

# Corrosion Behaviour of Carbon Steel In Presence of New Generation of Heterocyclic Compounds

## Case Study: The Egyptian Minerals and Salts Company (Emisal)

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### ABSTRACT

The Egyptian Minerals and Salts Company (EMISAL) located in Fayoum, Egypt, extract Sodium Sulfate from lake "Qaroun" water which contains Chloride and Sulfate ions as major components. The extraction process depends on the crystallization of Sodium Sulfate by cooling the lake saline solution up to  $-1^{\circ}\text{C}$ . The crystallization occurs through consecutive crystallizers. Each crystallizer contains a tube- side made from Aluminum bronze or Titanium and a shell side made from Nickel aluminum bronze. The saline solution (Brine solution) which is rich in both  $\text{Na}_2\text{SO}_4$  and  $\text{NaCl}$  passes inside the tube where the cooling solution passes in the shell side around the tube. The solution inside the tube is subjected to cooling and continuous circulations under the effect of the circulation pumps. Consequently, the brine solution temperature is lowered from  $25^{\circ}\text{C}$  to  $-1^{\circ}\text{C}$  and Sulfate is separated as  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  whereas  $\text{NaCl}$  is still soluble in the solution and then used as cooling solution in the first crystallization stage. In the second crystallization stage, the cooling solution is mono ethylene glycol –water mixture, which pumped from the refrigeration units in lines made from carbon steel, due to drastic conditions during circulation process and the degradation of glycol to different types of organic acid mainly have small partial size. Moreover glycol has physical affect also increases the corrosive behaviour, the carbon steel lines are subjected to continuous corrosion, which lead to appearance of rusted iron in the cooling solution which results in a reduced efficiency of the cooling process. The anti-corrosion activity of the newly synthesized phthalazin compounds were covered the electrochemical behaviours of steel alloy cured in solution content a mixture of mono ethylene glycol and water content 67% which obtained in cooling system.

**Keywords:** Monoethylene Glycol, Carbon Steel, Anti Corrosion, Phthalazin.

### I. INTRODUCTION

Dow Chemical Co., Midland, Mich., distributes a technical bulletin entitled, "Acidic Thermal Degradation of ethylene Glycol and Propylene Glycol" [1]. This advisory bulletin references the research of Dr. Walter Rossiter and his team of the National Bureau of Standards, now named "The National Institute for Standards and Technology (NIST)". Dr. Rossiter and his team conducted experiments that showed uninhibited ethylene glycol will degrade into five organic acids - glycolic, glyoxylic, formic, carbonic and oxalic- in the presence of heat, oxygen, copper and aluminum [2-4]. Copper and Aluminum act as catalysts in the presence of uninhibited ethylene glycol. The organic acids then will chemically attack Copper and Aluminum in as little as three weeks under the right conditions to form metal organic compounds in the fluid. Another extensive study

on the degradation of uninhibited ethylene glycol was conducted by John Beavers and Ronald Diegle of Battelle, Columbus Laboratories [5].

Corrosion of metals is a major industrial problem that has attracted many investigation and researches [6, 7]. The use of inhibitors is one of the most practical methods to protect metals against corrosion, especially in acidic media [8]. Most efficient inhibitors are organic compounds containing electronegative functional groups and  $\pi$ -electrons in triple or conjugated double bonds. Researchers conclude that the adsorption on the metal surface depends mainly on the physicochemical properties of the inhibitor group, such as the functional group, molecular electronic structure, electronic density at the donor atom *P*-orbital character and the molecular size [9-11]. A number of heterocyclic compounds containing Nitrogen, Oxygen and Sulphur either in the

aromatic or long chain Carbon system have been reported to be effective inhibitors <sup>[12, 13]</sup>. The planarity and the lone electron pairs in the hetero atoms are important features that determine the adsorption of molecules on the metallic surface <sup>[14]</sup>. The inhibition efficiency has been closely related to the inhibitor adsorption abilities and the molecular properties for different kinds of organic compounds <sup>[15- 19]</sup>. The power of the inhibition depends on the molecular structure of the inhibitor.

