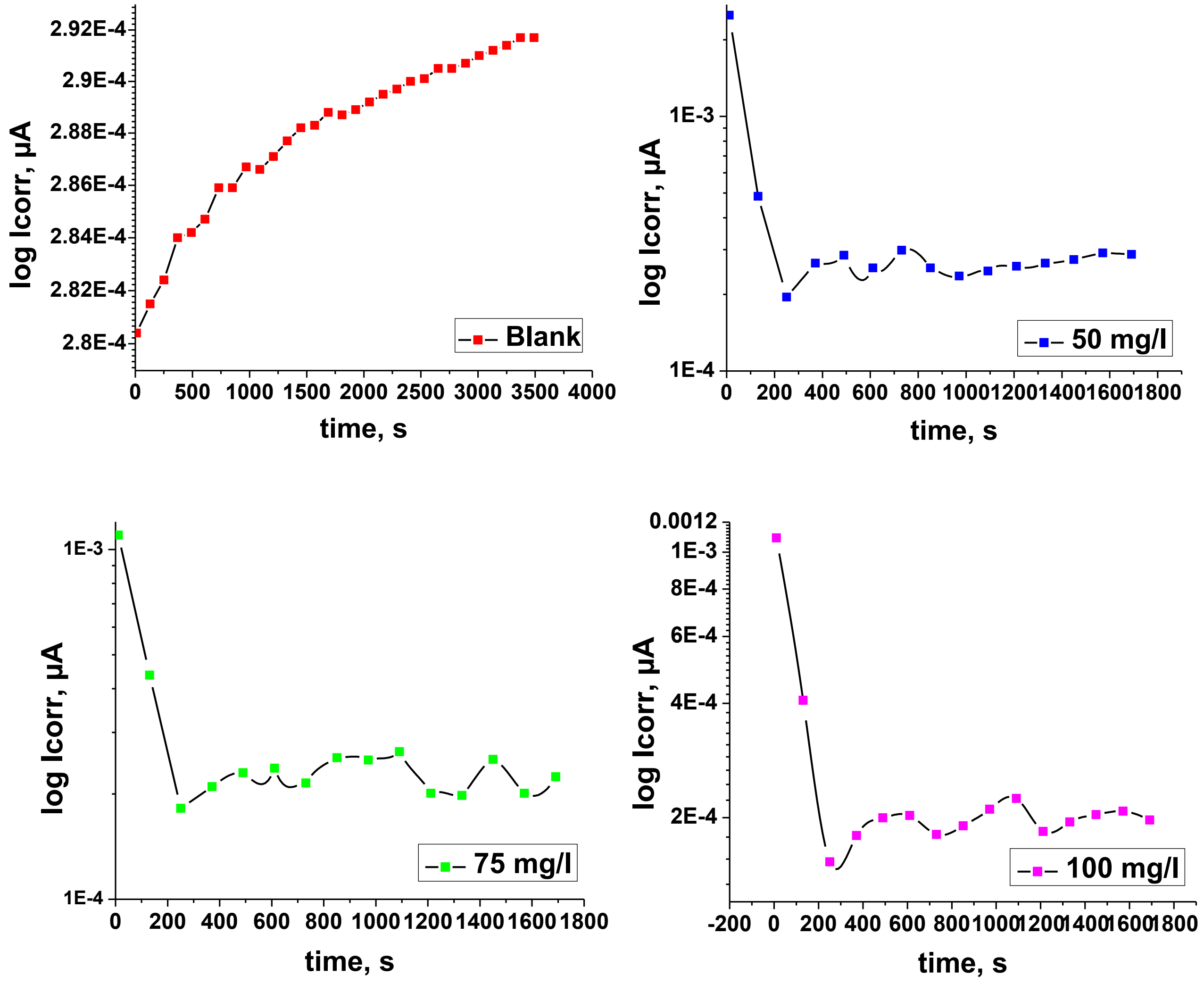


Fig.4. Time-versus corrosion current for №2 steel in 1M HCl medium in absence and presence of (3ar,6ar)-3a,6a-di-p-tolyltetrahydroimidazo[4,5-d]imidazole-2,5(1H,3H)-dithione inhibitor at various concentration (25 $^0$C).

