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ORIGINAL ARTICLE

Antihypertensive drugs as an inhibitors for corrosion of aluminum and aluminum silicon alloys in aqueous solutions

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Abstract The corrosion behavior of aluminum and three aluminum–silicon alloys in different concentrations of HCl solutions and its inhibition by antihypertensive drugs was studied using potentiostatic polarization measurements. As the acid concentration increases, the rate of corrosion increases. Aluminum is less susceptible to corrosion than any of Al–Si alloys. The inhibition efficiency of the drug compounds increases with their concentration up to a critical value. At higher additive concentrations the inhibition efficiency starts to decrease. The inhibitive action of these compounds is due to their formation of insoluble complex adsorbed on the metal surface. The adsorption follows Langmuir adsorption isotherms. It was found that the drugs compounds provide protection to Al and Al–Si alloys against pitting corrosion by shifting the pitting potential to more positive direction until critical drug concentrations (250 ppm). After this critical concentration the inhibition against to pitting corrosion starts to decrease.

1. Introduction

Aluminum and its alloys exhibit corrosion resistance in many environments and for this reason they find many important industrial applications. The corrosion resistance is due to the initial formation of a compact and adherent passive oxide film on the exposed surfaces. However, in the presence of insidious ions such as chloride ions, the protective oxide film can be locally destroyed, initiating metal dissolution. Again, the oxide film is amphoteric and hence dissolves readily in acidic solutions (Oguzie, 2009).

In an attempt to mitigate electrochemical corrosion of aluminum and its alloys, the main strategy is to effectively isolate the metal from corrosion agents. This can be achieved by

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the use of corrosion inhibitors. The use of inhibitors is one of the best known methods of corrosion protection. Most of the efficient acid inhibitors are organic compounds that contain mainly nitrogen, sulphur or oxygen atoms in their structure. Organic compounds used as inhibitors act through a process of surface adsorption, So the efficiency of an inhibitor depends not only on the characteristics of the environment in which its acts, the nature of the metal surface and electrochemical potential at the interface but also on the structure of the inhibitor itself, which includes the number of adsorption active centers in the molecule, their charge density, the molecular size, the mode of adsorption, the formation of metallic complexes and the projected area of the inhibitor on the metal surface (Chetouani et al., 2005; Okafor and Zheng, 2009).

Compounds with functional groups containing heteroatoms which can donate lone pairs of electrons are found to be particularly useful as inhibitors for aluminum corrosion (Khaled and Al-Qahtani, 2009; Obot and Obi-Egbedi, 2008; Lashkari and Arshadi, 2004; Zheludkevich, 2005; Maayta and Al-Rawashdeh, 2004; Amin et al., 2005; Obot et al., 2009). Also, compounds with π-bonds also generally exhibit good inhibitive properties by providing electrons to interact with the metal surface (Yildirim and Cetin, 2008; Hasanov et al., 2007; Umoren and Ebenso, 2008). Both features obviously can be combined within the same molecule such as drugs.

The use of drugs as corrosion inhibitors for metals in different aggressive environments is not widely reported. Few reports exist in the literature to date; these include the use of sulpha drug (El-Naggar, 2007). Some pharmaceutical compounds used for inhibition of Al in 0.5 mol L^{-1} H_3PO_4 (Fouda et al., 2009).

In the previous work, rhodanine azo sulpha drugs (Abdallah, 2002) and antibacterial drug (Abdallah, 2004) were used as corrosion inhibitors for corrosion of 304 SS and aluminum in hydrochloric solutions. They inhibit the corrosion by parallel adsorption on the surface of the metal due to the presence of more than one active center in the inhibitor molecule.

The aim of the present paper is to study the inhibiting action of some antihypertensive drugs on the general and pitting corrosion of Al and three alloys of Al–Si in hydrochloric acid solution using potentiostatic and potentiodynamic anodic polarization techniques. The mode of adsorption and the corrosion inhibition mechanism are also discussed.

2. Experimental methods

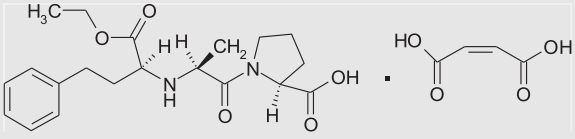
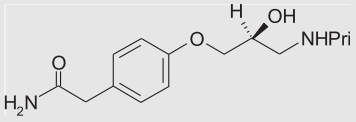
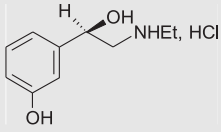
The chemical composition of the three of Al–Si alloys is presented in Table 1.

These electrodes in the form of a cylindrical rod were fixed to pyrex glass tubing by araldite (exposed surface area is 0.79 cm^2 for Al pure, 0.64 cm^2 for alloy I, 0.77 cm^2 for alloy II and 0.65 cm^2 for alloy III). Electrical contacts were made through thick copper wires soldered to the end of the electrodes not exposed to the solution. The electrodes were successively abraded with different grades of emery paper, degreased with acetone and finally washed twice with distilled water; complete wetting of the surface was taken as an indication of its cleanliness. All chemicals used were of A.R. quality. The

Table 1 Composition of pure Al and Al–Si alloys (by weight percent).