The primary step in the action of organic corrosion inhibitors in acid solutions is usually adsorption at the metal–solution interface. The adsorption process depends on the electronic characteristic of the molecules (adsorbate), the chemical composition of the solution, nature of the metal surface; temperature of the reaction and on the electrochemical potential at the metal–solution interface <sup>[20]</sup>. The adsorption requires the existence of attractive forces between the adsorbate and the metal. According to the type of forces, adsorption can be physisorption or chemisorptions or a combination of both <sup>[21]</sup>. Physisorption is due to electrostatic attractive forces between inhibiting organic ions or dipoles and the electrically charged surface of the metal. Chemisorptions is due to interaction between unshared electron pairs or P-electrons with the metal in order to form a coordinate type of bond. It may take place in presence of heteroatom (P, Se, S, N, O), with lone-pair electrons and/or aromatic rings in the adsorbed molecules <sup>[22- 27]</sup>. Many organic molecules are used to inhibit carbon steel corrosion.

The aim of this work is to study influence of the molecular structure on the inhibiting efficiencies of organic compounds in corrosion processes. The inhibiting efficiency of non-toxic phthalazin derivatives on carbon steel corrosion in mono ethylene glycol content water 67% was investigated. The investigation is performed using electrochemical method of potentiodynamic polarization, many mechanisms have been proposed for the inhibition of metal corrosion by organic inhibitors. Generally it has been assumed that the first stage in the action mechanism of the inhibitor in the acid media is based on its adsorption on the metal surface <sup>[28]</sup>. The processes of adsorption of inhibitors are influenced by the nature of the metal surface, the chemical structure of the organic inhibitor, the

distribution of charge in the molecule, the type of aggressive electrolyte, and the type of interaction between organic molecules and the metallic surface <sup>[29, 30]</sup>. In most inhibition studies the formation of donor–acceptor surface complexes between  $\pi$ - electrons of an inhibitor and the vacant d-orbital of a metal were postulated <sup>[31- 38]</sup>. Nitrogen-based compounds are effective inhibitors for carbon steel corrosion in aqueous solutions. The presence of lone pairs of electrons on the nitrogen atoms of the additional nitrogen atoms delocalized and thus produces a delocalization energy that stabilized the compound. Also, it is known that heterocyclic nitrogen compounds may also adsorb through electrostatic interactions between the positively charged nitrogen atom and the negatively charged metal surface <sup>[39]</sup>.

## II. EXPERIMENTAL

### 2.1. Metals and electrode

The working electrode prepared from commercially carbon steel used as a pipes in the refrigeration unit in the Egyptian Minerals and Salts Company (EMISAL), El-Fayoum, Egypt. The chemical composition is indicated in Table (I).

### 2.2. Surface pretreatment of the electrode

To achieve high reproducibility, the working electrode was always pretreated using the same procedure. The electrode was mechanically polished using successive grade emery papers 800/1000/1200/2000 and wrapped against smooth polishing cloth and then washed with deionized water (*DI*) water. The working electrode consists of massive rod of diameter corresponding to a circular surface area of a 0.28 cm<sup>2</sup>. The electrode was fitted into glass tubing of appropriate internal diameter by chemical resistant epoxy resin, leaving the front surface area to contact the solution.

**Table (I):** Chemical composition of carbon steel

| Element  | C    | Si   | Mn   | S    | P    | Cu   | Cr   | Ni   | Mo | Al   | Fe      |
|----------|------|------|------|------|------|------|------|------|----|------|---------|
| analysis | 0.34 | 0.26 | 0.93 | 0.02 | 0.04 | 0.01 | 0.01 | 0.02 | -  | 0.01 | balance |

### 2.3. The investigated corrosion inhibitors

The selected inhibitors were synthesized in the laboratory; they were prepared by 1 (mmol) with respect to their molecular weight. The stock solutions were made in (9:1) water: acetone to ensure solubility. The stock solutions were used for all experimental purposes.

Table (2): The investigated corrosion inhibitors

|  |  |
|--|--|
| 4-(3-bromo-4-methylphenyl)-2H-phthalazin-1-one (I)   |  |
| 4-(3-bromo-4-methylphenyl)-1-oxo-2H-phthalazin-2-yl] acetic acid hydrazide (II)                                    |  |
| 2-[(3-Methylpyrazol-5-one-1-yl) carbonyl methyl]-4-(3-bromo-4-methylphenyl)-2H-phthalazin-1-one (III)              |  |
| 2-[(3,5-Dimethyl-pyrazol-1-yl) carbonyl methyl]-4-(3-bromo-4-methylphenyl)-2H-phthalazin-1-one (IV)                |  |
| 2-[4-(3-bromo-4-methylphenyl)-1-oxo-2H-phthalazin-2-yl]-N-(1,3-dioxo-1,3-dihydroisoindol-2-yl)acetamide (V)        |  |
| Benzopyrolo-2-one-3-yl-4-[(3-bromo-4-methylphenyl)-2H-phthalazin-1-one-2-yl]acetyl hydrazone (VI)                  |  |
| [4-(3-bromo-4-methylphenyl)-1-oxo-2H-phthalazin-2-yl]acetic acid (2,3,4,5-tetrahydroxy-pentylidene)hydrazide (VII) |  |

|   |  |
|---|--|
| N-(3-(1H-imidazol-1-yl)propyl)-2-(4-(3-bromo-4-methylphenyl)-1-oxophthalazin-2(1H-yl)acetamide (VIII) |  |
| 4-(3-bromo-4-methylphenyl)phthalazine-1(2H)-thione (IX)   |  |

