Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2021.27050

221 (2021) 270–280
May

Inhibitive performance of dapoxetine drug for corrosion of aluminum alloy (AA6063) in acidic and alkaline solutions: experimental and theoretical studies using Materials Studio v7.0

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Received 9 August 2020; Accepted 16 January 2021

ABSTRACT

The inhibiting effect of the dapoxetine drug towards corrosion of aluminum alloy (AA6063) in 1.0 M HCl and 1.0 M NaOH solutions using weight loss, potentiodynamic polarization, and theoretical calculation. The results demonstrated that the inhibition efficiency (IE%) was increased with increasing the concentration of dapoxetine and lowering the temperature. IE% of dapoxetine is higher in 1.0 M HCl than in 1.0 M NaOH solution. The activation parameters of the corrosion process are endothermic, and the formation of the activated compound includes an association process. Inhibition was demonstrated in light of the horizontal adsorption of the complex formed between dapoxetine and the alloy surface on AA6063 according to the Langmuir absorption isotherm. The inhibition performance of Dapxitine on AA6063 was investigated using materials Studio v7.0. The quantum chemical descriptors are found to suitable to explain the performance of title molecule as corrosion inhibitors. Additionally, adsorption of dapoxetine on an aluminum alloy (Al) (111) has been investigated. The results of the current theoretical approach comply with that obtained experimentally.

Keywords: Corrosion inhibitor; Dapoxetine; Adsorption; Frontier molecular orbital; Fukui function

1. Introduction

The study of corrosion of aluminum (Al) and its alloys in an acidic medium is an important topic of interest for scientists. They are used in many industrial applications such as construction, electronics, packaging, and the aerospace industry. Although Al is corrosion resistant but does not have enough capacity to be used in aerospace. Therefore, it should be mixed with other metals such as silicon (Si). Al–Si alloys have a protective oxide layer on their surface. However, when exposed to high concentrations of acids or bases, corrosion occurs. There are several methods to overcome this problem, the most important of which is the use of corrosion inhibitors [1–8]. Most corrosion inhibitors applied to inhibit the corrosion of Al and its alloys are known to be organic molecules containing nitrogen, sulfur, or oxygen

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atoms [9–13]. The inhibitory effect of these compounds is due to the adsorption on the surface of the metal, which provides a barrier layer between the metal and the aggressive solution. The extent of inhibition depends on the nature of the metal used, the chemical composition of the additive, the hydrogen ion concentration, the temperature, the ability to form complex, and other factors [14–18]. These molecules give high inhibition efficiency, but unfortunately have a detrimental effect on humans and the environment.

Scientists have tended to use some drugs as corrosion inhibitors due to their economic properties, as they are cheap, easy to produce and purify, safe for human health and give high efficiency in inhibiting metals or alloys due to the presence of more active centers in their chemical composition, which facilitates the adsorption process [19–25].

In the present manuscript, we are investigating the inhibiting effect of dapoxetine drug toward the corrosion of aluminum alloy (AA6063) in acidic and alkaline solutions using weight loss, potentiodynamic polarization, and theoretical calculation The correlation between the inhibition efficiencies were obtained from experimental techniques and the theoretical calculations using materials Studio v7.0 were interpreted.

2. Experimental techniques

2.1. Chemical and electrochemical measurements

The measurements were performed with samples of aluminum alloy (AA6063). The chemical composition of this alloy is in weight % Si = 0.42, Fe = 0.17, Cu = 0.001, Mn = 0.009, Mg = 0.42, Ni = 0.001, Ti = 0.01, Zn = 0.001, Na = 0.0012, and the balance is Al.

For the chemical measurement such as weight loss (WL) carried out using coupons of dimension 1.0 × 3.0 × 0.2 cm^3. For electrochemical measurements such as potentiodynamic polarization (PDP), a cylindrical rod immersed in Araldite is used with an uncovered area to the medium 0.45 cm^2. Before any experiments, the coupons or the rod electrodes were furbished with some of degree emery papers ranging from 200 to 1,000 to get mirror surface, degreased with acetone, and finally washed with distilled water. All solutions used in this study were of analytical grade. Double distilled water was used for all preparation. The preferred temperature was altered within ±0.1°C.

WL measurements were accomplished as previously described [26]. Each experiment was repeated three times, to verify the reliability of the result (which was above 99% reproducible).

The percentage inhibition efficiency (IE%) and surface coverage (θ) which symbolize the part of the metal surface covered by the additive compounds were computed using the next equations:

$$\mathrm{IE}\% = \left[1 - \frac{W_{\mathrm{inh}}}{W_{\mathrm{uninh}}}\right] \times 100 \tag{1}$$

$$\theta = \left[1 - \frac{W_{\mathrm{inh}}}{W_{\mathrm{uninh}}}\right] \tag{2}$$

where W_{inh} and W_{uninh} are the weight losses of the 6063 Al alloy coupon in uninhibited and inhibited acid or alkaline solutions, respectively.

The rate of corrosion (R_{corr}) is calculated as g cm^{-2} h^{-1} from the following equation:

$$R_{\mathrm{corr}} = \frac{\mathrm{WL}}{At} \tag{3}$$

where WL in g, A is the surface area of coupon in cm^2 and t is the immersion time in h.

PDP experiments were achieved in a conventional cell with containing three electrodes, a working electrode (WE), the platinum counter electrode (PT), and a saturated calomel electrode (SCE) as a reference electrode. PDP measurements were performed out using a PS remote potentiostat with PS6 software at a scan rate of 1.0 mVs^{-1}. Some corrosion kinetics parameters, were calculated such as anodic (ba) and cathodic (bc) Tafel slopes, corrosion potential (E_{corr}), corrosion current density (I_{corr}). The values of I_{corr} are determined by extrapolation of anodic and cathodic Tafel lines with the E_{corr} for free acid and alkaline solutions and for each concentration of dapoxetine drug.