Sample	Alloy	Si	Fe	Cu	Mn	Mg	Ni	Ti	Zn	Cr	Na	Sr
Al	–	–	–	–	–	–	–	–	–	–	–	–
Alloy I	6063	0.42	0.17	0.001	0.009	0.42	0.001	0.010	0.001	0.000	0.0012	0.000
Alloy II	20556	7.01	0.110	0.000	0.000	0.318	0.001	0.091	0.001	0.000	0.0012	0.000
Alloy III	$AlSi_{11}MgSr$	10.85	0.110	0.000	0.001	0.176	0.001	0.094	0.001	0.000	0.0016	0.061

Table 2 The chemical structure of antihypertensive drugs.

Inhibitor	Name	Structure formula	Molecular formula
Compound I	Enalapril maleate		$C_{20}H_{28}N_2O_5{\cdot}C_4H_4O_4$ M. Wt. = 492.53
Compound II	Atenolol		$C_{14}H_{22}N_2O_3$ M. Wt. = 266.3
Compound III	Etilefrine hydrochloride		$C_{10}H_{15}NO_2$, HCl M. Wt = 217.7

solutions were prepared using twice distilled water and no trial was made to deaerate them. The electrochemical cell was all Pyrex and described elsewhere (El-Etre, 2007). The experiments were carried out at 25 ± 1 °C using air thermostat.

Potentiostatic and potentiodynamic anodic polarization measurements were carried out using PS remote potentiostat with PS6 software for calculation of some corrosion parameters e.g., corrosion current density ($i_{corr.}$) corrosion potential ($E_{corr.}$) and rate of corrosion ($R_{corr.}$). The corrosion parameters were calculated from the intercept of the anodic and cathodic Tafel lines. The potentiostatic and potentiodynamic anodic polarization measurements were carried out at scan rate of 10 mV $s^{-1}$and 1 mV s^{-1}, respectively. A three compartment cell with a saturated calomel reference electrode (SCE) and a platinum foil auxiliary electrode was used.

The inhibition efficiency (I.E.) and the surface coverage (θ) were calculated using the following equations:

$$\text{I.E.} = \left[1 - \frac{R_{\text{corr.add}}}{R_{\text{corr.free}}}\right] 100 \quad (1)$$

$$\theta = \left[1 - \frac{R_{\text{corr.add}}}{R_{\text{corr.free}}}\right] \quad (2)$$

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

Conductance measurements were carried out using YSI model 32 conductance meter of cell constant equal to 1.6.

The inhibitors used in this study were three compounds of antihypertensive drugs. The chemical structure of three compounds is shown in Table 2.

3. Results and discussion

3.1. Potentiostatic polarization

3.1.1. Effect of acid concentration

Fig. 1 shows the anodic and cathodic polarization curves of Alloy III in different concentrations of HCl solutions as an example. Similar curves were obtained for the other two alloys and Al pure (not shown) (see Table 3).

The effect of acid concentrations on the corrosion parameters such as $E_{corr.}$, $i_{corr.}$ and $R_{corr.}$ is summarized in Table 1. Inspection of this table reveals that $E_{corr.}$ is dependent of acid concentration. $E_{corr.}$ values shifted more negative potentials. The values of $i_{corr.}$ of Al and all the alloys increased with increase of acid concentrations and consequently the corrosion rate $R_{corr.}$ increases. At the same acid concentration the value of $i_{corr.}$ decreases in the following order III > II > I > Al. This indicates that alloy III has the highest susceptibility to corrosion and Al is less susceptible to corrosion than any of these alloys in agreement with previous results (Bohni and Uhlig, 1969).

3.1.2. Effect of antihypertensive drugs

The effect of addition of increasing concentration of three compounds of antihypertensive drugs (I–III) on the anodic and cathodic polarization curves of aluminum electrode and three of Al–Si alloys in 0.01 M HCl solution was studied. Similar curves to Fig. 1 were obtained (not shown). The corrosion parameters of Al and three Al–Si alloys such as $E_{corr.}$, $i_{corr.}$ and $R_{corr.}$ were calculated and listed in Tables 4–6, respectively. By the inspection of these tables, it is clear that the values of $E_{corr.}$ are changed by increasing the concentration of drugs. It is clear from Table 4 in presence of compound I. The values of $E_{corr.}$ are shifted to more positive potential. This indicates that this compound acted as an anodic inhibitor for Al, alloy I, alloy II and alloy III. In Table 5 compound II generally acted as cathodic inhibitors (except Al and alloy II, 1000 ppm compound II) On the other hand in Table 6 compound III generally acted cathodic inhibitor (except Al 1000 ppm compound III). When the additive concentrations increase from 50 up to 250 ppm the values of $i_{corr.}$ and hence $R_{corr.}$ decrease. Then at concentrations more than 250 ppm the values of $i_{corr.}$ and $R_{corr.}$ increase; consequently, the value of inhibition efficiency (IE) increases at concentrations up to 250 ppm. But at higher