The corrosion resistance of the steel surface is very low (around 16.5 ohm), but it slowly increased from 16.3 to 16.8 ohm in uninhibited 1M HCl medium, revealed in Fig.5. The reason is that $FeCl_3$, $FeCl_2$, $Fe(OH)_3$ and $Fe(OH)_2$ compounds were formed on the steel surface, and these forming thing layers covered some active sites on the steel surface and slowly blocked corrosion attacks to the steel surface; as a result, the corrosion resistance slowly goes up.

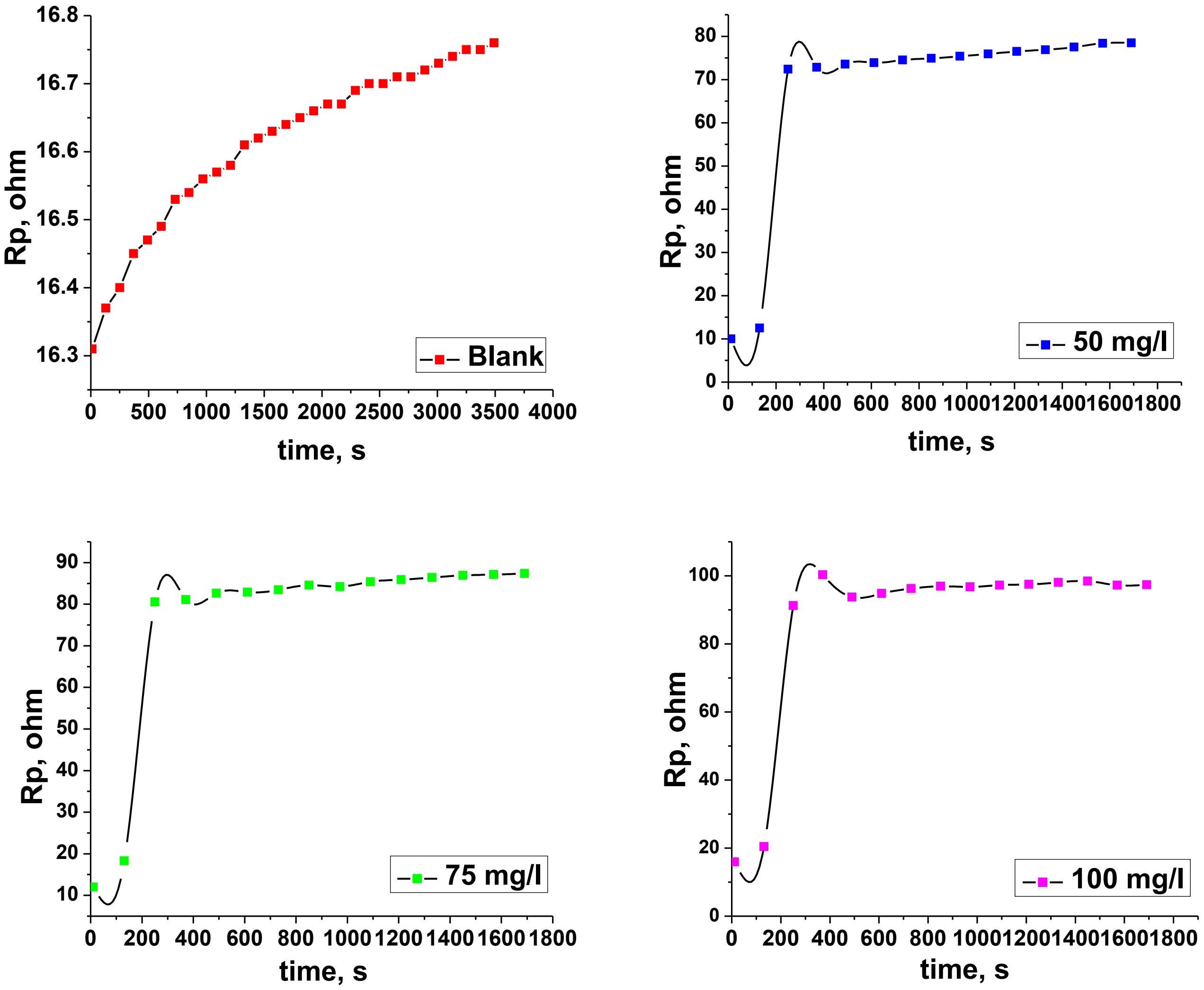


Fig.5. Time-versus corrosion resistance of for №2 steel in 1M HCl medium in absence and presence of (3ar,6ar)-3a,6a-di-p-tolyltetrahydroimidazo[4,5-d]imidazole-2,5(1H,3H)-dithione inhibitor at various concentration in (25 $^0$C).

