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Prazole Compounds as Inhibitors for Corrosion of Aluminum in Hydrochloric acid

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The influence of three compounds of anti-ulcer prazole drugs on the dissolution of aluminum electrode in 1.0M HCl solution was investigated using weight loss, hydrogen evolution reaction, galvanostatic polarization and electrochemical impedance spectroscopy techniques .The inhibition efficiency was found to increase with increasing the concentration of the inhibitors and with decreasing the temperature. The inhibition action of these compounds was explained in terms of adsorption on the aluminum surface. The adsorption process follows Langmuir isotherm .Some activated thermodynamic parameters were calculated. The polarization studies showed that these compounds are acting as mixed inhibitors. Electrochemical impedance spectroscopy technique exhibit one capacitive loop indicating that, the corrosion reaction is controlled by charge transfer process. The results obtained from different techniques are in good agreement.

Keywords: Prazole drugs, zinc, corrosion inhibitors.

1. INTRODUCTION

Corrosion of aluminum (Al) in hydrochloric acid solution and its control is an active area of research due to its high industrial importance. The control of this corrosion assumes greater significance, particularly by the use of inhibitors due to its easy methodology. The acid inhibitors find extensive applications in pickling, chemical and electrochemical etching of aluminum [1]. The corrosion inhibition of aluminum in acidic solutions is based on organic compounds containing nitrogen, oxygen, sulfur atoms and multiple bonds in the molecules that facilitate adsorption on the aluminum surface [2-10]. The inhibition efficiency of organic compounds is related to their adsorption properties. Adsorption depends on the nature and the state of the metal surface, on the type of

corrosive medium and on the chemical structure of inhibitor [11]. Studies reported that the adsorption of inhibitors mainly depends on some physicochemical properties of the molecule, related to its functional group, to the possible steric effects and electronic density of donor atoms, adsorption is also to depend on the possible interaction of π-orbital's of the inhibitors with d-orbital of the surface atoms which induce greater adsorption of inhibitor molecule on tip the surface of metal leading to the formation of a corrosion protection film [12].

Prazole compounds were used as anti-ulcer drugs. No data are recorded in the literature about the behavior of these compounds as inhibitors for metallic corrosion. These compounds were selected as inhibitors because: They are nontoxic, relatively cheap, and easy to produce in purities with proportion of more than 99 % and they are rich in donating atoms such as -N, -O and –S atoms. Continuation to our goal for searching for safe, eco-friendly and non-toxic corrosion inhibitor. The aim of the present investigation is to study the inhibitive action of prazole compounds towards the corrosion of aluminum in HCl solution using weight loss, hydrogen evolution reaction, galvanostatic polarization and electrochemical impedance spectroscopy (EIS) techniques.

2. EXPERIMENTAL METHODS

2.1. Materials

The working electrode used in this study was aluminum electrode with purity 99.99%..In weight loss and hydrogen evolution measurements Al coupons with dimension 1.0x2.0x0.1 cm^3 were used. For galvanostatic and electrochemical impedance spectroscopy techniques a cylindrical rod embedded in araldite with exposed surface area of 0.68 cm^2 was used. The electrode surface was polished with different grades of emery papers up to 600 grades in order to obtain a smooth surface, degreased in acetone, washed by distilled water and dried between two fitter papers. All chemicals used were of AR grade and used as received.

Weight-loss measurements were carried out as describe elsewhere [6]. The reaction vessel used for hydrogen evolution reaction and the measurements of the corrosion rate of Al in 1.0 M HCl solution in the absence and presence of prazole compounds were the same as explained elsewhere [5].

Galvanostatic polarization measurements were carried out on Al electrode in 1.0 M HCl in presence and absence of different concentrations of the inhibitors used at 25^oC using EG&G Potentiostate/Galvanostat model-173. Measurements were carried out in three compartment electrochemical cell. Pt counter electrode, saturated calomel electrode as reference electrode and Al working electrode. Solutions were not deaerated to make the conditions identical to weight loss measurements. All the experiments were carried out at 30±1^oC by using ultra circulating thermostat. E vs. log I curves were recorded. The corrosion kinetic parameters such as cathodic Tafel slope (β_c), and anodic Tafel slope (β_a) were calculated from the linear region of the polarization curves. The corrosion current density ($I_{corr.}$) was determined from the intersection of the linear parts of the cathodic and anodic curves with the corrosion potential ($E_{corr.}$). The percentage inhibition efficiency (% IE) was calculated from the following equation:

$$\% \text{ IE} = \left[1 - \frac{I_{add}}{I_{free}} \right] 100 \qquad (1)$$

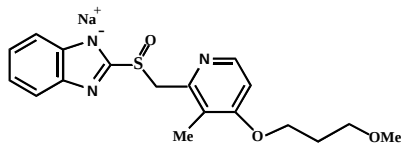
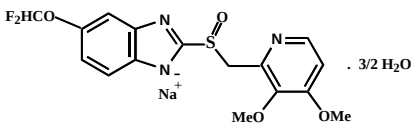
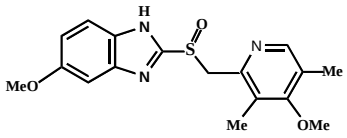
where I_{free} and I_{add} are the corrosion current densities in absence and presence of inhibitors.