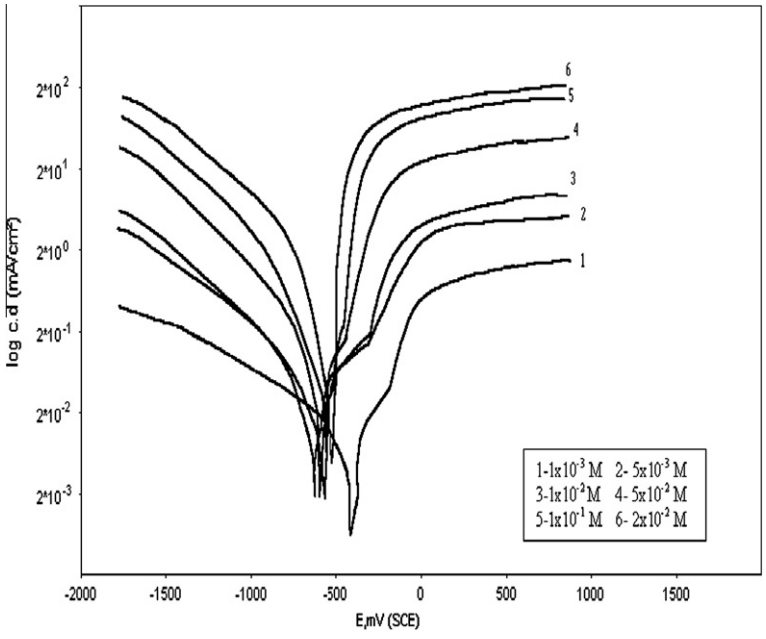


Figure 1 Anodic and cathodic polarization curves of alloy III in different concentrations of HCl solution.

Table 3 Corrosion parameters obtained from anodic and cathodic polarization curves of Al and Al–Si alloys in different concentrations of HCl solution at 25 °C.

Electrode sample	Acid Conc. (M)	$-E_{corr.}$, mV (SCE)	$i_{corr.} \times 10^{-6}$ (A cm^{-2})	$R_{corr.} \times 10^{-2}$ (mm/y)
Al	1×10^{-3}	588	1.65	15.05
	5×10^{-3}	636	5.60	22.25
	1×10^{-2}	736	9.00	29.66
	5×10^{-2}	587	13.90	45.80
	1×10^{-1}	677	17.30	48.40
	2×10^{-1}	681	19.60	52.30
Alloy I	1×10^{-3}	568	4.20	7.20
	5×10^{-3}	540	8.00	12.96
	1×10^{-2}	555	10.90	17.14
	5×10^{-2}	545	16.72	22.70
	1×10^{-1}	617	20.00	31.39
	2×10^{-1}	591	22.38	37.02
Alloy II	1×10^{-3}	577	6.42	10.08
	5×10^{-3}	652	10.95	14.90
	1×10^{-2}	593	13.57	18.70
	5×10^{-2}	620	19.68	27.50
	1×10^{-1}	608	22.60	31.40
	2×10^{-1}	591	24.48	34.70
Alloy III	1×10^{-3}	431	9.60	15.05
	5×10^{-3}	598	15.60	22.25
	1×10^{-2}	589	18.90	29.66
	5×10^{-2}	554	26.18	45.80
	1×10^{-1}	557	28.98	48.40
	2×10^{-1}	535	31.43	52.30

Table 4 Corrosion parameters obtained from anodic and cathodic polarization curves of Al and its alloys in 1×10^{-2} M of HCl solution containing different concentrations of compound I at 25 °C.

Alloy	Inhibitor Conc. (ppm)	$E_{corr.}$ mV (S.C.E)	$i_{corr.} \times 10^{-6}$ (A cm^{-2})	$R_{corr.} \times 10^{-2}$ (mm/y)	I.E. (%)	θ
Al	0	−736	9.00	12.78	–	–
	50	−713	3.80	5.400	57.70	0.5770
	100	−640	3.10	4.400	65.6	0.6560
	150	−570	2.10	3.200	76.83	0.76.83
	250	−518	1.70	2.500	80.33	0.8033
	500	−494	2.04	2.900	77.00	0.7700
	1000	−466	2.40	3.400	73.39	0.7339
Alloy I	0	−555	10.9	17.14	–	–
	50	−556	3.30	5.100	69.72	0.6972
	100	−642	2.40	3.820	77.98	0.7798
	150	−602	2.20	3.400	79.75	0.7975
	250	−535	1.70	2.700	81.10	0.8110
	500	−510	2.20	3.460	79.82	0.7982
	1000	−449	2.70	4.250	75.23	0.7523
Alloy II	0	−593	13.5	18.7	–	–
	50	−632	2.30	3.24	82.96	0.8296
	100	−569	1.60	2.23	88.15	0.8815
	150	−490	1.48	1.18	89.07	0.8907
	250	−440	1.20	1.59	91.11	0.9111
	500	−448	2.10	2.90	84.44	0.8444
	1000	−432	2.90	4.01	78.52	0.7852
Alloy III	0	−589	18.9	29.66	–	–
	50	−587	2.00	2.950	89.40	0.8940
	100	−474	1.50	2.400	92.06	0.9206
	150	−433	1.38	2.100	92.80	0.9280
	250	−436	1.20	1.870	93.70	0.9370
	500	−476	2.50	4.290	86.77	0.8677
	1000	−434	3.50	5.540	81.50	0.8150

Table 5 Corrosion parameters obtained from anodic and cathodic polarization curves of Al and its alloys in 1×10^{-2} M of HCl solution containing different concentrations of compound II at 25 °C.