2.2. Computational methodology

Geometry optimization on dapoxetine was applied using the DMol3 calculation model included in Materials Studio v7.0.[27] "Setup; geometry optimization, Fine; quality, Functional; LDA, all electrons in core treatment are considered, DNP Basis set". Both E_{HOMO} and E_{LUMO}; were computed as registered in Table 1 and given in Fig. 1.

The following parameters are calculated using equations represented in previous studies: I, A, χ, and η can be studied in terms of the E_{HOMO} and the E_{LUMO} [28]. As well as, Fukui indices (f^+ and f^-) which represent local nucleophilic and electrophilic attacks from DMol3 calculation [29].

Dapoxetine has been simulated on aluminum alloy Al(111) surface using the Monte Carlo method to calculate binding energy. First, dapoxetine was optimized using Forcite Model. Second, the molecular dynamic simulation for Al(111) surface was carried out with periodic boundary (lattice parameter A: 14.3 × 14.3 × 21.6 Å). The adsorption locator module has been applied to the dapoxetine Al(111) system to calculate binding energy between dapoxetine and Al(111) surface as follows:

$$E_{\mathrm{BE}}\left(\mathrm{kcal/mol}\right) = \left(E_M + E_{\mathrm{inh}}\right) - E_{\mathrm{inh}+M} \tag{4}$$

Considering, the binding energy is E_{BE}, the total energy of the metal crystal is E_M and is the total energy of Dapoxetine is E_{inh} and the energy of the two merged dapoxetine with Al is $E_{\mathrm{inh}+M}$.

The following descriptors were investigated Frontier molecule orbital density (FMO) E_{HOMO} and E_{LUMO} are the parameters used to calculate the energy gap ΔE, global hardness h, and global softness S, ionization potential I, electron affinity A, absolute electronegativity X, global electrophilicity index w, the back donation $\Delta E_{\mathrm{Back\text{-}donation}}$, the binding energy E_{BE}, and molecular electrostatic potential MEP.

3. Results and discussion

3.1. WL measurements

3.1.1. Effect of dapoxetine concentration

The effect of different concentrations of dapoxetine drug on the corrosion of AA6063 in 1.0 M HCl and 1.0 M NaOH solutions was demonstrated after the immersion period ranging from 1 to 4 h using WL measurements. The data acquired is registered in Table 2. Examination of this table denotes that the addition of dapoxetine reduces WL and increases IE%. This proves that the dapoxetine reduces the corrosion of 6063 Al in 1.0 M HCl and 1.0 M NaOH solutions. It was observed that IE% of dapoxetine in acidic medium is more than that in alkaline solution. The inhibitory effect of the studied dapoxetine can be explained by its adsorption on the surface of AA6063. The adsorption strength is related to its molecular structure. The existence of more than one active center in the drug structure led to the expectation that the adsorption of this drug was horizontal.

Figs. 2a and b represent the relationship between IE% and drug concentration for corrosion of AA6063 in 1.0 M HCl and 1.0 M NaOH solutions, respectively, at different immersion times ranging from 1 to 4 h. By examining this Fig. 2, it is evident that greater values of the IE% were obtained with increasing drug concentration. We also find that the IE% values increase from the lowest concentration to the highest concentration of drugs in a narrow concentration range. This observation indicated that the presence of low concentrations of dapoxetine inhibited the corrosion of AA6063 in acidic and alkaline solutions. The high IE% at low concentrations of the dapoxetine is good evidence of horizontal adsorption of the dapoxetine on the AA6063 surface. The influence of increasing the concentration of dapoxetine on the IE% value can be illustrated as follows. At low concentrations of the drug, there are a lot of free sites on the AA6063 surface of the drug compound to be adsorbed. Hence, any increase in the concentration leads to an increase in IE% value. On the other hand, at higher drug concentrations there are not enough free sites on the surface of AA6063 for the drug to be adsorbed. Hence, the effect of increased concentration on the inhibition efficiency is diminished.

It is important that the effect of inhibitor concentration on the inhibition efficacy does not differ completely in the alkaline medium. Fig. 2b shows an almost linear relationship in each concentration range. This result indicates that the adsorbed sites on the alloy surface are always more than enough regardless of the increase in the inhibitor concentration. The observed discrepancy between the results of the acidic and alkaline medium can be indicated by the nature of drug adsorption on the alloy surface. While dapoxetine is adsorbed horizontally in the acidic medium covering a large surface area of each molecule, it may be oriented so that it covers a smaller area in an alkaline medium.

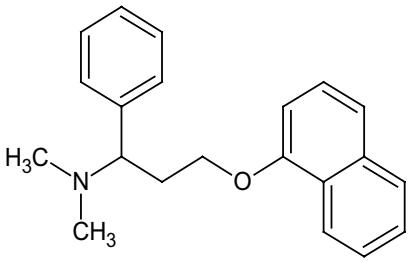
Fig. 3, the effect of immersion time on IE% for corrosion of AA6063 in 1.0 M HCl and 1.0 M NaOH solutions containing some concentrations of dapoxetine, respectively.

Obviously, it can be seen from these figures that, the behavior in a 1.0 M HCl solution is different from that of 1.0 M NaOH especially at low concentrations of dapoxetine.