On the other hand, the corrosion resistance is too large in inhibited 1M HCl medium (Fig.5) and depends on inhibitor concentration. For instance, it maintained around 70 ohms at 50 mg/l inhibitor concentration while it stabilized around 100 ohms at 100 mg/l inhibitor concentration (Fig.6). These obtained results suggest that (3ar,6ar)-3a,6a-di-p-tolyltetrahydroimidazo[4,5-d]imidazole-2,5(1H,3H)-dithione inhibitor is effective corrosion resistance molecules for №2 steel surface in aggressive environment.

EFM method gives good opportunities for deep understand anodic and cathodic Tafel constants change by period. In this research work, the time-versus Tafel betas (anodic and cathodic constants) for №2 steel in 1M HCl medium in absence and presence of (3ar,6ar)-3a,6a-di-p-tolyltetrahydroimidazo[4,5-d]imidazole-2,5(1H,3H)-dithione inhibitor at various concentration firstly investigated and resulted in Fig.6. Anodic and cathodic Tafel constants for №2 steel were recorded around 20 and 22 mV/decade and increased during the period in 1M HCl medium, reported that the electrochemical process is going on the steel surface.

Anodic and cathodic Tafel constants require an electrochemical half-reaction. Inhibitor molecules influence anodic and cathodic Tafel constants and changed them to large potential, and this action depends on inhibitor concentration. Anodic and cathodic Tafel constants of inhibited medium stabilized. This action shows the inhibitor impact on cathodic anodic half-reaction is stable.

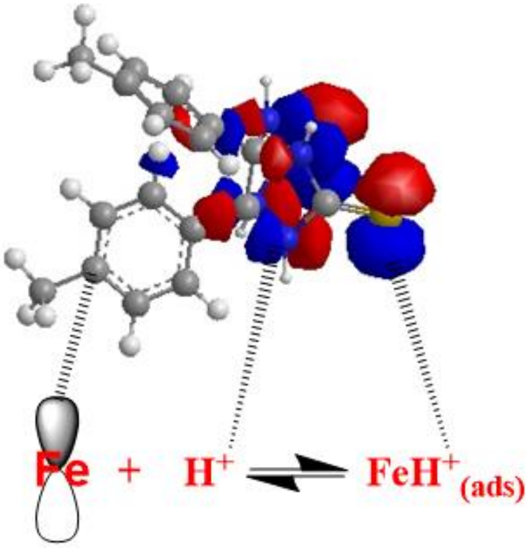
(3ar,6ar)-3a,6a-di-p-tolyltetrahydroimidazo[4,5-d]imidazole-2,5(1H,3H)-dithione inhibitor impacts on cathodic reaction on the steel surface, reaction mechanism is following:

$$Fe + H^+ \leftrightarrow FeH^+_{(ads)}$$

$$FeH^+_{(ads)} + e^- \leftrightarrow FeH_{(ads)}$$

$$FeH_{(ads)} + H^+ + e^- \leftrightarrow Fe + H_2$$

Inhibitor molecules connect with iron free d orbitals and donate delocalization electrons to $H^+$ and $FeH^+_{(ads)}$ ions on steel surface; as a result, these ions are neutralized, this mechanism is following:



**Cathodic site on steel surface**

On the other hand, the steel surface is positively charged with the potential of zero charges (PZC) and hydrated $Cl^-$ions can be adsorbed on this steel surface. Supplementary, iron is oxidized in anodic site on steel surface, this oxidized reaction is following:

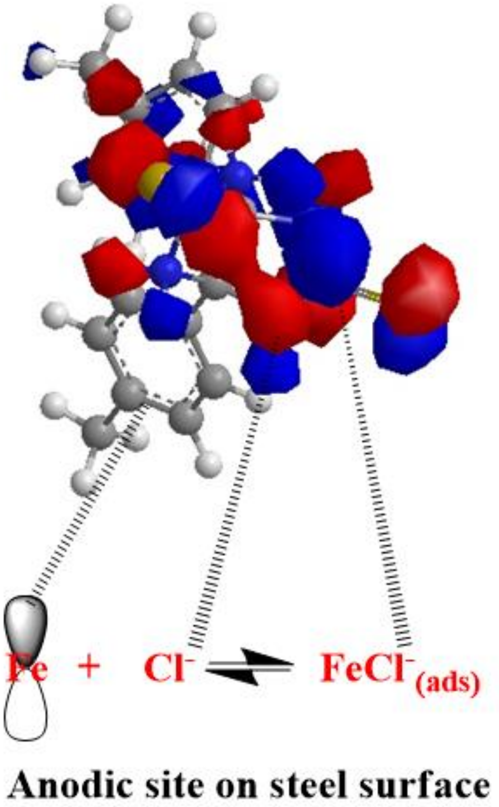
$$Fe + Cl^- \leftrightarrow FeCl^-_{(ads)}$$