Alloy	Inhibitor Conc. (ppm)	E_{com} mV (S.C.E)	$i_{corr.} \times 10^{-6}$ (A cm^{-2})	$R_{corr.} \times 10^{-2}$ (mm/y)	I.E. (%)	θ
Al	0	−736	9.00	12.78	–	–
	50	−682	4.80	6.900	46.34	0.4634
	100	−730	4.00	5.900	55.37	0.5537
	150	−715	3.37	4.790	62.50	0.6250
	250	−725	2.90	4.130	67.69	0.6769
	500	−733	3.40	4.770	62.22	0.6222
	1000	−731	4.20	5.850	53.33	0.5333
Alloy I	0	−555	10.9	17.14	–	–
	50	−690	4.90	7.400	55.43	0.5543
	100	−702	3.88	6.100	64.39	0.6439
	150	−685	3.20	4.990	70.36	0.7085
	250	−691	2.89	4.390	74.36	0.7436
	500	−674	3.50	5.600	67.90	0.6790
	1000	−656	4.30	6.800	60.50	0.6050
Alloy II	0	−593	13.5	18.7	–	–
	50	−640	6.60	9.16	51.11	0.5111
	100	−661	4.60	6.30	65.93	0.6593
	150	−630	3.90	5.14	71.25	0.7125
	250	−678	3.16	4.90	76.60	0.7660
	500	−666	4.75	6.61	64.80	0.6480
	1000	−517	6.40	8.90	52.60	0.5260
Alloy III	0	−589	18.9	29.66	–	–
	50	−623	5.00	7.850	73.50	0.7350
	100	−627	4.20	6.550	77.78	0.7778
	150	−640	3.90	5.900	78.79	0.7879
	250	−676	3.40	5.320	82.00	0.8200
	500	−622	4.10	6.480	78.30	0.7830
	1000	−622	4.70	7.340	75.13	0.7513

concentrations more than 250 ppm of drugs, the values of I.E. decrease. This indicates that the resistance to corrosion starts to decrease. At one and the same inhibitor concentrations the values of I.E. decrease according to the following sequence:

Compound I > Compound II > Compound III.

3.1.3. Adsorption isotherm

The adsorption of antihypertensive drugs on the surface of aluminum and its alloys can be interpreted by finding a suitable isotherm which describes the variation of experimentally obtained values of the amount of adsorbed substance by unit area of the metal surface with its concentration in bulk solution at constant temperature. The degree of surface coverage (θ) which represents the part of metal surface covered by drug molecules was calculated using the following Eq. (2).

The values of (θ) for different concentrations of the studied drug compounds have been used to explain the best isotherm for adsorption of drug compounds on the metal surface. It is regarded as substitutional adsorption process between the drug compound in the aqueous phase (drug aq.) and water molecules adsorbed on the metal surface $(H_2O)_{ads}$ (Moretti et al., 1999).

$$Drug_{(sol.)} + X(H_2O)_{ads} \rightleftharpoons Drug_{(ads)} + X(H_2O)_{sol} \quad (3)$$

where, X is the size ratio, that is, the number of water molecules replaced by one drug molecule. Attempts are made to fit (θ) values to various isotherms including, Frumkin, Temkin, Freundlich, Langmuir, Flory Huggins and Bockris-Swinkel isotherm. By far the results were best fitted by Langmuir adsorption isotherm according to the following equation:

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (4)$$

where K and C are the equilibrium constants of adsorption process and additive concentration, respectively. Plotting C/θ against C (Fig. 2) gave a straight line with unit slope value with correlation coefficient of 0.999, 0.996 and 0.998 for compounds I, II and III, respectively, indicating that the adsorption of antihypertensive drug on the surface of Al and Al–Si alloys follows Langmuir adsorption isotherm. From these results one can postulate that there is no interaction between the adsorbed species.

3.2. Potentiodynamic anodic polarization

3.2.1. Susceptibility of Al and its Alloys to pitting corrosion by chloride ions

Fig. 3 represents the potentiodynamic anodic polarization curves of Al electrode in different concentrations of NaCl solution at scan rate of 1 mV s^{-1}. Similar curves (not shown) were obtained for other three alloys.

Inspection of the curves of this figure reveals that:

(i) There is no any active dissolution oxidation peak was observed during the anodic scan. This reflects the stability of the air-formed oxide film on surface of aluminum or its alloys.

Table 6 Corrosion parameters obtained from anodic and cathodic polarization curves of Al and its alloys in 1×10^{-2} M of HCl solution containing different concentrations of compound III at 25 °C.