Electrochemical impedance spectroscopy (EIS) were carried out at open circuit potential (E_{ocp}) in the frequency range from10kHz to 100MHz with signal amplitude perturbation of 5 mV by using a computer potentiostat (AutoLab 30 Metro).

2.2. Inhibitors

The following three prazole compounds (Omeprazole, pantoprazole and rabeprazole sodium) were kindly provided from Misr Company for Pharmaceuticals and Chemical Industries, Egypt and were used as received without further purification. Their structures are recorded in Table 1.

Table 1. Chemical structures and names of prazole drugs.

Inh.	Structure	Name	Molecular Weight
I		Sodium salt of 2-((4-(3-methoxypropoxy)-3-methylpyridin-2-yl)methylsulfinyl)-1*H*-Benzimidazole (**Omeprazole**)	**345.42**
II		Sodium salt of 1-(2-((3,4-dimethoxypyridin-2-yl)methylsulfinyl)-1*H*-benzimidazol-6-yl)-2,2-difluoroethanone (**Pantoprazole Sodium Sesquihydrate***)*	**432.38**
III		5-methoxy-2-((4-methoxy-3,5-dimethylpyridin-2-yl)methylsulfinyl)-1*H*-benzimidazole (**Rabeprazole Sodium**)	**381.40**

3. RESULTS AND DISCUSSION

3.1. Weight loss measurements

Figure 1 represents the relation between time and weight loss of Al coupons in 1.0 M HCl solution devoid of and containing different concentrations of compound III as an example. Similar curves were also obtained for other two compounds (not shown). An inspection of Fig. 1 reveals that, the weight loss of Al in presence of the inhibitor varies linearly with time, and is much lower than that obtained in the blank solution. The linearity obtained indicates the absence of insoluble surface film

during corrosion and that the inhibitors were first adsorbed onto the surface and thereafter impede the corrosion process [14]. The corrosion rates (R_{corr}, mg cm^{-2} min^{-1})were calculated from the slope of the linear relationship obtained in Fig. 1.

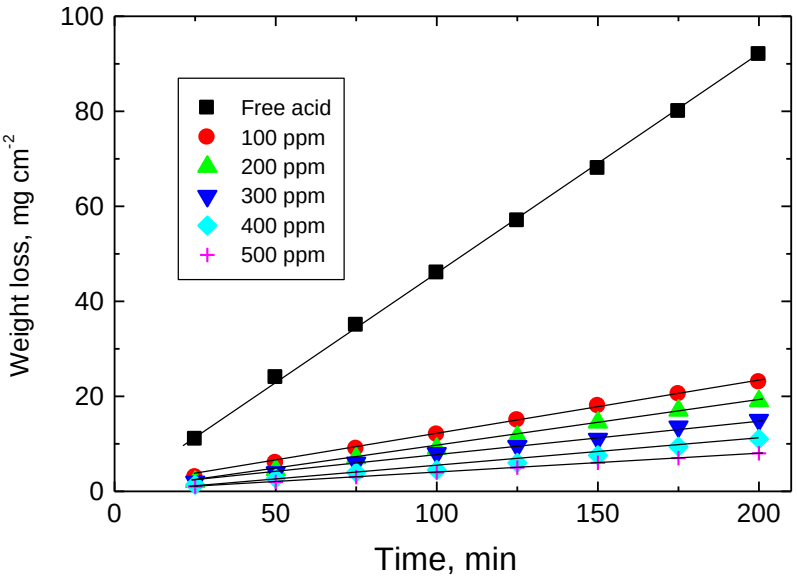


Figure 1. Weight-loss as a function of time of aluminum electrode in 1.0 M HCl solution without and with compound III.

The percentage inhibition efficiency (%IE) was calculated as follow:

$$\% \text{ IE} = \left[1 - \frac{R_{corr.add}}{R_{corr.\ free}} \right] 100 \qquad (2)$$

where,$R_{corr,free}$ and $R_{corr,add}$ are the rate of corrosion in the absence and presence of inhibitors.

