

## Effects of Water Soluble Rosin on the Corrosion Inhibition of Carbon Steel

Ayman M Atta<sup>1,2</sup>, Gamal A El-Mahdy<sup>1,3,\*</sup>, Husein S. Ismail<sup>2</sup> and Hamad A. Al-Lohedan

<sup>1</sup>Chemistry Department, College of Science, King Saud University, Riyadh 11541, Saudi Arabia

<sup>2</sup>Petroleum Applications Department, Egyptian Petroleum Research Institute (EPRI), Naser City 11727, Cairo, Egypt.

<sup>3</sup>Chemistry Department, Faculty of Science, Helwan University, Cairo, Egypt

\*E-mail: [Gamalmah2000@yahoo.com](mailto:Gamalmah2000@yahoo.com)

Received: 11 September 2012 / Accepted: 27 October 2012 / Published: 1 December 2012

---

New corrosion inhibitors, namely, rosin poly(oxyethylene) ester 4,5-dihydroimidazole maleate Adduct (RIMA-PEG), have been synthesized from rosin acid natural product. The chemical structure of the prepared RIMA-PEG was confirmed by FTIR analysis. The effectiveness of the synthesized compound as corrosion inhibitor for carbon steel in 1M hydrochloric acid solution was investigated using electrochemical methods. Experimental data indicated that RIMA-PEG has shown a strong inhibitive effect for the corrosion of carbon steel in 1M HCl solution.

---

**Keywords:** Open circuit potential, Acid solution, Carbon steel, FTIR, Polarization,

### 1. INTRODUCTION

Inhibitors based on organic materials are widely used in the corrosion protection of materials in several environments [1]. The use of inhibitors is one of the most practical methods for protection against corrosion, especially in acidic media [2-4]. Acid solutions are widely used in industry, the most important fields of application being acid pickling, industrial acid cleaning, acid descaling and oil well acidizing. Because of the general aggressivity of acid solutions, inhibitors are commonly used to reduce the corrosive attack on metallic materials. Most of the well-known acid inhibitors are organic compounds containing nitrogen, sulphur, oxygen, phosphorous and aromatic ring or triple bonds. It has been reported that the inhibition efficiency decreases in the order: O < N < S < P [5-6]. Moreover, many N-heterocyclic compounds have been proved to be effective inhibitors for the corrosion of metals and alloys in aqueous media. The influence of organic compounds containing nitrogen on the

corrosion of steel in acidic solutions has been investigated by several authors. Among them, azoles have been intensively investigated as effective steel corrosion inhibitors [7–9].

Synthesis of new materials from renewable natural resources has becoming a rapidly growing area, as these materials could potentially replace or partially replace environmentally and energy unfavorable plastics derived from petroleum chemicals [10-12]. We have focused on developing a new class of renewable polymers using gum rosin, due to its abundance, low cost as well as its potential ability to be converted into polymerizable monomers. Water-soluble synthetic polymers are a family of materials that have been developed commercially and studied scientifically at an accelerating pace in recent years. Many water soluble polymers, because of their amphipathic structure and surface activity, are used as surface active agents. In the previous work, nonionic surfactants were prepared from rosin acid and used as flow improver and oil spill dispersant for petroleum crude oil [13-15]. The present work, deals with synthesis of water soluble nonionic surfactants from rosin acid adducts.

This paper focuses on the efficiency of non-toxic modified rosin hydroimidazole, which is derivative of imidazole as steel corrosion inhibitor in hydrochloric acid. The investigation is performed using electrochemical methods.

## 2. EXPERIMENTAL

### 2.1. Materials

All materials were used without further purification. Rosin were heated at 150°C for 4 hours then heated at 200°C for 30 minutes in nitrogen atmosphere to isomerizes rosin acids to leveopimaric acid, then it were separated by crystallization from the cold acetone solution of commercial

rosin. Rosin acids with acid number 183mg KOH.g<sup>-1</sup> and melting point 167°C was obtained from commercial rosin [15]. The separation of the rosin acids from rosin was carried out to increase the yield and to remove terpens, which have the ability to react with maleic anhydride. Maleic anhydride (MA), ethylene diamine (EDA), p-toluene sulfonic acid (PTSA), poly (ethylene glycol), PEG, having molecular weights 400 and 600 designated as PEG 400 and PEG 600 were supplied from Aldrich Chemicals Co. (USA) and used as received.

The corrosive solution (1M HCl) was prepared by appropriate dilution of analytical grade 37% HCl with double distilled water. Corrosion tests were performed on a carbon steel sheet having the following chemical composition (wt %): 0.3% C, 0.02% Si, 0.03% Mn, 0.045% Sn, 0.04% P and the remainder Fe. A carbon steel disc of the same chemical composition was mounted in Teflon with an exposed surface area of 1 cm<sup>2</sup> was used in all electrochemical measurements. The prepared electrode was mechanically polished with different grades of silicon carbide papers, degreased in ethanol to obtain a fresh oxide-free surface, washed with bi-distilled water and dried at room temperature.