### 2.4. Materials and solutions

Analytical grade reagent and (DI) water were used. The media was prepared by the sequential addition of (330 ml) of mono ethylene glycol solution which has specific gravity (1.110-1.112 gm/cm<sup>3</sup>) to (670 ml) of the deionized (DI) water; the solution was stirred to complete miscibility. We get the recommended final concentration namely; a mixture of mono ethylene glycol and water content 67% and has specific gravity (1.040 gm/cm<sup>3</sup>) and PH = 6.

### 2.5. Electrochemical Cell

The cell was a three – electrode all – glass double jacket cell, with a platinum counter electrode and saturated calomel reference electrode. The working electrode was placed in the center of the cell in the manner that the electrode is adjacent to a platinum counter electrode and the reference electrode as presented in Fig. (I).

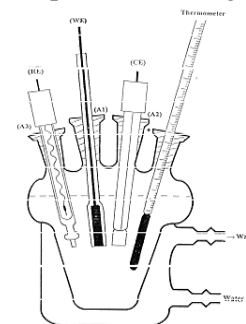


Figure 1. Double jacket all glass electrochemical cell

[WE = working electrode, RE = reference electrode and CE = counter electrode]

## 2.6. Electrochemical system

The electrochemical polarization measurements were performed using the volt lab 10 PGZ100" All-in-one" Potentiostat / Galvanostat system (made in France). The latest analog and microcomputer design advances to provide high performance, ease of use, and greater versatility in electrochemical measurements. The instrument is interfaced to an external IBM 1200 CPU computer. The Volta Master 4 software is designed to measure and analyze corrosion data, easily and reliably, using a variety of techniques cyclic voltammeter, potentiodynamic polarization. The experimental set up allows the direct application of the required techniques. In our experiments techniques, both linear polarization and Tafel techniques were used.

## 2.7. Potentiodynamic Polarization Techniques

The corrosion rate can be estimated usually by linear polarization and Tafel extrapolation. The potentiodynamic measurements were conducted at a scan rate of 20 mV/S. The resulting current is linearly plotted versus the potential and the slope of this potential-current function at corrosion potential, ( $E_{corr}$ ), is referred to as the polarization resistance, ( $R_p$ ), it is used with the Tafel constants to determine the corrosion current density, ( $i_{corr}$ ). The linear polarization technique is extremely rapid. The rapidity of the measurements makes the linear polarization very useful in that the applied potential is never far removed from the corrosion potential, so the surface of the specimen is not significantly affected by the experiment and can often be used for other studies. The Tafel plot technique provides another way of determining the corrosion rate that has been used. In a typical experiment, we program the entire potential scan to take place within  $\pm 200$  mV of  $E_{corr}$  with a scan rate of 20 mV/S. The corrosion rate is calculated and the results are displayed digitally.

## III. RESULTS AND DISCUSSION

The data presented and discussed in this chapter were covered the electrochemical behaviour of steel alloy cured in solution content a mixture of mono ethylene glycol and water content 67% which present in cooling

system in the Egyptian minerals & salts company (EMISAL).

During this part, the effects of different types of organic compound were studied. Electrolyte solution is a mixture of mono ethylene glycol and water content 67%, the electrode prepared from carbon steel used in cooling system. Linear polarization technique used to determine different function mainly related to the corrosion of steel alloy and can present the mechanism of corrosion and inhibition.

### 3.1. Electrochemical behaviour of steel alloy in absence of organic additive

The effect of electrolyte on the electrochemical behaviour of steel alloy was investigated under the polarization conditions. The linear polarization and Tafel extrapolation techniques were employed at scan rate 20 mV/S. The potentiodynamic polarization curves of the electrode at glycol solution were investigated and presented in Fig. (2). The values of different corrosion parameters data were calculated and presented in Table (3).