Alloy	Inhibitor Conc. (ppm)	$E_{corr.}$ mV (S.C.E)	$i_{corr.} \times 10^{-6}$ (A cm^{-2})	$R_{corr.} \times 10^{-2}$ (mm/y)	I.E. (%)	θ
Al	0	−736	9.00	12.78	–	–
	50	−750	5.40	7.690	39.80	0.3980
	100	−788	4.40	6.260	51.00	0.5100
	150	−790	3.90	5.530	56.75	0.5675
	250	−752	3.60	5.160	59.64	0.5964
	500	−836	4.40	6.170	51.11	0.5110
	1000	−609	5.40	7.570	40.00	0.4000
Alloy I	0	−555	10.9	17.14	–	–
	50	−716	5.70	8.980	47.61	0.4761
	100	−702	4.30	6.750	60.60	0.6060
	150	−710	3.90	6.080	64.53	0.6453
	250	−737	3.60	5.700	66.97	0.6697
	500	−675	4.10	6.500	62.38	0.6238
	1000	−658	5.20	8.210	52.23	0.5223
Alloy II	0	−593	13.5	18.7	–	–
	50	−654	7.00	9.70	48.15	0.4815
	100	−710	5.00	7.12	62.96	0.6296
	150	−745	4.85	6.70	64.04	0.6404
	250	−768	4.34	6.50	67.86	0.6786
	500	−662	5.70	7.95	57.78	0.5778
	1000	−656	7.00	9.70	84.15	0.8415
Alloy III	0	−589	18.9	29.66	–	–
	50	−695	6.80	10.80	64.00	0.6400
	100	−658	5.30	8.350	71.96	0.7196
	150	−668	4.50	6.700	74.30	0.7430
	250	−697	3.75	5.900	80.16	0.8016
	500	−756	4.70	7.340	75.13	0.7513
	1000	−604	5.50	8.600	70.90	0.7090

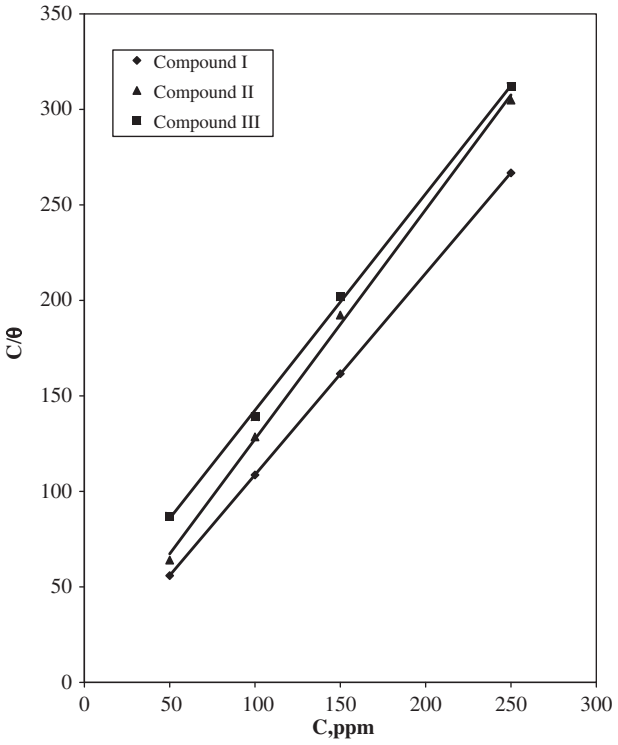


Figure 2 Langmuir adsorption isotherm for alloy III.

(ii) Increasing the sodium chloride concentrations causes the current flowing along the passive region to increase suddenly and markedly at some definite potential denoting the destruction of the passivating oxide film and the initiation of visible pits. The effect of increasing the chloride ions concentrations is the shift of the pitting potential into the active (negative) direction.

The dependence of $E_{pitt.}$ with the concentration of Cl^- ion is shown in Fig. 4. The relation presents sigmoid S-shaped curve that indicates a higher $E_{pitt.}$ value at the lower chloride ion concentrations. In this case, the rate of passive film formation prevails over that the film breakdown, which is clear from the small change of E_{pitt}. into the negative direction of potential. Thus, the metal surface may undergo a repassivation (Abdallah, 2004; Abd El-Haleem, 1979). However, at relatively higher Cl^- ion concentrations, E_{pitt} varies with Cl^- ion concentration according to a straight-line relationship in the following forms (Abdallah and Al-Karanee, 2009):

$$E_{pitt.} = a_1 - b_1 \log C_{Cl}^- \quad (5)$$

where a_1 and b_1 are constants depending on both the nature and type of the aggressive anion and of the electrode. This is due to the destruction of the passive film formed on the metal surface and the pits propagate without allowing to undergo the repassivation. At higher Cl^- ion concentrations, E_{pitt} shifted rapidly to more negative potential; it can be expected that