Inspection on Fig. 1a shows that, at high concentrations equal to or greater than 0.00005 M of dapoxetine, there is almost no time effect on IE%. This behavior can be explained in term of that the dapoxetine drug are immediately adsorbed on the surface of the alloy to reach its maximum available adsorption capacity in a very small period of time. On the other hand, IE% increases directly with time at concentrations below 0.00005 M. These results strongly

Table 1
Quantum chemical descriptors of dapoxetine

E_{HOMO} (eV)		–0.1827
E_{LUMO} (eV)		–0.0951
ΔE_{Gap} (eV)	$E_{LUMO} - E_{HOMO}$	0.0876
I (eV)	E_{HOMO}	0.1827
A (eV)	E_{LUMO}	0.0951
X (eV)	$(I + A)/2$	0.1389
h (eV)	$(I - A)/2$	0.1752
S (eV)$^{-1}$	$1/h$	5.7070
w	$m^2/2h$ where $m = -X$	0.0017
$\Delta E_{Back\text{-}donation}$	$h/4$	0.0438
ΔN	$\frac{X_{Al} + X_{inh}}{2(\eta_{Al} + \eta_{inh})}$	4.1979
E_{BE} k Cal mol^{-1}	$(E_M + E_{inh}) - E_{inh+M}$	–93.275



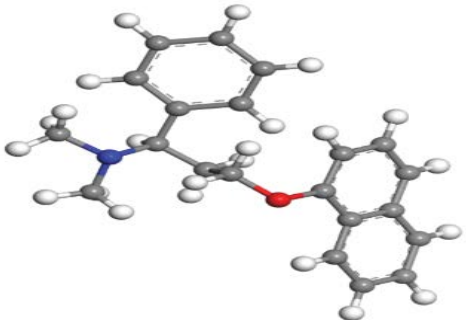


Fig. 1. Dapoxetine: colors; red, blue, gray, and white for O, N, C, and H atoms, respectively. The chemical formula: $C_{21}H_{23}NO$. Molar mass: 305.413 g mol^{-1}.

Table 2
WL and IE% for corrosion of AA6063 in 1.0 M HCl and 1.0 M NaOH solutions free and containing different molar concentrations of dapoxetine

Immersion time, h		Free 1.0 M HCl	Molar concentration of dapoxetine				
			5×10^{-6}	1×10^{-5}	5×10^{-5}	1×10^{-4}	5×10^{-4}
1	WL	0.0137	0.0127	0.0076	0.0012	0.0008	0.0002
	IE%		7.29	44.53	91.24	94.16	98.54
2	WL	0.1068	0.0933	0.0461	0.0046	0.0016	0.0012
	IE%		12.64	56.84	95.69	98.5	98.88
3	WL	0.1979	0.1319	0.0548	0.0076	0.0023	0.0014
	IE%		33.35	72.31	96.16	98.84	99.29
4	WL	0.2679	0.1329	0.0652	0.0093	0.003	0.0016
	IE%		50.39	75.66	96.53	98.88	99.40
		Free 1.0 M NaOH					
1	WL	0.0156	0.0145	0.0143	0.0133	0.0103	0.0008
	IE%		7.05	8.33	14.74	33.97	94.87
2	WL	0.0268	0.0243	0.0241	0.0226	0.0161	0.0011
	IE%		9.33	10.07	15.67	39.93	95.89
3	WL	0.0366	0.0325	0.0322	0.0307	0.0204	0.0014
	IE%		11.20	12.02	16.12	44.26	96.17
4	WL	0.0456	0.0392	0.0387	0.0337	0.0226	0.0016
	IE%		14.04	15.13	26	50.44	96.49

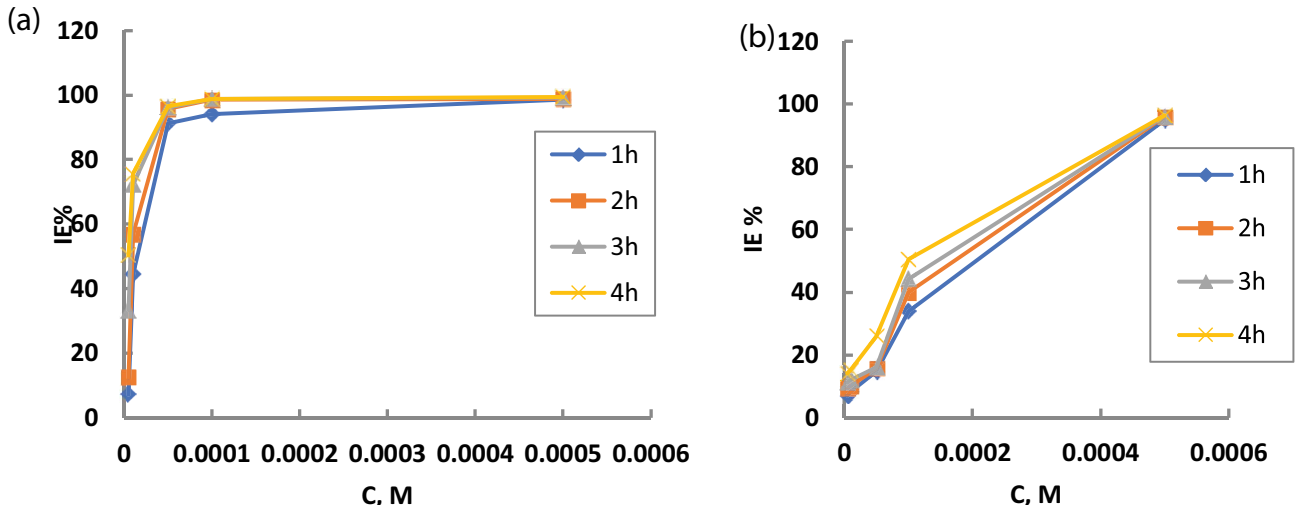


Fig. 2. Effect of various concentrations of dapoxetine on the IE% for AA6063 corrosion in (a) 1.0 M HCl and (b) 1.0 M NaOH solutions.

indicate that this concentration (0.00005 M) represents the one that can provide the maximum possible adsorption capacity.

The curves obtained in the alkaline solution (Fig. 1b) show a nearly independent behavior of IE on the exposure time. This result indicates that the dapoxetine molecules adsorb instantly, reaching their maximum possible adsorption capacity regardless of exposure time. It is important to mention here that the value of maximum possible adsorption capacity depends only on the concentration of the inhibitor.