In absence of organic additive, a low negative corrosion potential ( $E_{corr}$ ) was recorded, -124 mV, due to the acidic behaviour of glycol in water furthermore this acidity increases due to the degradation of glycol to different types of organic acid mainly have small partial size. Moreover glycol has physical affect also increases the corrosive behaviour. According to the Tafel plots, the corrosion process is mixed controlled with time due to the reduction of dissolved Oxygen is the most probable cathodic control and steel oxidation is anodic reaction. The current density notes 0.183 mA/cm<sup>2</sup>. The low values of  $i_{corr}$  are mainly due to the chemical corrosion process on the surface of electrode. The Polarization resistance in this case records 0.60 k $\Omega$ .cm<sup>2</sup>. Polarization resistance represents the resistance of the electrode to be polarized. According to Stern Gerry equation, the corrosion rate can be determined of steel in glycol solution. Corrosion rate gets high value compared to steel in water. Corrosion rate notes 2.13 mm/Y this value explain the highly aggressive properties of glycol solution. **Generally; glycol solution has corrosive properties due to the following reason:**

[1] It is relatively easy to degrade into five organic acids (glycolic, glyoxylic, formic, carbonic and oxalic) in the presence of heat, oxygen, copper and aluminum. Copper and aluminum act as catalysts. The organic acids then will chemically attack copper and aluminum in as little as three weeks under the right conditions to form metal organic compounds in the fluid.

[2] Acidic ethylene glycol effects on metals. The latter is much more corrosive toward metals. Corrosion of metals will commence at locations where metal ions are stripped away from the base metal by acidic, uninhibited ethylene glycol. The section of metal that has had its surface metal stripped away now becomes a metal oxide. Also, once metal ions are in solution, they can attach themselves to oppositely charged metals to form a galvanic corrosion cell. Rapid corrosion can commence at these sites in the cooling loop.

[3] Corrosion byproducts (metal oxides) then can be swept away to cause damage downstream. Typical problems associated with corrosion in a chiller cooling-loop system are clogging of a particulate filter, damage to mechanical seals and premature failure of the system. Corrosion already has occurred and internal system damage is likely to be present.

### 3.2. Electrochemical behaviour of steel alloy in presence of compound (I)

The effect of electrolyte in presence of organic compound **4-(3-bromo-4-methyl phenyl)-2H-phthalazin-1-one**, on the electrochemical behaviour of steel alloy was investigated under the polarization conditions. The linear polarization and Tafel extrapolation techniques were presented in Fig. (2). The data of different corrosion parameters were calculated and presented in Table (3).

The corrosion potential ( $E_{\text{corr}}$ ) is shifted to low negative values and recorded, -261 mV, which mainly due to the inhibition effect of organic compound (I). The current density was recorded as  $0.055 \text{ mA/cm}^2$ . The low values of  $i_{\text{corr}}$  are mainly due to the chemical and physical inhibition due to Compound (I) which is the starting nucleus for synthesis of all compounds mentioned in this research, showed high inhibition for the metal due to the electron pairs on the nitrogen atoms as well as  $\pi$ -

electrons on the aromatic rings. The Polarization resistance in this case records  $204 \text{ k}\Omega\cdot\text{cm}^2$  and sharply increases compared to absence of compound (I). According to Stern Gerry equation, the Corrosion rate reduced sharply and gets  $637.7 \text{ }\mu\text{m/Y}$  which jumped to less corrosion.

### 3.3. Electrochemical behaviour of steel alloy in presence of compound (II)

The potentiodynamic polarization curves of the studied electrode in glycol solution in the presence of **4-(3-bromo-4-methyl phenyl)-1-oxo-2H-phthalazin-2-yl] acetic acid hydrazide** were investigated and presented in fig. (2). The data were calculated and presented in Table (3).

The presence of compound (II) shifted the corrosion potential ( $E_{\text{corr}}$ ) to more negative values, -236 mV, which mainly due to the inhibition effect of organic compound (II). The current density was recorded as  $0.0026 \text{ mA/cm}^2$ . The low values of  $i_{\text{corr}}$  are mainly due to the chemical and physical inhibition due to Compound (II) which contain additional hydrazide group (-NH-NH<sub>2</sub>) which has larger electric density, which indicated that this functional group can adsorb on the surface of metal by donate electrons to vacant d-orbital of iron atoms.

Polarization resistance in this case records  $5.84 \text{ k}\Omega\cdot\text{cm}^2$  and sharply increases compared to absence of (II). According to Stern Gerry equation, the Corrosion rate reduced sharply and gets  $30.33 \text{ }\mu\text{m/Y}$  which jumped to less corrosion.