The calculated values of R_{corr} and % IE from the weight loss measurements are listed in Table 2. It is obvious that,as the concentration of prazole compounds increases the values of R_{corr} decreases and % IE increases. This indicted that the inhibiting effect of these compounds. At one and the same inhibitor concentration the values of % IE decreases in the following order: compound III > compound II > compound I.

3.2 .Adsorption isotherm

The adsorption of the anti-ulcer prazole drugs on the surface of aluminum electrode is regarded as substitutional adsorption process between drug compounds in the aqueous phase ($drug_{aq}$) and the water molecules adsorbed on the aluminum surface $(H_2O)_{ads}$

$$Drug_{(sol)} + X(H_2O)_{ads} \rightleftharpoons Drug_{(ads)} + XH_2O_{(sol)} \qquad (3)$$

where X is the size ratio, that is the number of water molecules replaced by one drug molecule.

The degree of surface coverage (θ) of Al electrode by adsorption of prazole drugs compounds was calculated using the following equation:

$$\theta = \left[1 - \frac{R_{corr.add}}{R_{corr.\ free}} \right] \quad (4)$$

The values of θ for different concentrations of the studied compounds (I - III) at 30 °C are inserted in Table 2. In order to prove the best adsorption isotherm.

Table 2. Effect of prazole drugs on the corrosion of aluminum in 1.0 M HCl solution using weight loss and hydrogen evolution measurements

Inhibitors	Concentration (ppm)	$R_{corr.}$, mg cm^{-2} min^{-1}	Θ	%I.E	
				Weight loss	Hyd. Evolution
Blank	0	0.540	--	--	--
Compound I	100	0.149	0.724	72.40	**73.45**
	200	0.103	0.809	80.92	**78.88**
	300	0.094	0.826	82.59	**81.28**
	400	0.072	0.867	86.66	**86.14**
	500	0.045	0.917	91.66	**90.15**
Compound II	100	0.125	0.768	76.85	**77.12**
	200	0.108	0.800	80.00	**80.15**
	300	0.084	0.844	84.44	**83.12**
	400	0.055	0.898	89.81	**90.22**
	500	0.040	0.926	92.59	**91.01**
Compound III	100	0.102	0.811	81.11	**80.08**
	200	0.088	0.837	83.70	**84.78**
	300	0.073	0.865	86.48	**86.21**
	400	0.041	0.924	92.40	**91.18**
	500	**0.033**	**0.939**	**93.88**	**94.09**

Attempts were made to fit θ values to various isotherms including Langumuir, Temkin, Frumkin, Freundlich and Flory Huggins isotherms. We found that the best result is applied by Langmuir adsorption isotherm. Figure 2 represents the relation between C/θ and C. A straight lines with unit slope value were obtained indicating that the adsorption of prazole drugs on the aluminum surface follows Langmuir adsorption isotherm. From these results, we conclude that there is no interaction between adsorbed species.

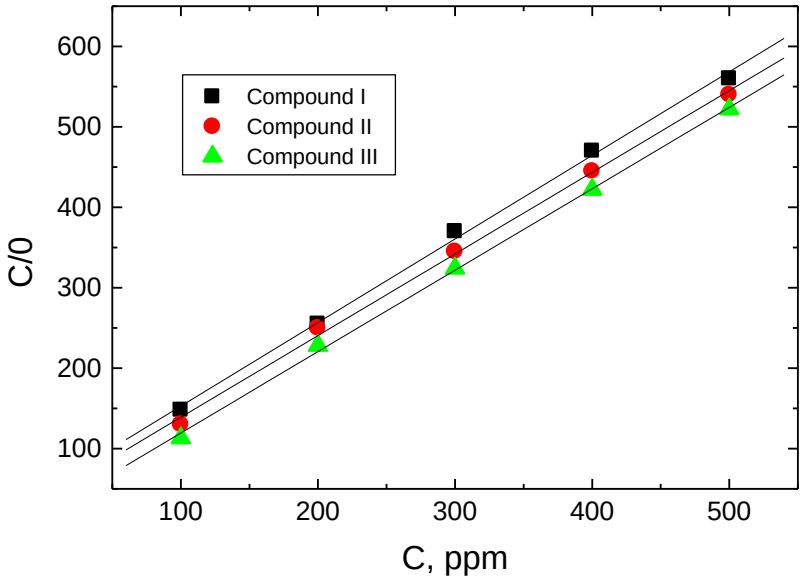


Figure 2. Langmuir isotherm for aluminum electrode in 1.0 M HCl solution in presence of prazole drug inhibitors.