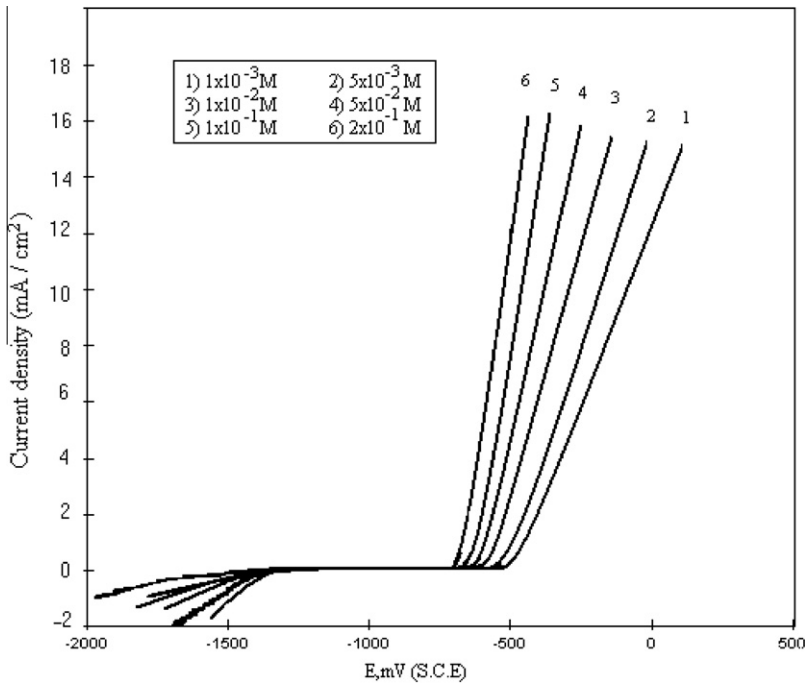


Figure 3 Potentiodynamic anodic polarization curves of pure Al in different concentrations of NaCl solutions.

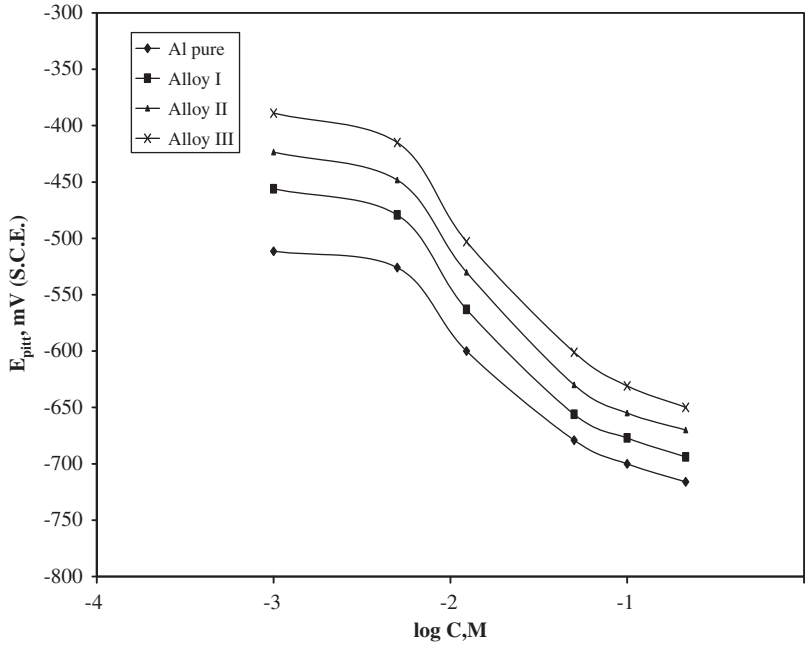


Figure 4 The relationship between pitting potential and logarithm of the concentrations of NaCl solution.

the film breakdown exceeds the film formation and the pit is continuously propagated.

Further inspection of the curves of Fig. 4 reveals that at one and the same Cl^- ion concentration the shift of pitting potential (E_{pitt}) to active (negative) values decreases in the following order:

Al > Alloy I > Alloy II > Alloy III

This sequence differs from that sequence obtained by general corrosion of Al and its alloys, where Al is more resistant to corrosion in HCl solution than Al–Si alloys. In general corrosion the oxide film formed by Al is thick, adherent and non porous. The addition of Si as an alloying element increases the rate of corrosion. Since Al is trivalent and Si is tetravalent, the excess of electron d delocalized throughout the lattice producing point defect. The point defect increases with

increasing Si content. This led to the decrease of the resistance of Al.

In the localized attack (pitting) by chloride ions, the presence of Si as an alloying element increases the pitting corrosion resistance of Al (Abd El-Rehim et al., 2004). This can be attributed to the incorporation of Si atoms in the passive film (Mzhar et al., 2001). This incorporation repairs the film defect and renders it more stable (Strehblow and Doherty, 1978). The above sequence may be attributed to that the chloride ions attack the passive film which contains mainly Al_2O_3 and SiO_2. The increase of Si content in the alloy led to form solid solutions consequently increases the resistance to pitting attack.

This sequence shows that pure Al has the highest susceptibility to pitting corrosion and alloy III is the less susceptible to pitting corrosion than any of other two alloys.