### 3.4. Electrochemical behaviour of steel alloy in presence of compound (III)

The electrochemical behaviour of steel alloy in presence of **2-[(3-Methylpyrazol-5-one-1-yl) carbonyl methyl]-4-(3-bromo-4-methyl phenyl)-2H-phthalazin-1-one**, was studied. The potentiodynamic polarization curves of the electrode in glycol solution and organic inhibitor were investigated and presented in Fig. (2).

The values of different corrosion parameters were calculated and presented in Table (3). The corrosion potential ( $E_{\text{corr}}$ ) recorded low negative values and

recorded, -521 mV, which mainly due to the inhibition effect of organic compound (III).

The calculated value of the corrosion current density,  $i_{\text{corr}}$ , of the steel alloy in the presence of Compound (III) showed lower current density and recorded 0.0074 mA/cm<sup>2</sup>. The low value of  $i_{\text{corr}}$ , are mainly due to the inhibition effect of Compound (III) which contain pyrazole ring which have two nitrogen hetero atoms and have one substituent methyl group. This result is linked to the electron donating effect of CH<sub>3</sub> group which increases the electron density on the pyrazole ring so it give good chance of adsorption on the electrode surface. Polarization resistance in this case records 1.8 kΩ.cm<sup>2</sup> and sharply increases compared to absence of compound (III). The sharp decrease in the corrosion rate, 86.4 μm/Y, indicates the inhibition effect of compound (III).

### 3.5. Electrochemical behaviour of steel alloy in presence of compound (IV)

The effect of electrolyte in presence of organic compound 2-[(3,5-Dimethyl-pyrazol-1-yl)carbonylmethyl]-4-(3-bromo-4-methyl-phenyl)-2H-phthalazin-1-one, on the electrochemical behaviour of steel alloy was investigated under the polarization conditions. The potentiodynamic polarization curves of the electrode in glycol solution and organic inhibitor were investigated and data presented in Fig. (2). The values of different corrosion parameters were calculated and presented in Table (3).

The corrosion potential ( $E_{\text{corr}}$ ) recorded low negative values and recorded, -592 mV, which mainly due to the inhibition effect of organic compound (IV). The current density was recorded as 0.0075 mA/cm<sup>2</sup>. The low values of  $i_{\text{corr}}$  are mainly due to the chemical and physical inhibition due to Compound (IV) which contain pyrazole ring which has two nitrogen hetero atoms and have two substituent methyl groups. Polarization resistance in this case records 0.871 kΩ.cm<sup>2</sup> and sharply increases compared to absence of (IV). According to Stern Gerry equation, Corrosion rate reduce sharply and get 87.87 μm/Y which jumped to less corrosion.

### 3.6. Electrochemical behaviour of steel alloy in presence of compound (V)

The effect of electrolyte in presence of organic compound 2-[4-(3-bromo-4-methyl-phenyl)-1-oxo-2H-phthalazin-2-yl]-N-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)acetamide, on the electrochemical behavior of steel alloy was investigated under the polarization conditions. The linear polarization and Tafel extrapolation techniques were presented in Fig. (2). The data of different corrosion parameters were calculated and presented in Table (3).

The corrosion potential ( $E_{\text{corr}}$ ) is shifted to low negative values and recorded, -218 mV, which mainly due to the inhibition effect of organic compound (V). The current density was recorded as 0.00031 mA/cm<sup>2</sup>. The low values of  $i_{\text{corr}}$  are mainly due to the chemical and physical inhibition due to Compound (V) the corrosion of metal was inhibited using Compound (V) which contain isoindol ring which has nitrogen hetero atom with lone pair of electron, two carbonyl group with high electronegativity and π-electrons in benzene ring.

The Polarization resistance in this case records 49.21 kΩ.cm<sup>2</sup> and sharply increases compared to absence of (V). According to Stern Gerry equation, the Corrosion rate reduced sharply and gets 3.701 μm/Y which jumped to less corrosion.

### 3.7. Electrochemical behaviour of steel alloy in presence of compound (VI)

The potentiodynamic polarization curves of the studied electrode in glycol solution in the presence of Benzopyrrolo-2-one-3-yl-4-[(3-bromo-4-methyl-phenyl)-2H-phthalazin-1-one-2-yl] acetyl hydrazone, were investigated and presented in fig. (2). The data were calculated and presented in Table (3).