3.3. Effect of temperature

Table 3. Effect of rising temperature on the corrosion rate and inhibition efficiency for the corrosion of aluminum in 1.0 M HCl solution in absence and presence of 500 ppm of prazole drugs using weight loss measurements

Inhibitors	Temperature ° C	$R_{corr.}$ mV. (SCE)	%IE
Blank	30	0.540	--
	40	0.680	--
	50	0.820	--
	60	0.980	--
Compound I	30	0.045	**91.66**
	40	0.093	**86.32**
	50	0.163	**80.12**
	60	0.269	**72.55**
Compound II	30	0.040	**92.59**
	40	0.076	**88.82**
	50	0.146	**82.19**
	60	0.237	**75.81**
Compound III	30	0.033	**93.88**
	40	0.072	**89.41**
	50	0.137	**83.29**
	60	**0.225**	**77.04**

The effect of rising temperature on the corrosion rate of Al in 1.0 M HCl solution in the absence and presence of 500 ppm of prazole drugs using weight loss measurements over temperature range from 30-60 ºC. Similar figures were obtained to figure 1 (not shown). The effect of rising temperature on the corrosion rate and the inhibition efficiency is given in Table 3. Inspection of this table reveals that, as the temperature increases the corrosion rate of Al increases and hence the inhibition efficiency of the prazole drugs compounds decreases.

This is due to the desorption aided by increasing the temperature. This behavior reveals is physical adsorption [15].

The apparent activation energy Ea, the enthalpy of activation ΔH^* and the entropy of activation ΔS^* for the corrosion of aluminum 1.0 M HCl solution devoid of and containing 500 ppm of polymer compounds were calculated from Arrhenius- type equation[16]:

$$R_{corr.} = A \exp(-E_a/RT) \quad (5)$$

and transition state equation:

$$R_{corr.} = RT/Nh \exp(\Delta S°/R) \exp(-\Delta H°/RT) \quad (6)$$

where A is the frequency factor h is the plank's constant, N is Avogadro's number and R is the universal gas constant.

Figure 3 represents the relation between log $R_{corr.}$ vs. 1/T for Al electrode in 1.0 M solution in the absence and presence 500 ppm of the studied inhibitors. Straight lines were obtained with slope equal to $-E_a / 2.303R$ The of E_a values were obtained from the slope of the straight lines and equal to 32.29 kJmol^{-1}in 1.0 M HCl solution and 41.61**,** 47.61 and 50.36 kJ mol^{-1} in presence of compound I, II and III, respectively. It is clear that the presence of the tested compounds increase the activation energy values. These results indicate that the prazole compounds act as inhibitors through increasing activation energy of aluminum dissolution by making a barrier to mass and charge transfer by their adsorption on aluminum surface.

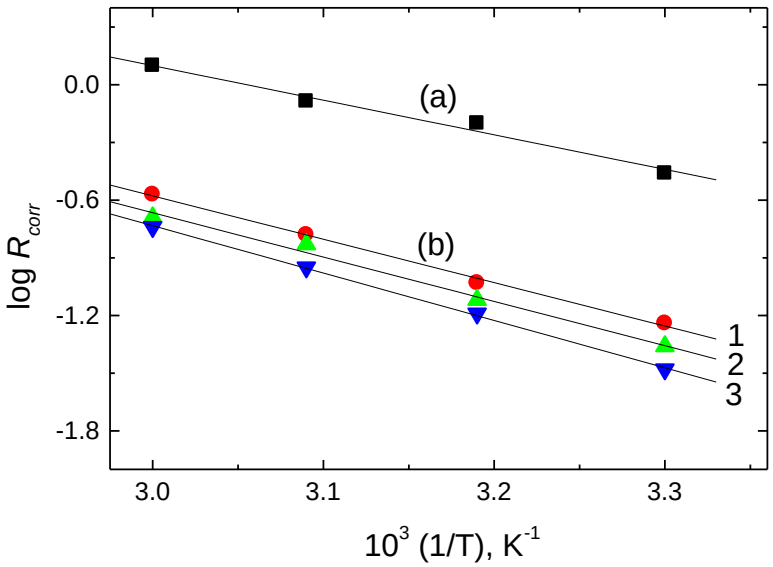


Figure 3. log R_{corr}-1/T curves for aluminum electrode in 1.0 M HCl in absence and presence of prazole drug inhibitors. a) 1.0 M HCl. b) 1- Compound I, 2- Compound II and 3- Compound III