3.1.2. Impact of rising temperature

The effect of increasing temperature on the corrosion rate of AA6063 in the free 1.0 M HCl solution and free 1.0 M NaOH and containing 0.0005 M of dapoxetine in a temperature range of 303–343 K was studied using weight loss measurements and after immersion time 4 h. Curves similar to Fig. 1 were obtained but not shown. At higher temperatures, the corrosion rate increases and the IE% decreases. This is due to the desorption of the inhibitor molecules is assisted by increasing temperature. This behavior

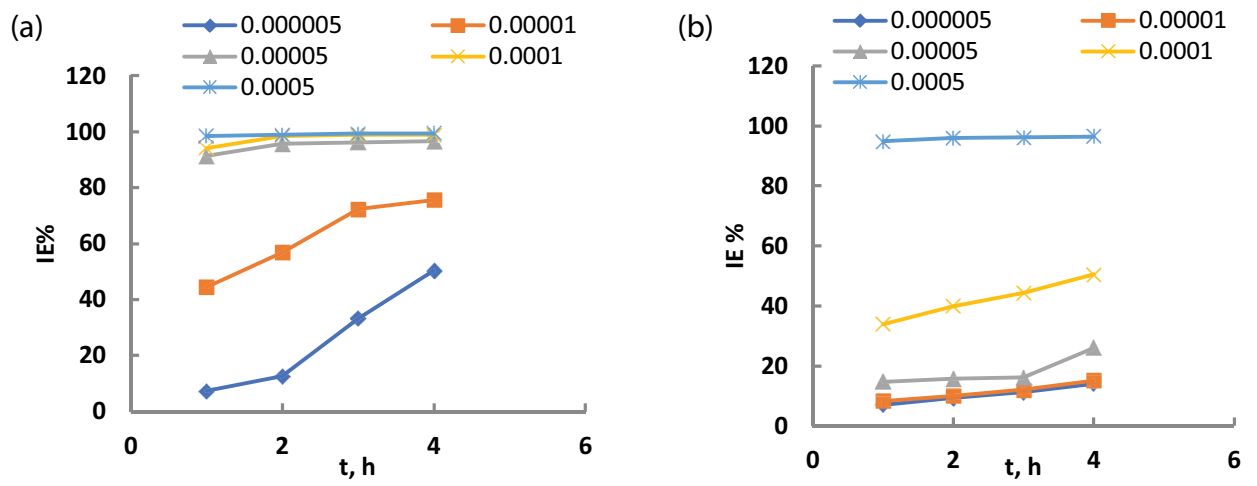


Fig. 3. Impact of immersion time on the IE% of dapoxetine for corrosion of AA6063 in (a) 1.0 M HCl and (b) 1.0 M NaOH solutions.

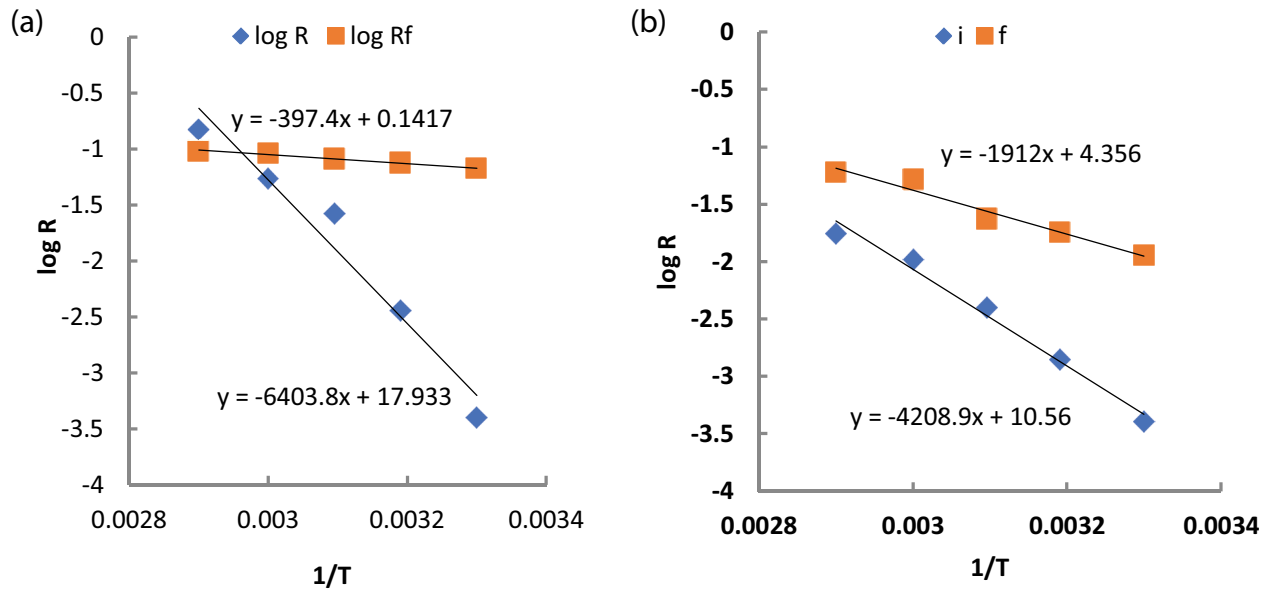


Fig. 4. Arrhenius plot for the corrosion of AA6063 in the free (a) 1.0 M HCl and (b) 1.0 M NaOH solutions and in the presence of 0.0005 M of dapoxetine.

indicates that the adsorption of dapoxetine on the AA6063 surface occurred through physical adsorption mode.