3.2.2. Inhibition of pitting corrosion

The effect of increasing addition of the studied drug compounds on the potentiodynamic anodic polarization curves of Al and its alloys in 1×10^{-2} M NaCl solution was studied. Similar curves (not shown) to those of Fig. 3 were obtained in the presence of these compounds. In their presence, the pitting potential was shifted toward a more positive direction until concentration of drug was up to 250 ppm. This indicates that inhibitive effect of these compounds for pitting corrosion. At higher concentrations (more than 250 ppm) of drugs, there is a shift of E_{pitt}., into the active (negative) direction. This shift indicates that the resistance to pitting corrosion is decreased.

Fig. 5 represents the relationship between E_{pitt} and log $C_{\text{inh.}}$ From the curves of this figure, it is clear that the increase of the concentration of the antihypertensive drugs until a critical concentration (250 ppm) causes a shift of pitting corrosion potential into the noble (positive) direction, in accordance with the following equation:

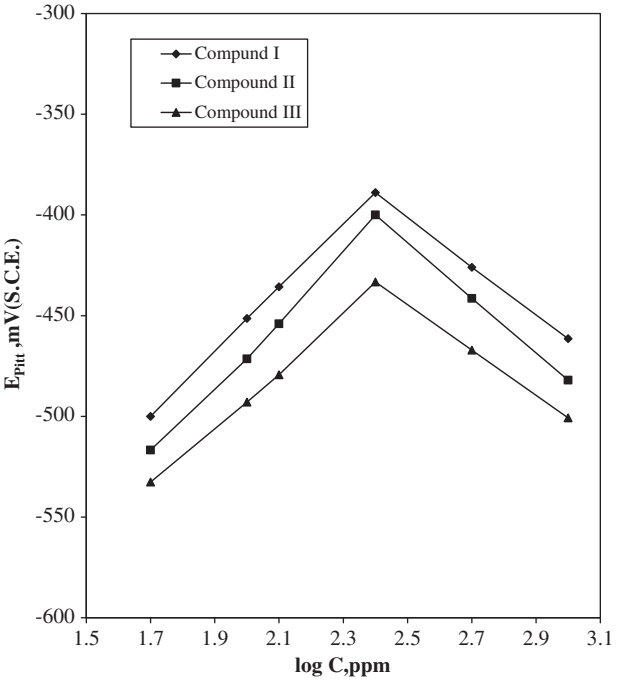


Figure 5 The relationship between pitting potential and logarithm of the concentrations of inhibitor compounds in 1×10^2 M NaCl solution for alloy III.

$$E_{\text{pitt.}} = a_2 + b_2 \log C_{\text{inh.}} \quad (6)$$

where a_2 and b_2 are constants depending on the type of inhibitors and aggressive anions as well as the metal or alloys under test. This denotes that at this critical concentration these compounds start to lose their inhibiting effect.

Some authors (Shams El-Din et al., 1977; Abd El Haleem et al., 1995) attributed the above observation to the hydrolysis of inhibitor to produce corrosion promoting species. However, one may attribute the lose of inhibiting effect toward pitting aluminum and its alloys in presence of high concentrations of antihypertensive sites drugs (more than 250 ppm) due to the competition for adsorption sites on the metal surface. The accumulation of the inhibitors molecules on the metal surface which creates a steric hindrance effect (Schweinsberg et al., 1988). Such effect leads to loosely attack the layer which stimulates corrosion rather than inhibition.

4. Mechanism of inhibition

The inhibition of the general and the pitting corrosion of pure aluminum and aluminum silicon alloys in hydrochloric acid solutions by some antihypertensive drugs as measured by potentiostatic polarization and potentiodynamic anodic polarization were found to depend on both the concentration and the nature of the inhibitors. As the concentration of the inhibitors increases the observed corrosion parameters led to:

(i) Decrease of corrosion density.
(ii) Increase of inhibition efficiency.
(iii) Increase of surface coverage.
(iv) Shift of pitting potential to positive direction.

The inhibition efficiency of antihypertensive drugs against the corrosion of Al and Al–Si alloys in 1×10^{-2} M HCl was explained on the basis of the adsorption of the inhibitors at the electrode-solution interface (Mohmoud et al., 1996). Since the drug compounds contain more than one active center in their chemical structures, they will improve the adsorption process, and consequently inhibit the metals against corrosion. However, the inhibition efficiency of the studied compounds depends on many factors, which include the number of adsorption active centers in the molecule, charge density, molecular size, structure and mode of interaction with metal surface and ability to form complexes (Fouda et al., 1986).

To illustrate the mechanism of interaction of antihypertensive drugs with metal ions, the stoichiometry of the expected Al-drugs complexes was estimated by conductance measurements. Conductometric titration curves were obtained by titrating 50 ml of 1×10^{-3} M Al^{3+} with a solution of 1×10^{-4} M drugs compound as a titrant. The conductance ml-added curves (Fig. 6) are characterized by breaks at molar ratio of 1.0 metal cation: 1.0 drugs additives for compounds I, II and III (cation-ligand).