Figure 4 represents the plot of log ($R_{corr.}$/T) vs. (1/T).Straight lines were obtained with slope equal to – ΔH° / 2.303 R and an intercept of log[(R/Nh) - (ΔS°/2.303R)]. The values of ΔH°obtained from the straight line equal 47.86 $kJmol^{-11}$in 1.0 M HCl solution and 57.44**,** 67.01 and 72.75 $kJmol^{-1}$ in presence of compound I, II and III, respectively. The positive signs of ΔH° reflect the endothermic nature of the aluminum corrosion process. The values of ΔH° are different for studied compounds which means that their structure affect the strength of its adsorption on the metal surface. The values of ΔS° calculated from the intercept of straight lineare equal to 225.8 $JK^{-1}mol^{-1}$ in 1.0 M HCl and 272.7, 285.2, 312.8 $JK^{-1}mol^{-1}$ in presence of compound I, II and III, respectively. The negative values of ΔS° in the absence and presence of the inhibitors implies that, the activated complex is the rate determining step and represents association rather than dissociation. It also reveals that an increase in the order takes place in going from reactants to the activated complex [13]. The order of inhibition efficiency of prazole compounds are agree with that obtained from the increase in E_a and ΔH° values and decrease in ΔS° values.

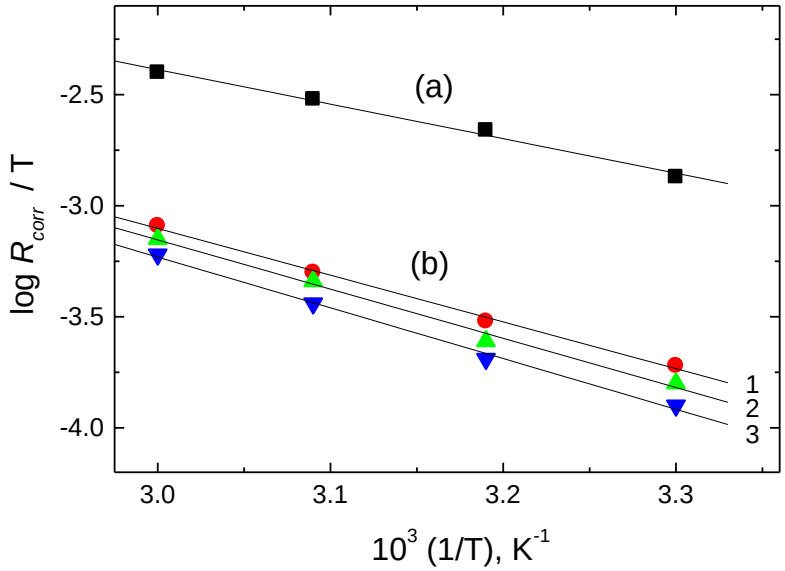


Figure 4. log corrosion rate / T vs. 1/T plots for aluminum electrode in 1.0 M HCl in absence and presence of prazole drug inhibitors.a) 1.0 M HCl. b) 1- Compound I, 2- Compound II and 3- Compound III.

3.3. Hydrogen evolution measurements

Figure 5 represents the relation between the volume hydrogen evolved during the corrosion of Al in 1.0 M HCl solution in the absence and presence of different concentrations of compound III as an example. Similar curves were also obtained for other two compounds (not shown). An inspection of Fig. 5 reveals that, the volume of hydrogen at the beginning is small and at a certain time the volume of H_2 starts to increase suddenly due breakdown of the pre-immersion of Al_2O_3 film formed on the Al

surface. This time is called incubation time. The incubation time increased as the concentration of inhibitors increases.

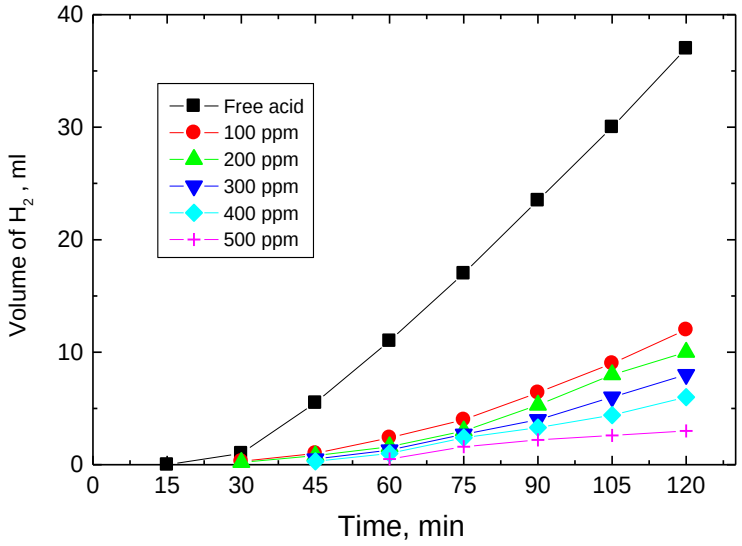


Figure 5. Hydrogen evolution during corrosion of aluminum electrode in 1.0 M HCl solution without and with compound III.