The activation thermodynamic parameters, for example, the apparent activation energy E_a, the change in enthalpy of activation ΔH^* and the change in the entropy of activation ΔS^* of the corrosion of 6063 Al in the free 1.0 M HCl solution and the free 1.0 M NaOH and in the presence of 0.0005 M of dapoxetine were computed from Arrhenius and transition sate equations [30,31] and inserted in Table 3.

$$R_{corr} = A_{exp}\left(\frac{-E_a}{RT}\right) \tag{5}$$

$$\frac{R_{corr}}{T} = \frac{RT}{Nh} / e^{(\Delta S^*/R)} e^{(-\Delta H^*/RT)} \tag{6}$$

where R_{corr} is the rate of AA6063 corrosion, A is the frequency factor, N is the Avogadro's number, and R is the gas constant.

Figs. 4a and b show an Arrhenius plot ($\log R_{corr}$ vs. $1/T$) for AA6063 in the (A) 1.0 M HCl solution and (B) 1.0 M NaOH solution for the free devoid of and containing 0.0005 M of dapoxetine. The values of E_a obtained from the slope of the straight lines are registered in Table 2. It appears from Table 3, that the values of E_a increase in the presence of dapoxetine than those in free acid or alkaline solutions. This result is due to a formation of a barrier of the adsorbed dapoxetine that prevents the mass and charge transfer between the alloy and the corrosive medium.

Fig. 5 symbolizes the relation between the $\log(R_{corr}/T)$ and $1/T$ for AA6063 in the (A) 1.0 M HCl solution and (B) 1.0 M NaOH solutions devoid of and containing 0.0005 M

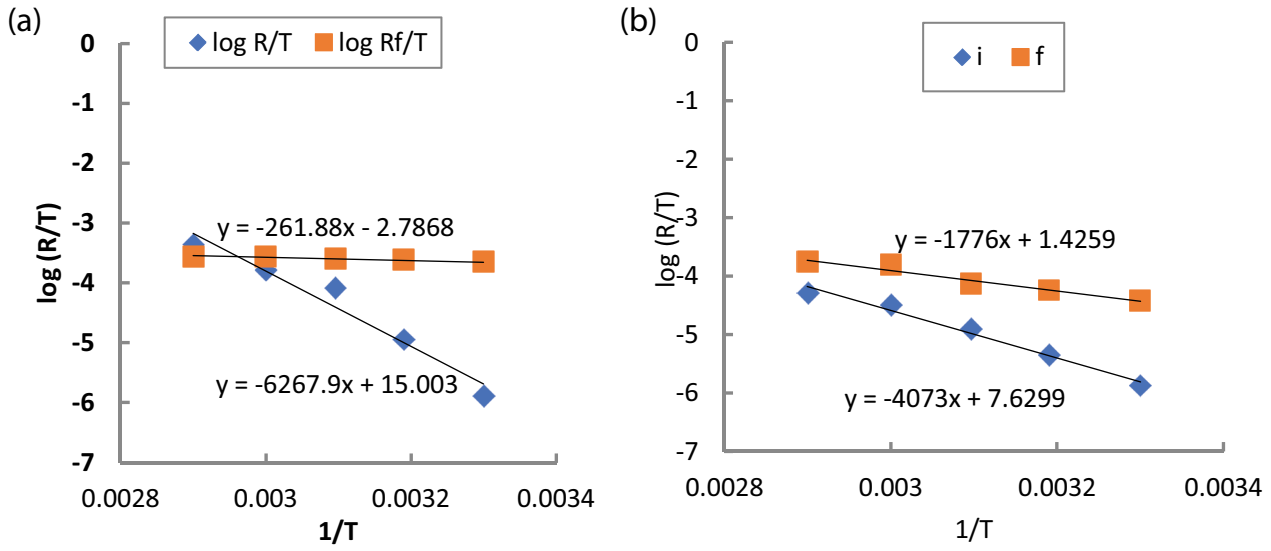


Fig. 5. Transition state plot for the corrosion of AA6063 in the free (a) 1.0 M HCl and (b) 1.0 M NaOH solutions and in the presence of 0.0005 M of dapoxetine.

of dapoxetine. A straight lines were obtained in both cases with a slop of ($-\Delta H^*/2.303\ R$) and an intercept of [$\log(R/Nh) + \Delta S^*/2.303R$]. The obtained values of ΔH^* and ΔS^* are recorded in Table 3.

The positive values of ΔH^* in the case of 1.0 M HCl or 1.0 M NaOH solution reflect that the activation process during the AA6063 corrosion is of an endothermic nature. The values of ΔS^* in acidic or alkaline-free solutions and in the presence of the dapoxetine are negative. This indicates that the activation complex is the rate-determining step represents a correlation rather than disintegration, indicating that a decrease in disturbance takes place when moving from reactants to the activated complex [32].

3.2. PDP measurements

PDP curves of AA6063 in 1.0 M HCl and 1.0 M NaOH-free solutions including some dapoxetine concentrations at a scanning rate of 1.0 mV/s were represented in Figs. 6a and b. It is obvious from these figures that, as the concentration of the drug increases, both the cathodic and anodic polarization curves are converted to lower current densities, indicating the inhibitory action of dapoxetine toward the corrosion of AA6063 in the acidic and alkaline solutions. Some corrosion parameters such as ba, bc, E_{corr}, I_{corr}, and IE% were computed and inserted in Table 4. The values of IE% were computed from the following equation:

$$\mathrm{IE}\% = \left(1 - \frac{I_{corr}}{I^{\circ}_{corr}}\right) \times 100 \tag{7}$$

where I°_{corr} and I_{corr} are the corrosion current density in free and inhibited solutions, respectively.

From the data in Table 4, it is apparent that in the presence of dapoxetine the values of E_{corr}, ba, and bc change slightly. This result denotes that the dapoxetine does not affect the mechanism of AA6063 corrosion, Thus, dapoxetine acts as mixed-type inhibitor. Such inhibitor type acts by adsorption on both anodic and cathodic sites on the AA6063 surface. The values of I_{corr} decrease and hence the values of IE% increase proving the inhibiting action of the dapoxetine. Further inspection of Table 4 reveals that at the same concentration of dapoxetine the values of IE% are higher in the acidic solution than those in alkaline solutions. This result is in consistence with that obtained from the weight loss measurement.