## 2.2. Preparation of Rosin 4,5-dihydroimidazole (RI)

Rosin 4,5-dihydroimidazole (RI) may be prepared by melt method as follows: EDA (1.12 mol) was mixed with purified rosin acid (1mol) in a flask fitted with a water condenser with a drying tube, a thermometer and an N<sub>2</sub> purge tube. The mixture was heated with stirring in the presence of N<sub>2</sub> atmosphere. During reaction, the temperature of the reaction mixture was raised to 135°C and kept there for 2 hours and the reaction temperature raised up to 180 °C for another 2h. The condenser was replaced with Dean Stark separator to remove the water formed during imidization. The reaction mixture was poured into excess water. The precipitate was filtered, washed thoroughly with water and then with diethylether to remove unreacted rosin and EDA. It was finally dried at 40°C under vacuum. The produced monomer was designated as RI. It is

light brown powder; yield was 95%; melting point was 78°C and nitrogen contents were calc. 2.64; found 2.55, calc. 5.01; found 5.22, calc. 1.92; found 1.88 and calc. 3.70; found, 3.75, respectively.

## 2.3. Preparation of rosin 4,5-dihydroimidazole maleic anhydride adduct

Synthesis of rosin 4,5-dihydroimidazole maleic anhydride adduct (RIMA) was prepared as following: RI (1mol) was melted and heated at

120°C, 200 ml of glacial acetic acid and (1 mol) of maleic anhydrid were added to RI. PTSA (1%) based on total weight of reactant was added to the reaction mixture after. The temperature was kept at 120 °C for 1 hour and the reaction left for 3 hours at 170 °C. The reaction temperature was cooled below 5°C to obtain brown powder of adduct. The powder was

washed several times with glacial acetic acid.

## 2.4. Preparation of rosin poly(oxyethylene) ester 4,5-dihydroimidazole maleate Adduct (RIMA-PEG)

A mixture of freshly distilled PEG 400 or PEG 600 (1.1 mol), RIMA (1 mol), PTSA (1%) based on total weight of reactants and 100 ml xylene were placed in 0.5 L round-flask fitted with Dean Stark apparatus. The mixture was allowed to reflux until the theoretical water was collected. Xylene was distilled off from the reaction product by rotary evaporator under reduced pressure. The product was separated by salting out use saturated NaCl solution and extracted with isopropanol using separating funnel. The purified products were isolated after evaporation of isopropanol.

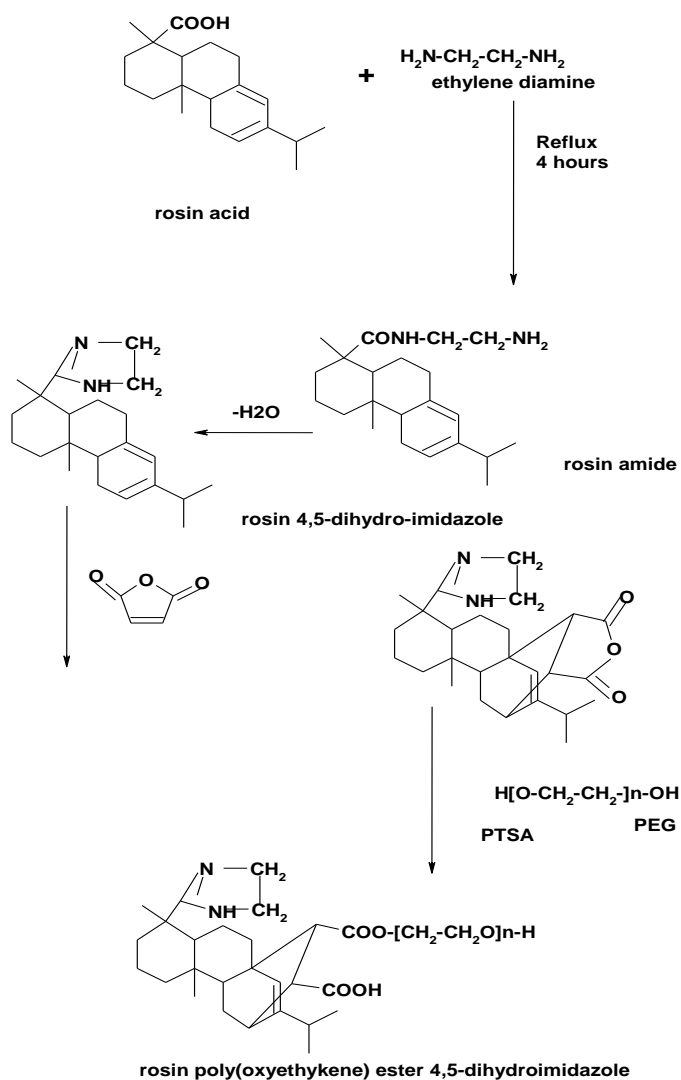
## 2.4. Measurements

The acid values of the synthesized resins were determined by the conventional acetic anhydride- pyridine method. Infrared spectra of the prepared compounds were recorded in polymer/KBr pellets using Mattson-Infinity series FTIR Bench Top 961.

The potential of carbon steel electrodes was measured against the saturated calomel electrode (SCE) in 1M HCl solution in the absence and presence of various inhibitor concentrations until the steady open circuit potential is attained. Potentiodynamic polarization studies were carried out using Volta lab 40 (Tacussel-Radiometer PGZ301) potentiostat and controlled by Tacussel corrosion analysis software model (Voltmaster 4) at a scan rate of 5mVs<sup>-1</sup> under static condition. A platinum electrode and saturated calomel electrodes (SCE) were used as auxiliary and reference electrodes, respectively. The working electrode was prepared from a cylindrical carbon steel rod insulated with polytetrafluoroethylene tape (PTFE). The area exposed to the aggressive solution was 1cm<sup>2</sup>. All the experiments were carried out at temperature from 25 to 50 °C. AC impedance measurements were performed using Tacussel-Radiometer.