After incubation time the corrosion of Al is varied linearly with time according to the following equation:

$$V_{H2} = Kt \qquad (7)$$

where V_{H2} is the volume of hydrogen evolved, t is the time and K is the specific rate constant of the corrosion reaction. The corrosion rate was obtained from the slope of the straight portion of curves after incubation time.

Values of % IE for three compounds of prazole compounds were calculated and given in Table 2. The order of inhibition efficiency at the same concentration of inhibitors decreased in the following order: compound III > compound II > compound I

3.4. Galvanostatic polarization measurements

Figure 6 represents the galvanostatic anodic and cathodic curves for Al in 1.0 M HCl solution in the absence and presence of different concentrations of compound III as an example. Similar curves were also obtained for other two compounds (not shown). The electrochemical parameters such as anodic ($ß_a$) and cathodic ($ß_c$) Tafel constants, corrosion potential ($E_{corr.}$), corrosion current density ($I_{corr.}$) and percentage inhibition efficiency (%IE) were obtained and given in Table 4.

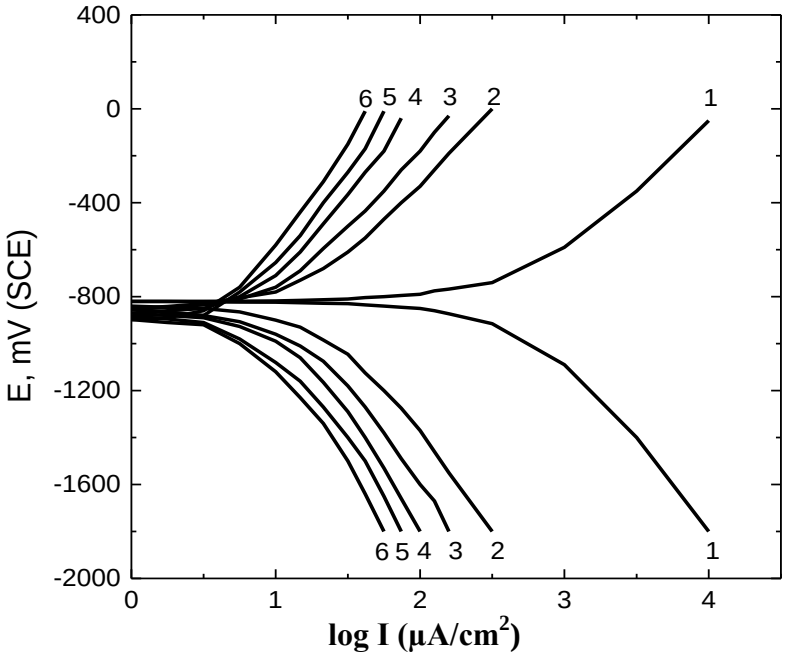


Figure 6. Galvanostatic polarization curves of aluminum electrode in 1.0 M HCl containing different concentrations of compound III at 30 °C. (1) 0.00 (2) 100 (3) 200 (4) 300 (5) 400 (6) 500ppm

Inspection of Table 4 reveals that, the values of $ß_a$ and $ß_c$ were changed slowly with addition of prazole compounds. This indicates that, these compounds affect both anodic dissolution of aluminum and hydrogen evolution reaction.

Table 4. Corrosion parameters obtained from galvanostatic polarization technique for aluminum electrode in 1.0 M HCl solution in absence and presence of different concentrations of prazole drug inhibitors.

Inhibitors	Concentration (ppm)	$ß_a$ m V dec^{-1}	$ß_c$ m V dec^{-1}	$-E_{corr}$ mV. (SCE)	$I_{corr.}$, $mAcm^{-2}$	%IE
Blank	0	795	820	810	458	--
Compound I	100	812	832	812	115	**74.89**
	200	822	844	815	106	**76.85**
	300	834	855	817	83	**81.87**
	400	850	870	822	60	**86.89**
	500	860	883	825	45	**90.17**
Compound II	100	810	840	816	102	**77.72**
	200	826	848	822	89	**80.56**
	300	830	862	829	68	**85.15**
	400	840	875	835	52	**88.64**
	500	860	890	844	39	**91.48**
Compound III	100	809	850	815	96	**79.03**
	200	832	866	820	78	**82.96**
	300	845	880	829	56	**87.77**
	400	862	905	837	45	**90.17**
	500	**890**	**920**	**845**	**30**	**93.49**

These results proved that the prazole compounds acts as a mixed–type inhibitors [17]. The values of E_{corr} is shifted slowly to negative potentials and the values of $I_{corr.}$ decrease indicating the inhibiting effect of these compounds. The percentage inhibition efficiencies of the three tested compounds decreases in the following order: compound III > compound II > compound I.