$$FeCl^-_{(ads)} \leftrightarrow FeCl_{(ads)} + e^-$$

$$FeCl_{(ads)} \leftrightarrow FeCl^+_{(ads)} + e^-$$

$$FeCl^+_{(ads)} \leftrightarrow Fe^{2+} + Cl^-$$

Supplementary, inhibitors neutralize $Cl^-$ and $FeCl^-_{(ads)}$ ions~~, t~~. This neutralize mechanism is the following:



It was clear from experimental results, (3ar,6ar)-3a,6a-di-p-tolyltetrahydroimidazo[4,5-d]imidazole-2,5(1H,3H)-dithione inhibitor molecules can decrease $H^+$, $FeH^+_{(ads)}$, $Cl^-$ and $FeCl^-_{(ads)}$ ions diffusion on the steel surface and deplete intergranular corrosion speed. Inhibitor molecules can adsorb on the steel surface by physical and chemical adsorption. Physical adsorption of (3ar,6ar)-3a,6a-di-p-tolyltetrahydroimidazo[4,5-d]imidazole-2,5(1H,3H)-dithione inhibitor molecules on the metal surface occur by the electrostatic interaction between positive charged nitrogen, sulfur heteroatoms and $H^+$, $FeH^+_{(ads)}$, $Cl^-$ and $FeCl^-_{(ads)}$ ions. Next, it occurred that chemical adsorption on the metal surface by donor-acceptor interaction between (3ar,6ar)-3a,6a-di-p-tolyltetrahydroimidazo[4,5-d]imidazole-2,5(1H,3H)-dithione inhibitor molecules and Fe atoms. In this process, the delocalized $\pi$ electrons in the aromatic ring and unpair electrons of heteroatoms are shared to free d orbitals of iron atoms on the metal surface.