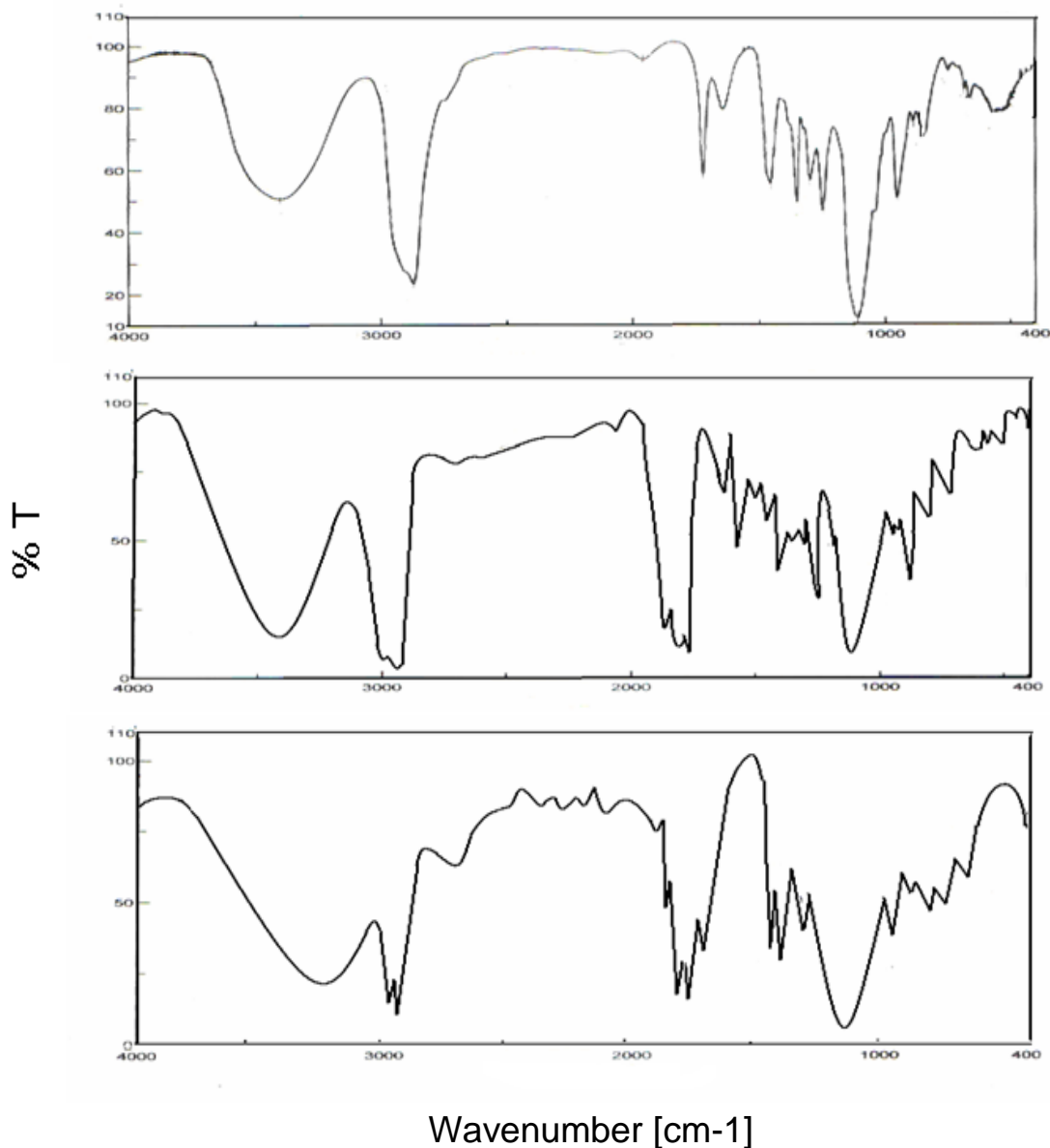
### 3. RESULTS AND DISCUSSION

#### 3.1. Identification of chemical structure of the prepared RIMA-PEG



**Figure 1.** Preparation of RIMA-PEG derivatives

Rosin have been used as a source with a lower cost for production of new applicable materials [16-19]. The present study was intended to modify the chemical structure of rosin to produce new water soluble corrosion inhibitors.