3.5. Electrochemical impedance spectroscopy (EIS)

The corrosion behavior of Al in 1.0 M HCl solution in the absence and presence of different concentrations of compound III is studied by EIS technique as an example. Similar curves were also obtained for other two compounds (not shown). The equivalent circuit models used to fit the experimental results were as previously reported [4]. Figure 7 shows the complex-plane impedance plots (Nyquist plots) for Al in 1.0 M HCl solution without and with various concentrations of inhibitor at 30 ^{o}C. As it can be seen from this Figure 7, the Nyquist plots contain depressed semi-circle with the center under the real axis, whose size increases with the inhibitor concentration, indicating a charge transfer process mainly controlling the corrosion of Al. Such behavior, is characteristic for solid electrodes and often refers to a frequency dispersion, has been attributed to roughness and other in homogeneities of the solid surface [18,19]. It is apparent, from these plots that the impedance response of Al in uninhibited acid solution has significantly changed after the addition of inhibitor compound in the corrosive solutions.

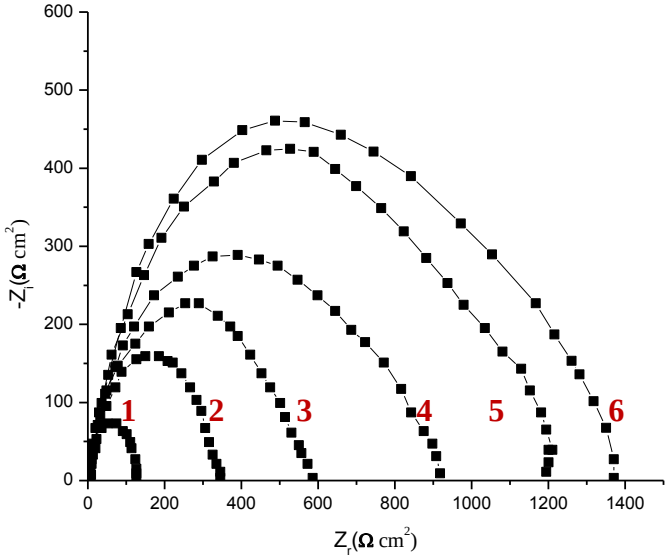


Figure 7. The Nyquist plots for Al in 1.0 M HCl solution in the absence and presence of compound III at 30 ^{o}C. (1) 0.00 (2) 100 (3) 200 (4) 300 (5) 400 (6) 500 ppm.

This indicated that the impedance of the inhibited substrate has increased with increasing concentration of inhibitor. The characteristic parameters associated to the impedance diagrams (R_{ct} and C_{dl}) and % IE are given in Table 5. The percentage inhibition efficiency % IE was calculated from the following equation.

$$\% \text{ IE} = \left[\frac{(1/R_{ct})_0 - (1/R_{ct})}{(1/R_{ct})_0} \right] 100 \qquad (8)$$

where $(R_{ct})_0$ and (R_{ct}) are the uninhibited and inhibited charge transfer resistance, respectively [20].

Table 5. Electrochemical parameters obtained from by electrochemical impedance spectroscopy technique for aluminum electrode in 1.0 M HCl solution in absence and presence of various concentrations of prazole drug .

Inhibitors	Concentration (ppm)	R_{ct} Ω cm²	C_{dl} µF cm^{-2}	%IE
Blank	0	126	131.2	-
Compound I	100	286	76.5	**55.94**
	200	478	69.6	**73.64**
	300	822	50.4	**84.67**
	400	1068	41.2	**88.20**
	500	1285	28.6	**90.19**
Compound II	100	295	71.5	**57.28**
	200	512	58.8	**75.39**
	300	898	44.6	**85.96**
	400	1145	29.8	**88.99**
	500	1328	21.8	**90.51**
Compound III	100	351	66.8	**64.10**
	200	582	51.5	**78.35**
	300	925	38.4	**86.37**
	400	1205	23.0	**89.45**
	500	**1398**	**16.6**	**90.98**

3.6. Inhibition mechanism

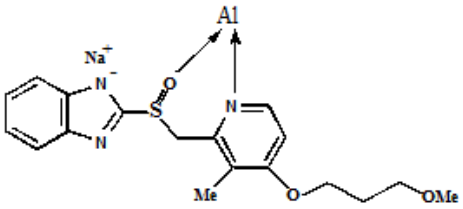
Inhibition of the aluminum corrosion in 1.0 MHCl solution by anti-ulcer prazole drugs using different techniques was found to depend on the concentration, temperature, chemical structure of inhibitors. There are some corrosion parameters were founded by increasing the concentration of inhibitors e.g. decrease of weight loss, increase of surface coverage, decrease of hydrogen evolved, decrease of corrosion current density, increase of charge transfer resistance, decrease of capacitance of double layer and increase of inhibition efficiency.