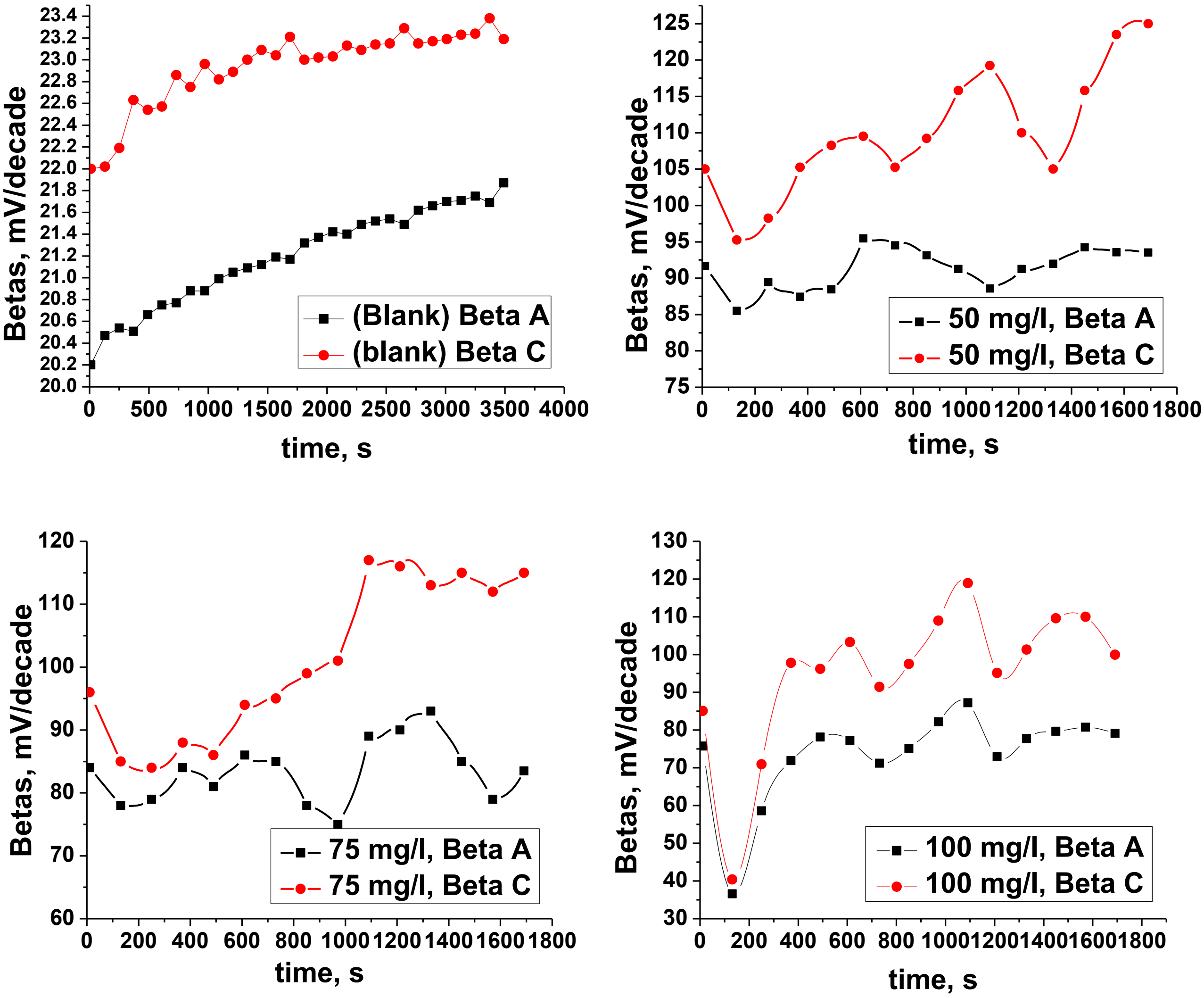


Fig.6. Time-versus Tafel betas for №2 steel in 1M HCl medium in absence and presence of (3ar,6ar)-3a,6a-di-p-tolyltetrahydroimidazo[4,5-d]imidazole-2,5(1H,3H)-dithione inhibitor at various concentration (25 $^0$C).