The presence of compound (VI) shifted the corrosion potential ( $E_{\text{corr}}$ ) to more negative values, -236 mV, which mainly due to the inhibition effect of organic compound (VI). The current density was recorded as 0.008 mA/cm<sup>2</sup>. The low values of  $i_{\text{corr}}$  are mainly due to the chemical and physical inhibition due to Compound (VI) which has the benzopyrrol ring, where this ring has larger electron density and possess π-electrons.

Polarization resistance in this case records 261 kΩ.cm<sup>2</sup> and sharply increases compared to absence of (VI).

According to Stern Gerry equation, the Corrosion rate reduced sharply and gets 97.41  $\mu\text{m}/\text{Y}$  which jumped to less corrosion.

### 3.8. Electrochemical behaviour of steel alloy in presence of compound (VII)

The electrochemical behaviour of steel alloy in presence of 4-(3-bromo-4-methyl-phenyl)-1-oxo-2H-phthalazin-2-yl]acetic acid (2,3,4,5 -tetrahydroxy-pentylidene)hydrazide, was studied. The potentiodynamic polarization curves of the electrode in glycol solution and organic inhibitor were investigated and presented in Fig. (2).

The values of different corrosion parameters were calculated and presented in Table (3). The corrosion potential ( $E_{\text{corr}}$ ) recorded low negative values and recorded, -319 mV, which mainly due to the inhibition effect of organic compound (VII).

The calculated value of the corrosion current density,  $i_{\text{corr}}$ , of the steel alloy in the presence of Compound (VII) showed lower current density and recorded 0.000079  $\text{mA}/\text{cm}^2$ . The low value of  $i_{\text{corr}}$ , are attributed to the higher molecular weight (M.wt. 519) of Compound (VII) and the presence of additional sugar group with multiple hydroxyl groups which may be an additional adsorption centre, thus the electron donating ability of the active sites increases and its adsorption on the metal surface increases.

Polarization resistance in this case records 19.78  $\text{k}\Omega.\text{cm}^2$  and sharply increases compared to absence of compound (VII). The sharp decrease in the corrosion rate, 919.1  $\text{nm}/\text{Y}$  indicates the inhibition effect of compound (VII).

### 3.9. Electrochemical behaviour of steel alloy in presence of compound (VIII)

The effect of electrolyte in presence of organic compound N-(3-(1H-imidazol-1-yl) propyl)-2-(4-(3-bromo-4-methylphenyl)-1-oxophthalazin-2(1H)-yl)acetamide, on the electrochemical behaviour of steel alloy was investigated under the polarization conditions. The potentiodynamic polarization curves of the electrode in glycol solution and organic inhibitor were investigated and data presented in Fig. (2). The values of

different corrosion parameters were calculated and presented in Table (3).

The corrosion potential ( $E_{\text{corr}}$ ) recorded low negative values and recorded, -341mV, which mainly due to the inhibition effect of organic compound (VIII). The current density was recorded as 0.035  $\text{mA}/\text{cm}^2$ . The low values of  $i_{\text{corr}}$  are mainly due to the chemical and physical inhibition due to Compound (VIII). Polarization resistance in this case records 176.45  $\text{k}\Omega.\text{cm}^2$  and sharply increases compared to absence of (VIII). According to Stern Gerry equation, Corrosion rate reduce sharply and get 412.6  $\mu\text{m}/\text{Y}$  which jumped to less corrosion.

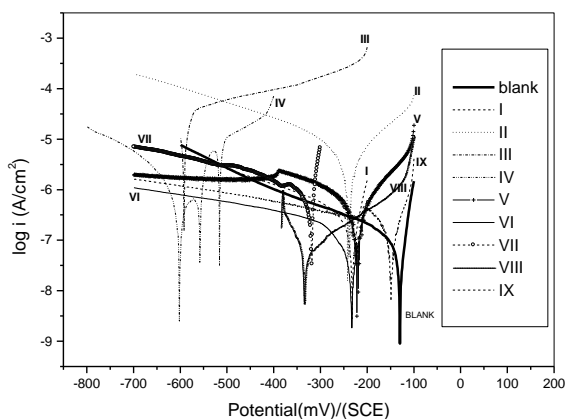
### 3.10. Electrochemical behaviour of steel alloy in presence of compound (IX)

The effect of electrolyte in presence of organic compound 4-(3-bromo-4-methylphenyl) phthalazin-1(2H)-thione, on the electrochemical behaviour of steel alloy was investigated under the polarization conditions. The potentiodynamic polarization curves of the electrode in glycol solution and organic inhibitor were investigated and data presented in Fig. (2). The values of different corrosion parameters was calculated and presented in Table (3).