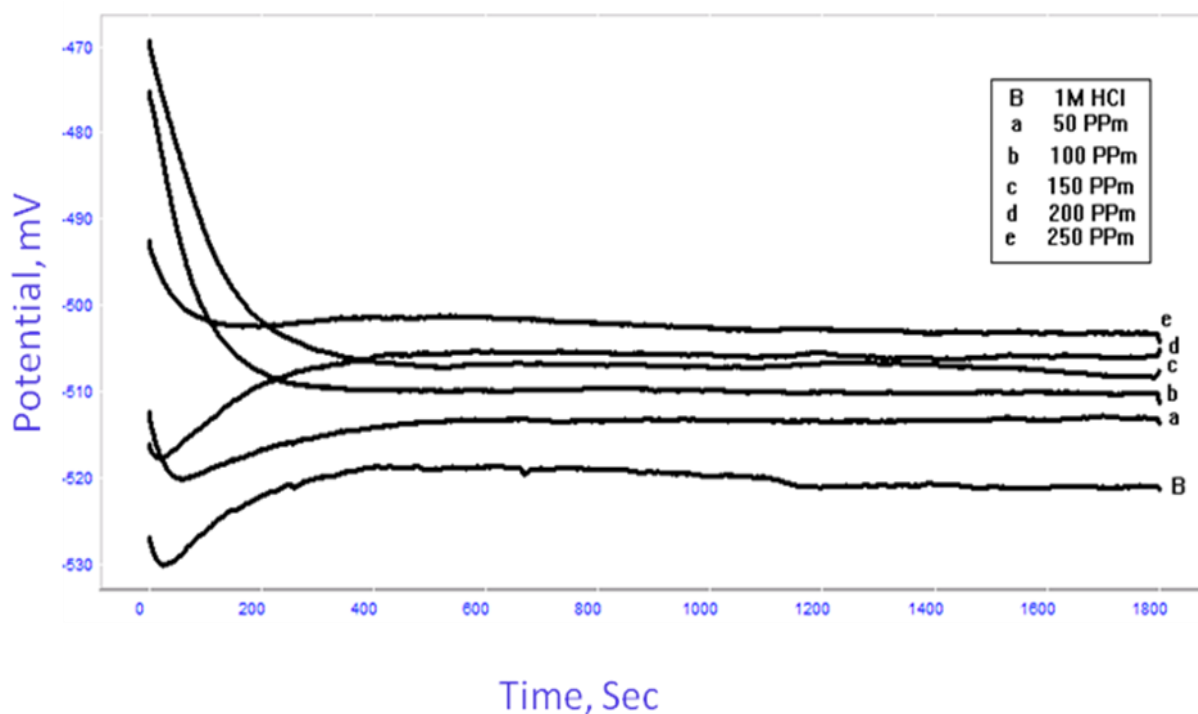


**Figure 2.** FTIR spectra of: (a) RI, (b) RIMA (c) RIMA-PEG400

The reaction procedure was illustrated in Fig.1. Rosin has been recognized to have excellent solubility and compatibility with a variety of other synthetic resin. This is because rosin acids have a hydrophobic skeleton containing unsaturated alicyclic in combination with hydrophilic carboxylic groups. The condensation of rosin acids with EDA can produce rosin imidazole derivative (RI). The reaction scheme indicates the formation of rosin imidazole after heat treatment of rosin acid to produce rosin 4,5-dihydroimidazole as illustrated in the experimental section. The formation of RI from rosin

acid was confirmed from reduction of acid number of rosin acid from 183 to 6 mg KOH.g<sup>-1</sup> which indicated the disappearance of acid group of rosin acid after condensation with EDA. The chemical structure of RI was confirmed from FTIR analysis. The FTIR spectrum of RI was represented in Fig. (2a). The appearance of new bands at 1620 and 3350 cm<sup>-1</sup>, which attributed to C=N and -NH stretching vibration of imidazole ring. The formation of rosin imidazole maleic anhydride Diels Alder adduct was produced from reaction of RI with MA as illustrated in the experimental section. The chemical structure of RIMA adduct was illustrated from FTIR spectrum which represented in Fig. (2b). The appearance of new absorption bands at 1810 and 1780 cm<sup>-1</sup> assigned to C=O stretching of MA anhydride group indicated the formation of RIMA adduct. The esterification of RIMA with PEG 400 and PEG 600 in the presence of PTSA as a catalyst was illustrated in Fig. 1. FTIR spectrum of RIMA-PEG600 ester was represented in Fig. (2c). The disappearance of absorption bands at 1810 and 1780 cm<sup>-1</sup> in spectrum of RIMA (figure 1b) and appearance of new bands at 1754 and 1100 cm<sup>-1</sup> which attributed to C=O and C-O stretching vibration of ester indicated the esterification of RIMA with PEG 400 and PEG 600.

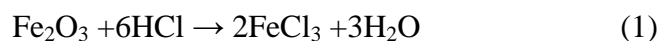
### 3.2. Open circuit potential measurements