The mechanism of the inhibition processes of Al by prazole drugs is mainly the adsorption one. The adsorption process of prazole compounds on the aluminum surface depends on many factors which include molecular size, presence of active centers in the chemical structure of inhibitor, charge density and ability to form complexes [21]. The presence of hetro atoms in the chemical structure of prazole compounds makes its adsorption by formation of coordinate bonds through the transfer of lone pairs of electron of heteroatoms to the Al surface These species can be adsorbed by the metal surface

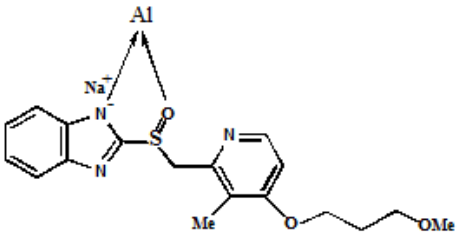
because of attractive forces between the negatively charged metal and the positively charged inhibitor molecules.

There are two types of possible complexes for prazole compound may be formed as illustrated in the following

for compound I

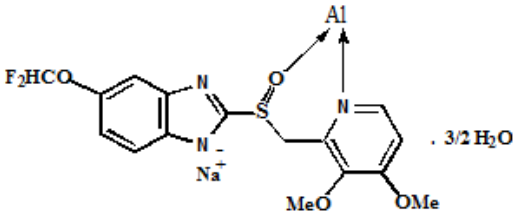


(B)

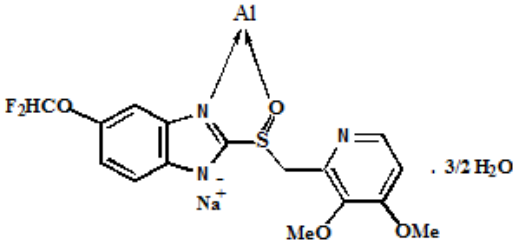


(A)

for compound II

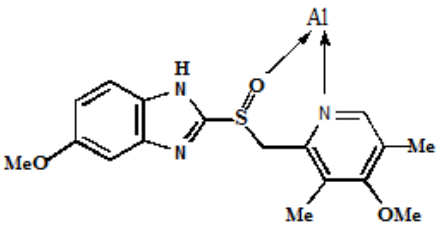


(A)

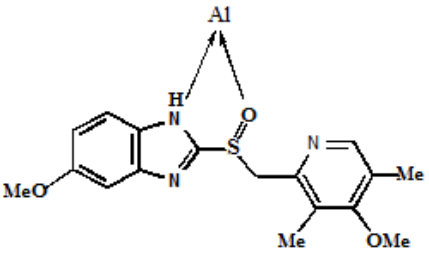


(B)

and for compound III



(A)



(B)

Complex A is more stable than complex B due to the formation of chelated six membered rings with Al ion. The complex B is less stable due to the formation of five membered rings. It is well known that the six membered ring is more stable than five membered ring. This is due to the high donation of π- electron.

The order of inhibition efficiency obtained from different techniques used decrease in the following order: compound III > compound II > compound I. It obvious that, the compound III is more efficient inhibitor for corrosion of Al in 1.0 M HCl solution than other two compounds. This is

attributed to the presence of two methoxy groups and two methyl groups in the chemical structure of inhibitors. These groups are electro donating group which enhance the adsorption process. The electro donation of methoxy is more than methyl group. This is due to increase the localization of lone pair of electron and electron density on N-atom. This increase the chance to make stable six membered ring with Al surface. On the other hand, the compound II contains two methoxy but compound I contains one methoxy and one methyl groups. So, the electro donation of compound II is more than compound I and hence increases the inhibition efficiency of compound II than compound I.

4.CONCLUSION

1-Prazole compounds inhibit the corrosion of aluminum in 1.0M solution.

2-The percentage inhibition efficiency increases with increasing the concentration of inhibitor and with decreasing temperature.

3-The inhibition action of prazole compounds due to the formation of insoluble complex adsorbed on the aluminum surface.

4-The adsorption process obeys Langmuir isotherm.

5- Electrochemical impedance spectroscopy indicates that the corrosion reaction is controlled by charge transfer process.

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