The corrosion potential ( $E_{\text{corr}}$ ) recorded low negative values and recorded, -145 mV, which mainly due to the inhibition effect of organic compound (IX).

It is clearly observed that the presence of Compound (IX) reduce the current density value to 0.087  $\text{mA}/\text{cm}^2$ , although Compound (IX) has (C=S) group which is very active center presented in this compound; it is the least effective among the investigated compounds. This may be due to its lower molecular weight (M.wt 331) and the low number of active sites.

Polarization resistance in this case records 88.42  $\text{k}\Omega.\text{cm}^2$  and sharply increases compared to absence of (IX). According to Stern Gerry equation, the Corrosion rate reduced and gets 1.01  $\text{mm}/\text{Y}$  which jumped to less corrosion.



**Figure 2 :** Potentiodynamic polarization curves for steel alloy in naturally aerated mono ethylene glycol solution, in absence/present of additive to the electrolyte solution at 25 c<sup>0</sup>.

**Table (3):** Corrosion parameters of steel alloy in mono ethylene glycol solution, in absence/present of additive to the electrolyte solution at 25 c<sup>0</sup>.

| S/NO. | Compound                              | E(i=0) (mV) | i <sub>Corr</sub> (mA/cm <sup>2</sup> ) | Rp(kΩ.cm <sup>2</sup> ) | Corrosion Rate | The inhibition efficiency (%I) |
|-------|---------------------------------------|-------------|---|-------------------------|----------------|--------------------------------|
| 1     | Mono ethylene glycol solution (Blank) | -124        | 0.183                                   | 0.60                    | 2.13 (mm/Y)    | -----                          |
| 2     | Compound (I)                          | -261        | 0.055                                   | 204                     | 637.7(μm/Y)    | 69.9                           |
| 3     | Compound (II)                         | -236        | 0.026                                   | 5.84                    | 30.3 (μm/Y)    | 98.6                           |
| 4     | Compound (III)                        | -521        | 0.0074                                  | 1.80                    | 86.40 (μm/Y)   | 95.9                           |
| 5     | Compound (IV)                         | -592        | 0.0075                                  | 0.871                   | 87.87 (μm/Y)   | 95.9                           |
| 6     | Compound (V)                          | -218        | 0.00031                                 | 49.21                   | 3.701 (μm/Y)   | 99.8                           |
| 7     | Compound (VI)                         | -236        | 0.008                                   | 261                     | 97.41 (μm/Y)   | 95.6                           |
| 8     | Compound (VII)                        | -319        | 0.000079                                | 19.78                   | 919.1 (nm/Y)   | 99.96                          |
| 9     | Compound (VIII)                       | -341        | 0.035                                   | 176.45                  | 412.6 (μm/Y)   | 80.9                           |
| 10    | Compound (IX)                         | -145        | 0.087                                   | 88.42                   | 1.01 (mm/Y)    | 52.4                           |

#### IV. CONCLUSION

Based on the results obtained, the following conclusions can be drawn: The newly synthesized phthalazin derivatives compounds can be used as nontoxic corrosion inhibitor for carbon steel corrosion in glycol solution. Heterocyclic compounds containing nitrogen, oxygen and sulphur have particularly considered as efficient corrosion inhibitors in acidic media. Also the results show that in presence of phthalazin derivatives, the galvanic current and galvanic potential were

decreased, it was found that in presence phthalazin derivatives, the galvanic current shifts to more positive direction and galvanic potential shifts to more negative direction.