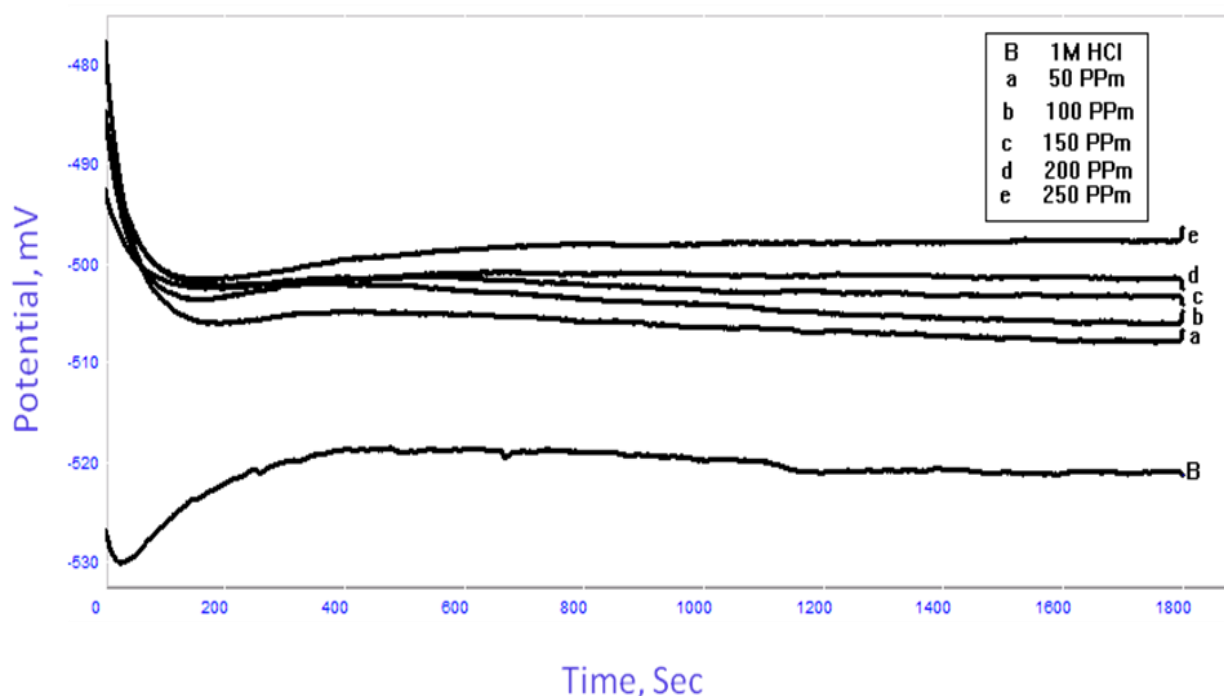
**Figure 3.** Open circuit potential–time plot for carbon steel in 1M HCl in absence and presence of RIMA-PEG400 at 25 °C.

The potential of carbon steel electrodes immersed in 1M HCl solution was measured as a function of immersion time in the absence and presence of different concentrations of RIMA-PEG400 and RIMA-PEG600 as shown in Figs. 3 and 4, respectively. It is clear that the potential of carbon steel

electrode immersed in 1M HCl solution (blank curve) tends towards more negative potential firstly, giving rise to short step. This behavior was reported by West [20], which represents the breakdown of the pre-immersion air formed oxide film presents on the surface according to the following equation:



This is followed by the growth of a new oxide film inside the solution, so that the potential was shifted again to more noble direction until steady state potential is established.



**Figure 4.** Open circuit potential–time plot for carbon steel in 1M HCl in absence and presence of different concentrations of RIMA-PEG600 inhibitors at 25 °C.

Addition of inhibitor molecules to the aggressive medium produces a negative shift in the open circuit potential due to the retardation of the cathodic reaction during the initial stage of measurements. Further addition of the Inhibitor molecules produces a positive shift in  $E_{\text{corr}}$ . As the concentration of the inhibitor increases, the corrosion potential was shifted to more noble direction.

### 3.3. Potentiodynamic polarization measurements

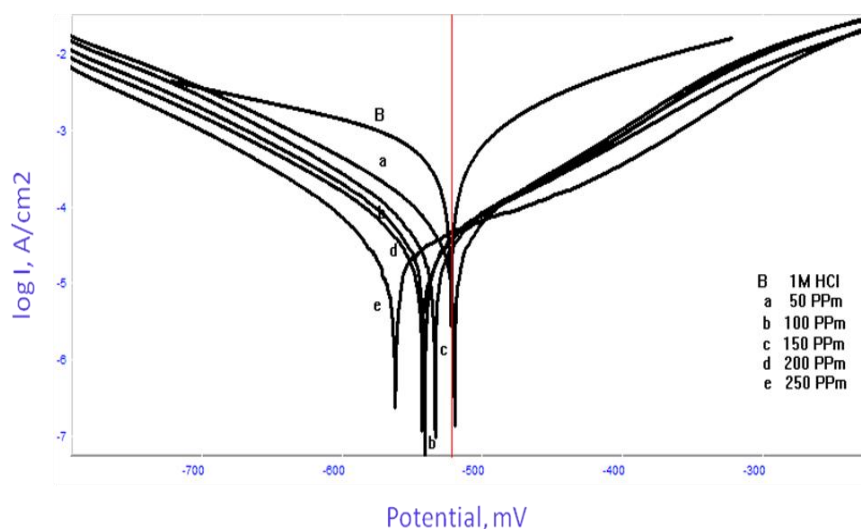
The effect of inhibitor concentration and temperature on both anodic and cathodic curves of carbon steel in 1M HCl solution was studied using potentiodynamic polarization technique. Evaluation of corrosion inhibition efficiencies (I %) can also be performed through electrochemical experiments.

**Table 1.** Parameters of potentiodynamic polarization of Carbon steel electrode in 1M HCl containing various concentrations of RIMA-PEG 400 at 25 °C.