3.3. Adsorption isotherm and inhibition mechanism

Dapoxetine drug inhibits the corrosion of AA6063 in 1.0 M HCl or 1.0 M NaOH solutions by adsorption of its molecules on the alloy surface. The adsorption process assumes as an alternative process in which the dapoxetine drug (Dap), in the aqueous phase replaces the "z" adsorbed on the surface of AA6063 [33] vis:

Table 3
Thermodynamic activation parameters for corrosion of AA6063 in free and inhibited in 1.0 M HCl and 1.0 M NaOH solutions

Solution	E_a (kJ mol^{-1})	ΔH^* (kJ mol^{-1})	ΔS^* (J mol^{-1} K^{-1})
Free 1.0 M HCl	7.60	5.01	–30.18
1.0 M HCl + 0.0005 M of dapoxetine	122.61	120.01	–10.78
Free 1.0 M NaOH	36.60	34.00	–20.48
1.0 M NaOH + 0.0005 M of dapoxetine	79.97	77.98	–6.20

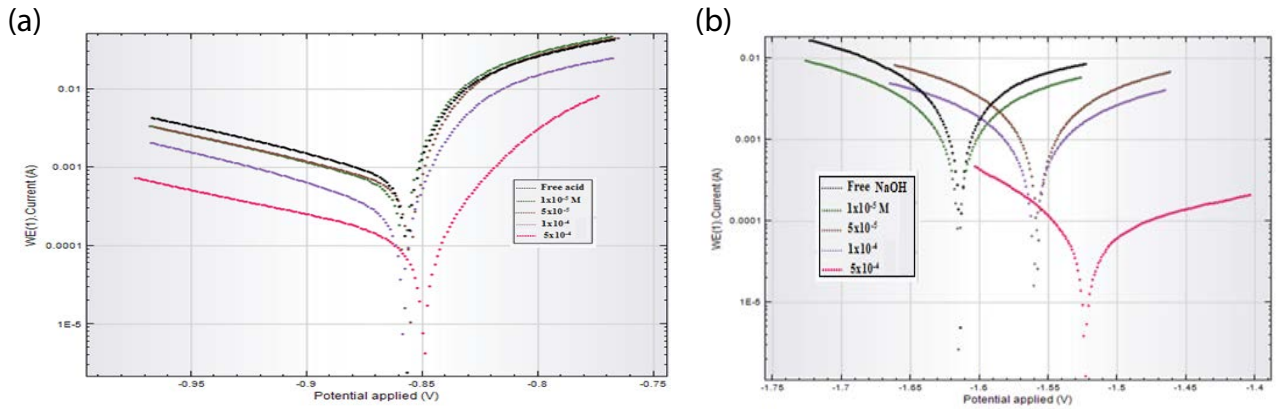


Fig. 6. PDP curves of AA6063 in free (a) 1.0 M HCl solution and (b) 1.0 M NaOH solution and containing different concentrations of dapoxetine.

Table 4
Corrosion parameters of AA6063 corrosion in free 1.0 M HCl and 1.0 M NaOH solutions and in the presence of different concentrations of dapoxetine

Drug concentration, M	$-E_{corr}$	β_a	$-\beta_c$	I_{corr}	IE%
	mV (SCE)	mV decade^{-1}	mV decade^{-1}	mA cm^{-2}	
1.0 M HCl	925	134	120	3.27	–
1.0 M HCl + 1 × 10^{-5}	931	142	112	1.91	41.59
1.0 M HCl + 5 × 10^{-5}	892	147	62	1.05	67.89
1.0 M HCl + 1 × 10^{-4}	904	126	76	0.62	81.04
1.0 M HCl + 5 × 10^{-4}	860	162	46	0.14	95.72
1.0 M NaOH	1,612	131	171	2.85	–
1.0 M NaOH + 1 × 10^{-5}	1,614	148	173	1.80	36.84
1.0 M NaOH + 5 × 10^{-5}	1,551	164	147	1.36	58.41
1.0 M NaOH + 1 × 10^{-4}	1,554	157	139	0.78	76.15
1.0 M NaOH + 1 × 10^{-4}	1,525	87	235	0.21	92.63

$$Dap_{(aq)} + zH_2O_{(sur)} \rightarrow Dap_{(sur)} + zH_2O_{(aq)} \quad (8)$$

where z is recognized as the size ratio and simply equals the number of adsorbed water molecules replaced by a one dapoxetine molecule. The strength of the adsorption depends on several factors, for example, the chemical composition of the compound used as an inhibitor. The type and the nature of the metal or alloy surface used, the nature and the concentration of the electrolyte are used as a corrosive solution, the presence of active centers that accelerate adsorption, the inhibitor ability to form complex, and other factors. In order to obtain the appropriate isotherm for the adsorption of the dapoxetine on the AA6063, the values of the surface coverage, θ, for some concentrations of the dapoxetine drug will be included in different adsorption isotherm. The best correlation among the experimental results obtained from the adsorption of dapoxetine on the AA6063 surface fit the Langmuir adsorption isotherm due to the following equation:

$$\frac{C}{\theta} = C + \frac{1}{K_{ads}} \quad (9)$$

where C is the concentration of dapoxetine used as an inhibitor, K_{ads} is the equilibrium constant of adsorption.

Fig. 7a and b illustrate plots between C/θ and C. A straight line is obtained for each with a slope equals to unity indicating that the dapoxetine adsorption on the AA6063 in 1.0 M HCl or 1.0 M NaOH solutions follows Langmuir isotherm. This assumes monolayer adsorption with no interaction between the molecules adsorbed on the surface of AA6063.