#### V. ACKNOWLEDGEMENTS

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## VI. REFERENCES

- [1]. Technical Bulletin, Dow Chemical Co. "Acidic Thermal Degradation Products of Ethylene Glycol and Propylene Glycol," Form No. C98030.
- [2]. W.J. Rossiter, J.R. Clifton and P.W. Brown (1985), "Degraded Aqueous Glycol Solutions: pH Values and the Effects of Common Ions on Suppressing pH Decreases," National Bureau of Standards, Solar Energy Materials, 12 (1), 77.
- [3]. W.J. Rossiter, P.W. Brown and K.G. Galuk (1987), "Characterization of Potential Thermal Degradation Products from the Reactions of Aqueous Ethylene Glycol and Propylene Glycol Solutions with Copper Metal," National Bureau of Standards, Solar Energy Materials, 16 (4), 309.
- [4]. W.J. Rossiter, P.W. Brown and K.G. Galuk (1986), "A Mass Spectrometric Investigation of the Thermal Oxidative Reactivity of Ethylene Glycol," National Bureau of Standards, Solar Energy Materials, 13 (3), 197.
- [5]. John Beavers and Ronald Diegle (1981), "The Effect of Degradation of Glycols on Corrosion of Metals Used in Non-Concentrating Solar Collectors," International Corrosion Forum proceedings.
- [6]. S.Tarab, A.M.Al.Turkustani (2006), Portugaliae Electrochimica Acta, 24, 53.
- [7]. N.O.Eddy, E.E.Ebenso (2010), Pigment and Resin Tech, 39, 77.
- [8]. S.A.Umoren, I.B.Obot, and N.O. Obi-Egbedi (2009), Mater. Sci, 44(1), 274.
- [9]. I.B.Obot and N.O.Obi-Egbedi (2008), Surface Review and Letters, 15(6), 903.
- [10]. I.B.Obot and N.O. Obi-Egbedi (2008), Colloids and surfaces A: Physicochem. Eng. Aspects, 330, 207.
- [11]. H.Ju, Z.P.Kai and Y. Li (2008), Corros. Sci.50, 865.
- [12]. N.O.Eddy and S.A.Odoemelam (2008), Adv. Nat. & Appl. Sci., 2(1), 35.
- [13]. S.A.Umoren, I.B.Obot, E.E.Ebenso and N.O.Obi-Egbedi (2008), Int. J. Electrochem. Sci. 3, 1029.
- [14]. S.S. Abd El-Rehim, M.A.M. Ibrahim and F.F.J. Khaled (1999), Appl. Electrochem., 29, 593.
- [15]. H.L.Wang, R.B.Liu and J.Xin (2004), Corros. Sci.46, 2455.
- [16]. S.Rengamati, S.Muralidharan, M.Anbu Kulamdainathan, S.Venkatakrishna Iyer (1994), J Appl. Electrochem., 24, 355
- [17]. E.E.Ebenso, Bull. (2003), Electrochem, 19, 209.
- [18]. N.Khalil, (2003), Electrochim. Acta, 48, 2635.
- [19]. S.L. Granese (1988), Corros. 44, 322.
- [20]. G. Trabanelli (1987), in: F. Mansfeld (Ed.), Corrosion Mechanism, Marcel Dekker, New York, p. 119.
- [21]. D.P. Schweinsberg, G.A. Nanayakkara, D.A. Steinert (1988), Corros. Sci. 28, 33.
- [22]. M. Ohsawa, W. Sue'Taka (1979), Corros. Sci.19, 709.
- [23]. J. Penninger, K. Wippermann, J.W. Schultze (1987), Werkst. Korros.38, 649.
- [24]. J.W. Schultze, K. Wippermann (1987), Electrochim. Acta. 32, 823.
- [25]. H.A. El-Rahman (1991), Corrosion 47, 424.
- [26]. M.M. Singh, R.B. Rastogi, B.N. Upadhyay (1994), Corrosion, 50, 620.
- [27]. G. Quartarone, T. Bellomi, A. Zingales (2003), Corros. Sci. 45, 715.
- [28]. R.R. Annand, R.M. Hurd, N. Hackerman (1965), J. Electrochem. Soc.112, 138.
- [29]. B. Sathianandhan, K. Balahrishnan, N. Subramyar, Br. (1970), Corros. J. 5, 270.
- [30]. F. Zucchi, G. Trabanelli, G. Brunor (1992), Corros. Sci. 33, 1135.
- [31]. J. Uhrea, K. Aramaki (1991), J. Electrochem. Soc. 138, 3245.
- [32]. J. O'M Bockris, B. Yang (1991), J. Electrochem. Soc.138, 2237.
- [33]. G. Banerjee, S.N. Malhatra (1992), Corrosion 48, 10.
- [34]. S. Kertit, A. Elkhely, J. Aride, A. Srhiri, A. Ben-Bachir, M. Etman (1989),J. Appl. Electrochem.19, 83.
- [35]. G.K. Gomma, M.H. Wahdan (1994), J. Mater. Chem. Phys. 39, 142.
- [36]. G.K. Gomma, M.H. Wahdan (1994), Bull. Chem. Soc. Jpn., 67, 2621.
- [37]. M.S. Abdel Aal, M.H. Wahdan, G.K. Gomma (1995), Mater. Chem. Phys. 39, 290.
- [38]. G.K. Gomma, M.H. Wahdan (1995), Ind. J. Chem. Technol., 2 , 107.
- [39]. Z.A. Iofa, G.N. Tomashov (1960), Zh. Fiz. Khim 34, 1036.