Conc. (ppm)	$-E_{corr}$ , mV	$I_{corr}$ , mA/Cm <sup>2</sup>	$R_p$ , ΩCm <sup>2</sup>	$\beta_a$ , mV/dec	$B_c$ , mV/dec	C.R mmy	I%
0	521	0.703	40.75	122.1	249.9	8.22	-
50	518	0.11	290.9	108.	120	1.33	84.35
100	541	0.092	154.47	117.8	118	1.08	86.91
150	532	0.089	302.27	108.3	109	0.981	87.33
200	542	0.074	293.63	121.7	119.3	0.873	89.47
250	559	0.071	1180	152.6	119.1	0.836	89.90

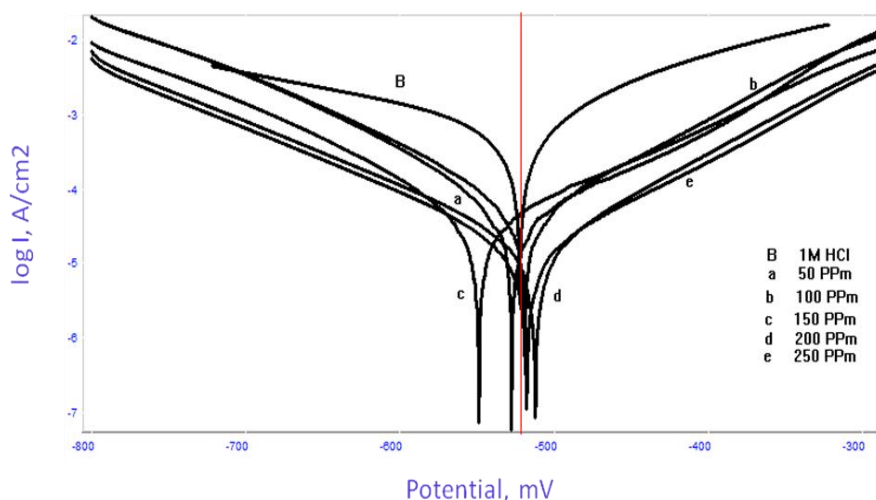
**Table 2.** Parameters of potentiodynamic polarization of Carbon steel electrode in 1M HCl containing various concentrations of RIMA-PEG600 inhibitor at 25 °C.

Conc. (ppm)	$-E_{corr}$ , mV	$I_{corr}$ , mA/Cm <sup>2</sup>	$R_p$ , ΩCm <sup>2</sup>	$\beta_a$ , mV/dec	$B_c$ , mV/dec	C.R mmy	I%
0	521	0.703	40.75	122.1	249.9	8.22	-
50	527	0.093	446.77	107.0	110.0	1.09	86.77
100	518	0.086	153.65	105.7	112.5	1.000	87.76
150	551	0.063	398.87	139.5	115.7	0.737	91.03
200	511	0.021	474.13	94.1	118.1	0.248	97.01
250	517	0.02	2470	98.9	120	0.240	97.15



**Figure 5.** Polarization curves of carbon steel recorded in 1 M HCl containing different concentrations of RIMA-PEG400 at 25 °C





**Figure 6.** Polarization curves of carbon steel recorded in 1 M HCl containing different concentrations of RIMA-PEG600 inhibitors at 25 °C.

The obtained results were illustrated in Figs. 5 and 6. Also, the electrochemical parameters such as  $I_{corr}$ ,  $E_{corr}$ ,  $\beta_a$ ,  $\beta_c$  and  $R_p$  associated with polarization measurements for carbon steel at different concentrations of the additive were simultaneously determined from the polarization curves using Voltmaster 4 corrosion software. The extrapolation of Tafel straight line allows the calculation of the corrosion current density ( $I_{corr}$ ).

**Table 3.** Influence of temperature on the electrochemical parameters for carbon steel electrode immersed in 1 M HCl without inhibitor addition.

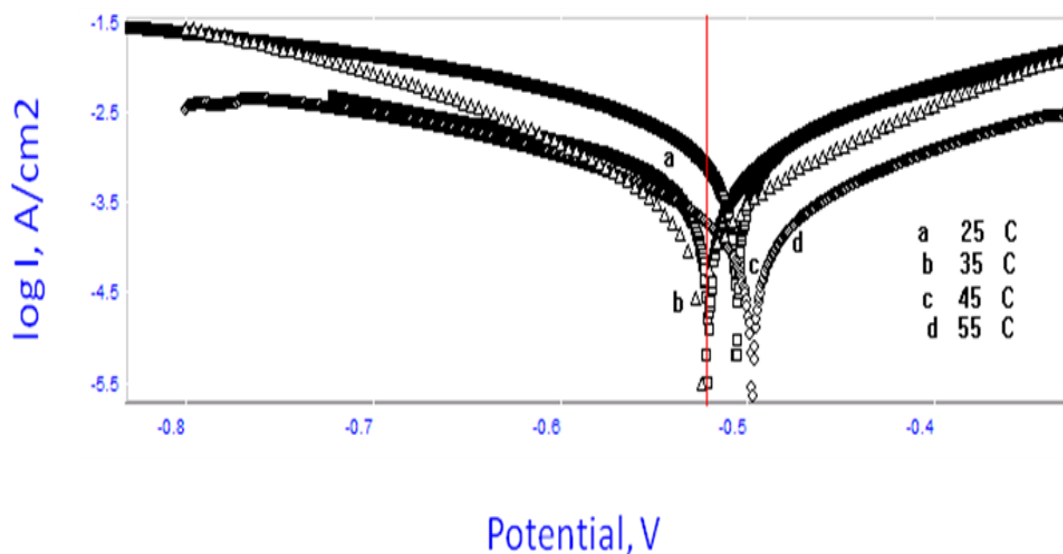
Temperature (°C)	$-E_{corr}$ , mV	$I_{corr}$ , mA/Cm <sup>2</sup>	$R_p$ , $\Omega$ Cm <sup>2</sup>	$\beta_a$ , mV/dec <sup>-1</sup>	$\beta_c$ , mV/dec <sup>-1</sup>	C.R mmy
25	521	0.703	40.75	122.1	249.9	8.22
35	506	2.5	21.00	266.7	273.3	29.91
45	529	5.2	8.04	243.6	236.6	61.98
55	551	7.7	6.49	250	303	90.42