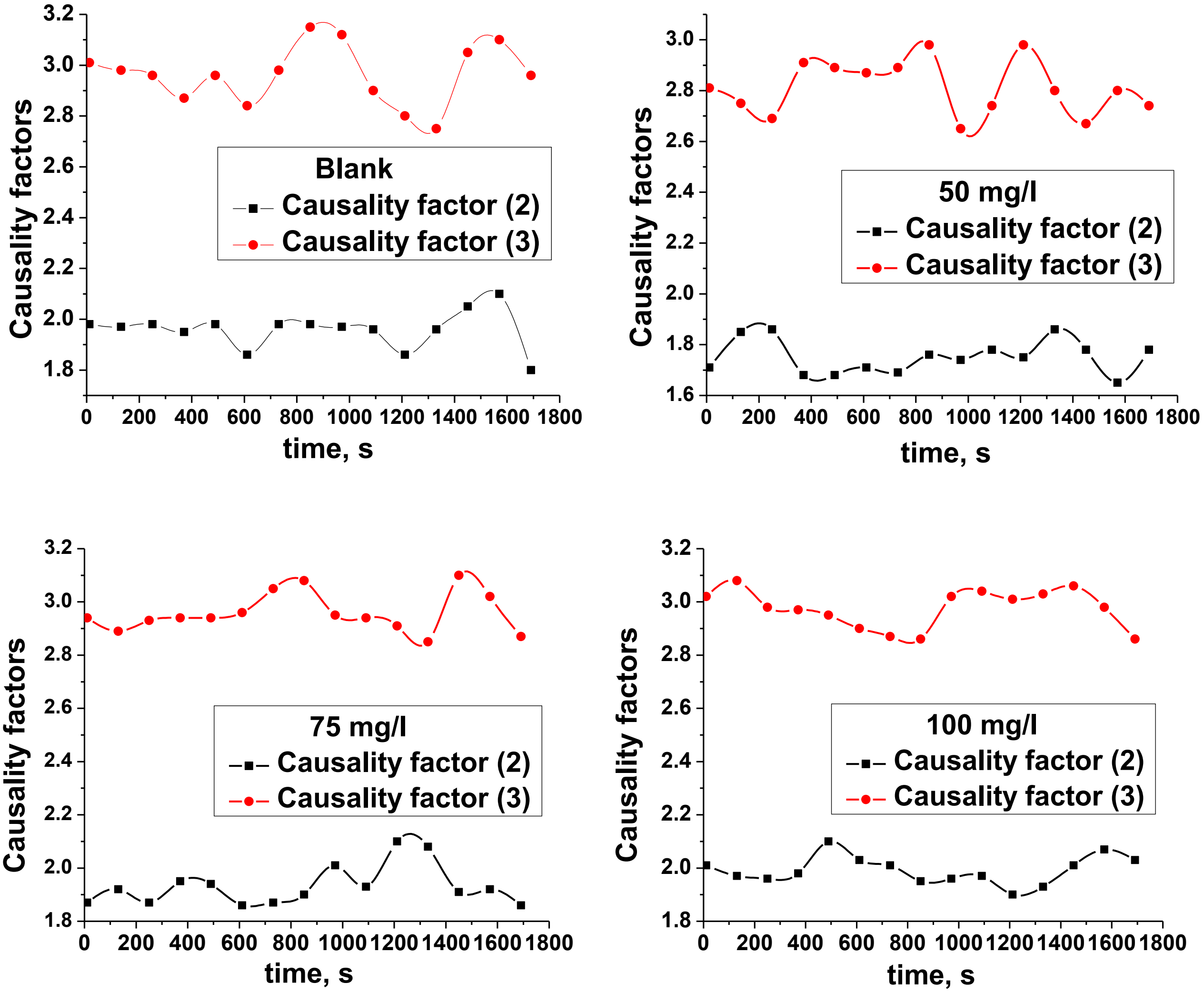


Fig.7. Time-versus causality factors for №2 steel in 1M HCl medium in absence and presence of (3ar,6ar)-3a,6a-di-p-tolyltetrahydroimidazo[4,5-d]imidazole-2,5(1H,3H)-dithione inhibitor at various concentration (25 $^{0}$C).

EFM results from accurate degrees were determined by causality factors (2) and (3) values. It was found that the experimental EFM causality factors (2) and (3) values for №2 steel in 1M HCl medium in absence and presence of (3ar,6ar)-3a,6a-di-p-tolyltetrahydroimidazo[4,5-d]imidazole-2,5(1H,3H)-dithione inhibitor at various concentration were similar to theoretical causality factors (2) and (3) values (Fig.7), meaning that obtained EFM test results were more accurate. In this research, it was also studied that the experimental EFM causality factors (2) and (3) values were stabilized around 2 and 3 respectively during period, suggests that the obtained results accurate degrees were valuable at different times.

## Conclusions

In this research work, the anti-corrosion properties, the EFM intermodulation spectrums, EFM charts, time-versus corrosion rate, corrosion current, corrosion resistance, anodic and cathodic Tafel constants of (3ar,6ar)-3a,6a-di-p-tolyltetrahydroimidazo[4,5-d]imidazole-2,5(1H,3H)-dithione inhibitor for carbon steel in 1M HCl environment were investigated and resulted on following opinions:

intermodulation spectrums indicated that the current peaks fluctuated around 10-15 µA for carbon steel in inhibited medium, suggest that the inhibitor molecules impact anodic and cathodic electrochemical half-reaction on the metal surface, and decrease current-connection abilities of steel surface to the potential downside;

it was shown by EFM chart, when (3ar,6ar)-3a,6a-di-p-tolyltetrahydroimidazo[4,5-d]imidazole-2,5(1H,3H)-dithione inhibitor adds to the corroded environment the current is fluctuated between +140µA and -131 µA during a given period, suggest that inhibitor molecules form thing layer and dramatically reduce free ions number on the carbon steel surface;

an inhibitor efficiency for carbon steel surface is over 80%, and maximally decreased corrosion rate, corrosion current and maximally increased corrosion resistance of steel surface in 1M HCl environment;

inhibitor molecules influenced anodic and cathodic Tafel constants and changed them to large potential, and this action depends on inhibitor concentration. Anodic and cathodic Tafel constants of inhibited medium stabilized, this action show the inhibitor impact on cathodic anodic half-reaction is stable;

EFM results' accurate degrees were determined by causality factors (2) and (3) values. The experimental EFM causality factors (2) and (3) values were stabilized around 2 and 3 respectively during a given period, suggests that the obtained results accurate degrees were valuable at different time.

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