It is known that (Amin, 1995) the shape of the conductometric curve depends on the concentrations of all the species present during the titration process as well as on some other factors such as viscosity, dielectric constant, solvation, complexation and proton transfer.

The inhibition process of antihypertensive drugs can be attributed to the formation of insoluble complexes. The three

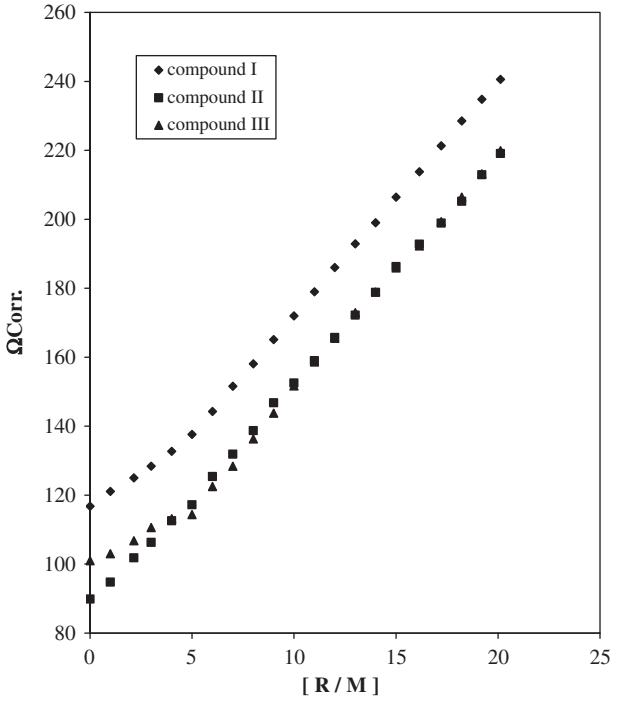
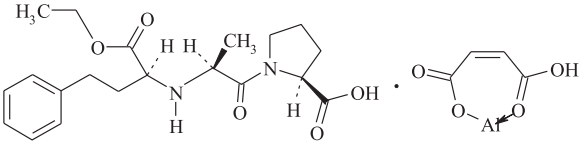


Figure 6 Conductometric titration of 50 ml of $1 \times 10-4$ M antihypertensive drugs (R) against 1×10^{-3} M $AlCl_3$ (M).

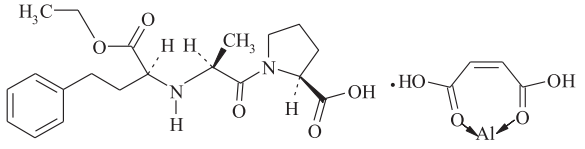
compounds of antihypertensive drugs can react with Al^{3+} ion according to the following reaction:

Compound I (high molecular weight) which gives the highest inhibition efficiency, can react with Al^{3+} ion via one of three routes to give structures I, II or III.

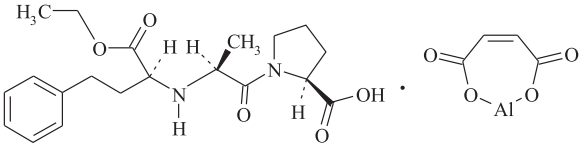
Structure (I)



Structure (II)

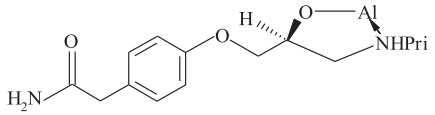


Structure (III)



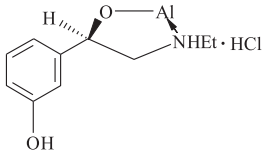
Structure I contains one covalent bond (O–Al) and one coordination bond (O → Al). Structure II contains two coordination bonds (O → Al). On the other hand, structure III contains two covalent bonds. Since the covalent bond (O-Al) is stronger than the coordination bond (O → Al), thus, structure III is the most expected complex to be formed.

Compound II interacts with the metal ion to give the following structure.



As seen, this structure contains two bonds; one of them is coordination (N → Al) and the other is covalent bond (O–Al).

Compound III reacts with the metal ions and the following structure may be obtained.



The last structure contains two bonds; one of them is coordination bond (N → Al), while the other bond (O–Al) is covalent.

In view of the above observations, one can conclude that the inhibition efficiencies (I.Es) of antihypertensive drugs (I–III) decrease in the order:

Compound I > Compound II > Compound III.

This sequence is in a good agreement with the results obtained experimentally from the two techniques.

5. Conclusion

(1) Antihypertensive drugs act as inhibitors for general and pitting corrosion of Al and Al–Si alloys.
(2) The inhibition efficiency increases with increasing drug concentrations up to a critical value and starts to decrease in presence of higher additives' concentrations due to steric hindrance effect.
(3) The drug compound acts as corrosion inhibitor due to the formation of insoluble complex adsorbed on the metal surface.
(4) The adsorption process follows Langmuir adsorption isotherm.
(5) Al–Si alloys are more resistant to pitting corrosion than Al in chloride-containing solution.

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