The values of  $I_{corr}$ , the corrosion potential ( $E_{corr}$ ),  $E$  (%), cathodic and anodic Tafel line as function of inhibitors concentrations are given in Tables ( 1-2). The degree of surface coverage ( $\theta$ ) and the percentage inhibition efficiency ( $I\%$ ) were calculated using the following Equations.

$$\theta = 1 - i / i_0 \tag{2}$$

$$I \% = (1 - I / i_0) \times 100 \tag{3}$$

where  $i_0$  and  $i$  are the corrosion current densities determined by the intersection of the extrapolated Tafel lines to the corrosion potential,  $E_{corr}$ . Tafel lines of nearly equal slopes were obtained as can be seen from Tables 1 and 2. As reflected from the plots the additive exhibits a significant effect on the current–potential relations.



**Figure 7.** Effect of temperature on the cathodic and anodic polarization for carbon steel in 1 M HCl without inhibitor addition.

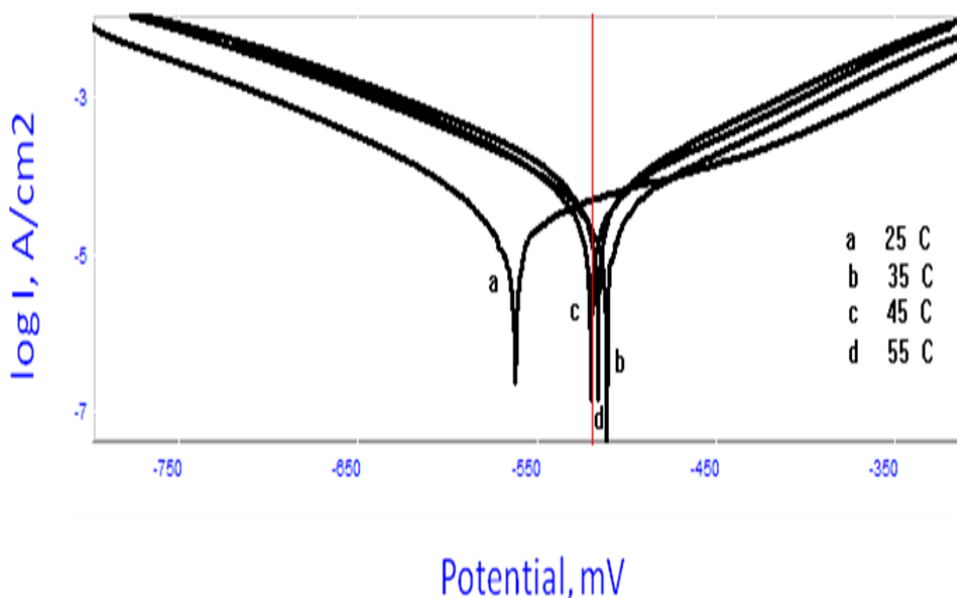
It can be seen that the Tafel lines are shifted to more negative and more positive potentials for the cathodic and anodic process, relative to the blank curve. This means that the additive affects both anodic dissolution of the metal and cathodic evolution of hydrogen (i.e. mixed-type inhibitor). It is clear from Fig. 5 that both the cathodic and the anodic reaction are inhibited and the inhibition increases as the inhibitor concentration increases.

**Table 4.** Influence of temperature on the electrochemical parameters for carbon steel electrode immersed in 1 M HCl in the presence of 250 ppm of RIMA-PEG400 inhibitor.

Temperature (°C)	$-E_{corr}$ , mV	$I_{corr}$ , mA/Cm <sup>2</sup>	$R_p$ , ΩCm <sup>2</sup>	$\beta_a$ , mV/dec <sup>-1</sup>	$\beta_c$ , mV/dec <sup>-1</sup>	C.R mmy	I%
25	559	0.071	1180	152.6	119.1	0.836	89.90
35	510	0.087	396.0	101.7	122.4	1.013	96.52
45	518	0.114	290.9	108.3	120.1	1.331	97.80
55	515	0.169	275.1	114.1	134.1	1.979	97.80

In addition, the slopes of the cathodic and anodic Tafel lines are approximately constant and independent on the inhibitor concentration. This behavior suggests that the inhibitor molecules affect the corrosion rate of carbon steel without changing the metal dissolution mechanism [21]. Also, the

addition of inhibitor molecules causes a decrease in  $I_{\text{corr}}$ , which increases with increasing inhibitor concentration indicating that the additive compound can be used as corrosion inhibitor of mild steel. The values of inhibition efficiency increased markedly with increase of inhibitor concentration indicated that a higher coverage of inhibitor on the surface was obtained in a solution with higher concentrations of inhibitor.



**Figure 8.** Effect of temperature on the cathodic and anodic polarization for carbon steel in 1 M HCl containing 250 ppm of RIMA-PEG400 inhibitor.