The standard free energy of adsorption (ΔG°_{ads}) was determined using the next equation:

$$55.5\ \text{K} = \exp\left(\frac{-\Delta G^\circ_{ads}}{RT}\right) \quad (10)$$

The values of ΔG°_{ads} are equal to –42.15 and –33.32 kJ/mol in 1.0 M HCl and 1.0 M NaOH solutions, respectively, indicate that the strong adsorption of dapoxetine on the surface of 6063 AA in acid and alkali solutions, the negative sign of ΔG°_{ads} indicates that this adsorption is spontaneous [34].

The inhibiting effect of dapoxetine toward the dissolution of AA6063 in 1.0 M HCl and 1.0 M NaOH solutions

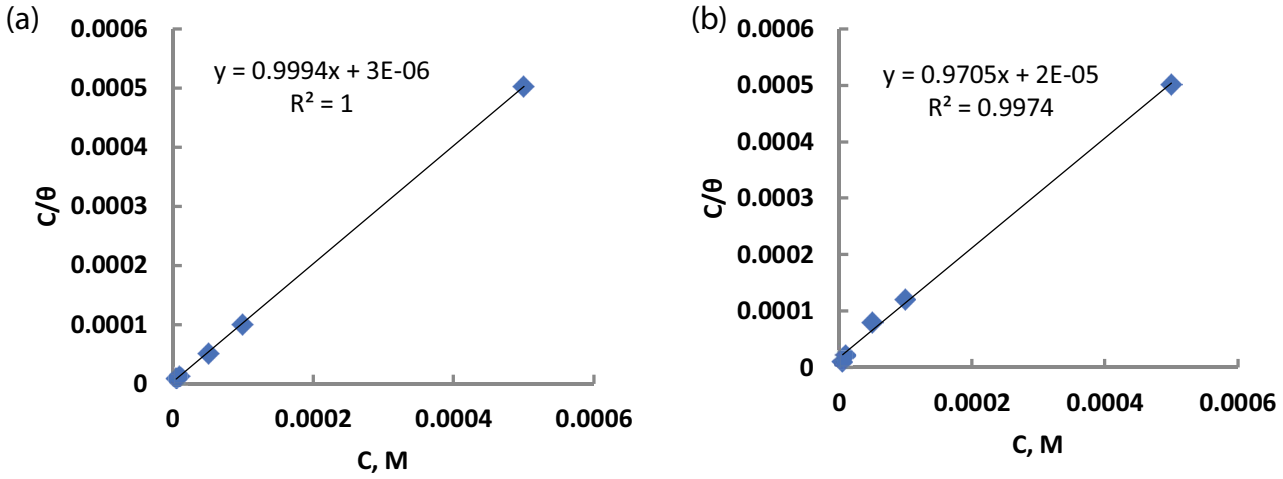


Fig. 7. Langmuir adsorption isotherm for AA6063 in (a) 1.0 M HCl and (b) 1.0 M NaOH solutions containing different concentrations of dapoxetine.

as measured by chemical and electrochemical measurements depend on the type of the alloy used, the corrosion medium concentrations, the chemical structure of the drug used, and its capability to form complex. The formation of the complex between dapoxetine and the surface of AA6063 occurs by transferring electrons from the oxygen and nitrogen atoms in the dapoxetine molecule to the alloy surface to form the coordinate bonds as shown in Fig. 8. This complex is adsorbed horizontally on the alloy surface.

The IE% of dapoxetine is higher in 1.0 M HCl solution compared to 1.0 M NaOH solution due to the corrosion product in acidic solution. AA6063 is dissolved in HCl solution forming an insoluble product of $AlCl_3$ on the surface of AA6063 which has reduced the surface area exposed to the aggressive acid solution. Therefore, the corrosion rate decreases, and thus IE% increases.

3.4. Theoretical studies

FMO density distributions of dapoxetine are represented in Fig. 9. The electron density of both HOMO and LUMO is shown to be distributed over the a naphthol moiety indicating that a naphthol moiety has a tendency for the molecule to donate electrons to lower empty molecular orbital energy. In addition, this moiety tends to form the feedback bond depending on E_{LUMO} which indicates the ease of accepting electrons from the *d* orbital of the metal.

Electron transfer ΔN occurs once an electron exchanges from an atom or a molecule to another chemical structure which commonly involves a transition metal complex. It has been reported that the values of ΔN can explain the inhibition effect resulting from electrons donation [28].

Molecular electrostatic potential MEP as shown in Fig. 10, the blue color indicates to partial negative charge distributed on α naphthol moiety and phenyl ring. However, the partial positive charge is distributed on the terminal hydrogen atoms.

The electronic flow happens from lower electronegativity dapoxetine to higher value Al surfaces. So, the ΔN from the dapoxetine molecule to the atoms of metal was estimated [22,35]. In this study, the electronegativity of bulk aluminum were used x_{AA} = 1.61 eV based on Pauling scale and a global hardness of η_{AA} = 0, by assuming that for a metallic bulk $I = A$, The value of ΔN indicates that the

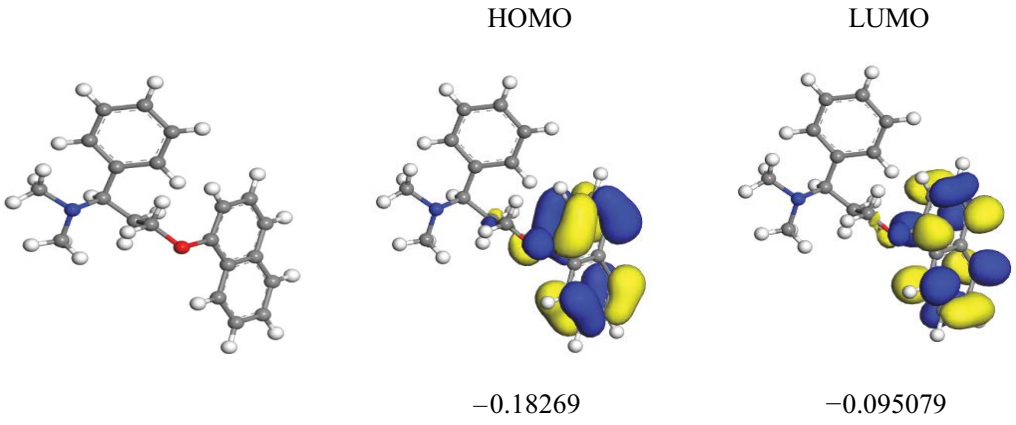


Fig. 8. Proposed complex formed between dapoxetine and metal ion.