The investigation of temperature on the corrosion process of carbon steel can modify the interaction between the carbon steel electrode and the inhibitor in acidic medium. Polarization curves for carbon steel in 1 M HCl without and with 250 ppm of RIMA-PEG400 inhibitor at different temperature range 25–55 °C were represented in Figures 7 and 8, respectively. Corresponding data are given in Tables 3-4. Careful inspection of data indicated that, the corrosion current density increased with increasing temperature both in uninhibited and inhibited solutions and the values of the efficiency of inhibitors are nearly constant in the studied temperature range. The data indicated that the prepared inhibitors act as an efficient inhibitor in the different ranges of temperature studied. The data presented in Table 4 reveals that the rate of corrosion generally increased with increase in temperature. The results can be explained on the basis that increasing temperature enhances the transfer rate of the aggressive ions, which in turn enhances the corrosion rate. It is clear also that the inhibition efficiency at different temperatures increases with increasing temperature and hence the surface coverage increases with increasing temperature. The high efficiency of these surfactants at different temperatures suggests that the mode of adsorption is chemisorbed. It can be concluded that the surfactant molecule covers a large area, thereby inhibiting iron corrosion. The chemisorbed layer is assumed to cover the entire surface leading to high efficiency. The results obtained here are in

consistent with data reported previously for increasing the efficiency of the inhibitor with temperature and to the mode of adsorption [22-27].

#### 4. CONCLUSIONS

The main conclusions of the present study could be summarized in the following points:

1- Water soluble imidazole derivative of rosin acid (RIMA-PEG) was synthesized and characterized by FTIR spectroscopy.

2- RIMA-PEG has shown a strong inhibitive effect for the corrosion of carbon steel in 1M HCl solution,

3- The strong inhibitive effect of RIMA-PEG can be attributed to the strong capability of RIMA-PEG to be adsorbed on the metallic surface.

4- RIMA-PEG acts as an efficient inhibitor at different ranges of temperatures.

#### ACKNOWLEDGMENT

The authors extend their appreciation to the Deanship of Scientific Research at King Saud University for funding the work through the research group Project No. RGP-VPP-148.

#### References

1. Hackerman, *Langmuir* 3 (1987) 922.
2. K.C. Emregül, O. Atakol, *Mater. Chem. Phys.* 82 (2003) 188.
3. S.A. Ali, M.T. Saeed, S.U. Rahman, *Corros. Sci.* 45 (2003) 253.
4. F. Bentiss, M. Traisnel, H. Vezin, H.F. Hildebrand, M. Lagrenee, *Corros. Sci.* 46 (2004) 2781.
5. B.D.C. Donnelly, T.C. Downie, R. Grezeskowiak, H.R. Hamburg, D. Short, *Corros. Sci.* 18 (1977) 109.
6. N.C. Subramanyam, B.S. Sheshardi, S.A. Mayanna, *Corros. Sci.* 34 (1993) 563.
7. F. Bentiss, M. Traisnel, M. Lagrenee, *Corros. Sci.* 42 (2000) 127.
8. M. Elachouri, M.S. Hajji, S. Kertit, E.M. Essassi, M. Salem, R. Coudert, *Corros. Sci.* 37 (1995) 381.
9. H.-L. Wang, R.-B. Liu, J. Xin, *Corros. Sci.* 46 (2004) 2455.
10. C. K. Williams, M. A. Hillmyer, *Polym. Rev.* 48 (2008) 1.
11. A. I. Corma, A. S. Velty, *Chem. Rev.* 107 (2007) 2411.
12. D. R. Dodds, R. A. Gross, *Science*, 318(2007)1250.
13. A. M. Atta, A. M. Ramadan, K. A. Shaffei, A. M. Nassar, N. S. Ahmed, M. Fekry, *J. Disper. Sci. Technol.*, 30 (2009) 1100.
14. A.M. Al-Sabagh, T.T. Khidr, A.M. Atta, *Pet. Sci. Technol.*, 20 (2002) 693.
15. A. M. Atta, M. E. Abdel-Rauf, N.E. Maysour, A. K. Gafer, *J. Disper. Sci. Technol* 31 (2010)583.
16. A.M. Atta, I.F. Nassar, H. M. Bedawy, *React. & Func. Poly.* 67 (2007) 617.
17. A.M. Atta, R. Mansour, M.I. Abdou, A.M. Sayed, *J. Polym. Adv. Techol.* 15 (9) (2004) 514.
18. A.M. Atta, R. Mansour, M.I. Abdou, A.M. Sayed, *J. Polym. Res.* 12 (2005) 127.
19. A.M. Atta, S.M. Elsaed, R.K. Farag, *Prog. Org. Coat.* 66 (2006) 1596.
20. J.M. West, *Electrodeposition and Corrosion Process*, second ed., Van Nostrand Reinhold, London, 1970, p. 93.
21. C.E. Kaan, H. Mustafa, *Corros. Sci.* 48 (2006) 797.

22. A. Popova, *Corros. Sci.* 49 (2007) 2144–2158.
23. A. Popova, E. Sokolova, S. Raicheva, M. Christov, *Corros. Sci.* 45 (2003) 33.
24. A. Popova, M. Christov, A. Vasilev, *Corros. Sci.* 49 (2007) 3276.
25. I.A. Ammar, F.M. El Khorafi, *Werk. Korro.* 24 (1973) 702.
26. T. Szauer, A. Brandt, *Electrochim. Acta* 26 (1981) 1209.
27. M A. Amin, M.A. Ahmed , H.A. Arida , T. Arslan d, M. Saracoglu and F. Kandemirli , *Corro. Sci.* 53 (2011) 540.