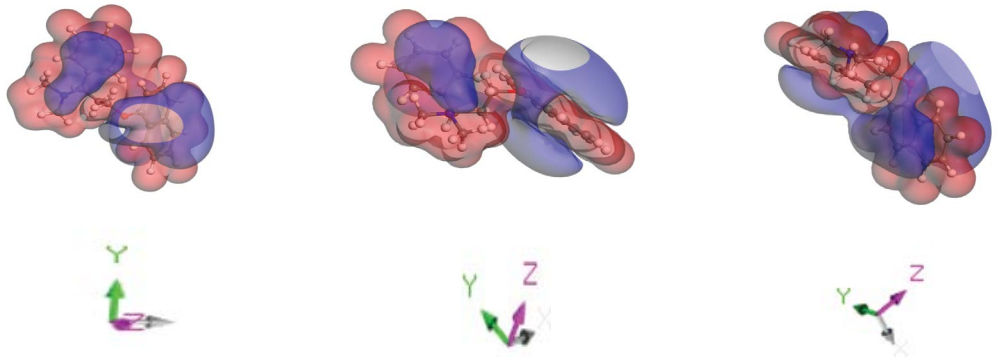


Fig. 9. MEP of dapoxetine around different *a*, *y* and *z* axis.

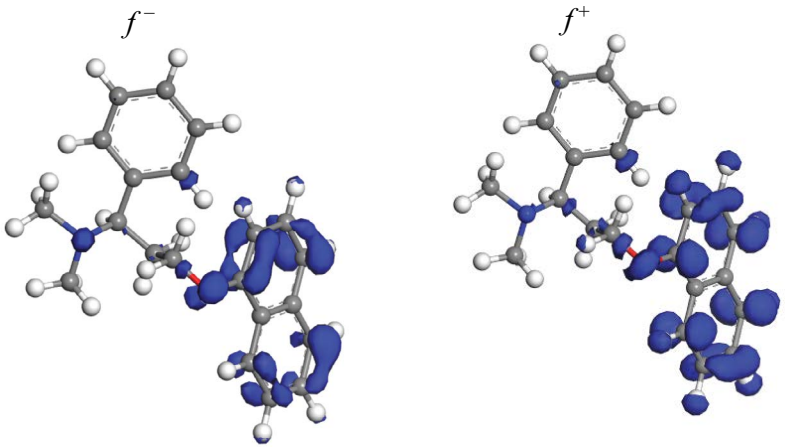


Fig. 10. Graphical representation of Fukui functions of dapoxetine.

inhibition efficiency was due to electron donation which agrees with Lukovits's study [36].

Condensed Fukui functions shown in Fig. 11 allow us to distinguish each part of dapoxetine molecule. It is evident that the α naphthol moiety is responsible for both the nucleophilic f^+ and the electrophilic f^- attack, in addition to the electrophilic attack are found in N atom.

The most stable dapoxetine conformation adsorbed on Al(111) as illustrated in Fig. 12 was obtained by adsorption locator model. The given adsorption energy of the investigated molecule is –93.275 k Cal/mol. It is observed that the adsorbed moieties are a naphthol and amino group which they are responsible for electron transfer from dapoxetine to Al(111) surface.

4. Conclusions

Dapoxetine acts as an effective inhibitor for the corrosion of AA6063 in 1.0 M HCl and 1.0 M NaOH solutions. The inhibition efficiency increases with increasing the concentration of dapoxetine and decreasing the temperature and it is higher in the acid medium than in the alkaline medium. Dapoxetine acts as a mixed inhibitor in acid and alkaline medium. The formation of the activated complex is endothermic and includes an association process. The inhibitive action of dapoxetine has been explained by its adsorption through the active centers present in its structure on the surface of AA6063. The adsorption obeys Langmuir adsorption. There is good agreement between the results obtained from theoretical calculations and experimental techniques.

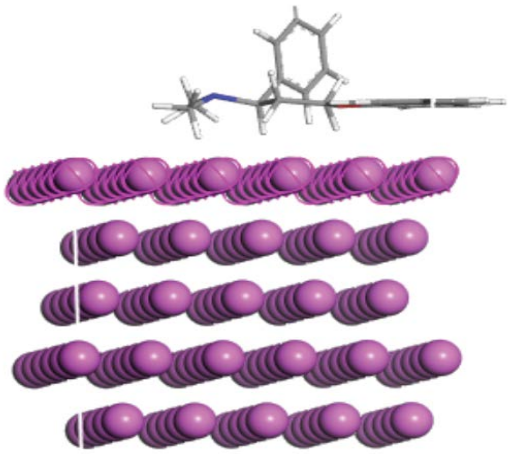
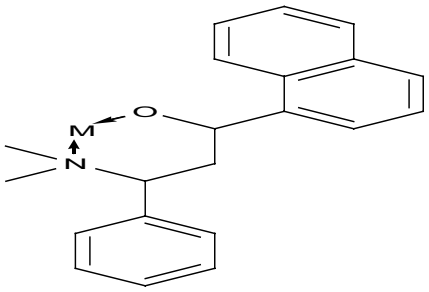


Fig. 11. Adsorption configuration at equilibrium of dapoxetine on Al(111) obtained by molecular dynamic simulation.



Scheme 1. Formation of the complex between the dapoxetine and AA6063 surface.

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