Desalination and Water Treatment
www.deswater.com

20 (2010) 35–44
August

doi: 10.5004/dwt.2010.1576

Effect of some new diazole derivatives on the corrosion behaviour of steel in 1 M HCl

Y. Abboud[a,b]*, B. Ihssane[a], B. Hammouti[c], A. Abourriche[a,b], S. Maoufoud[a], T. Saffaj[d], M. Berrada[a], M. Charrouf[a], A. Bennamara[a], H. Hannache[b]

[a]*Laboratoire de Biomolécules et Synthèse Organique, Faculté des Sciences Ben M'sik, Casablanca, Morocco*
Tel. +212 22 70 46 71/72/73; Fax +212 22 70 46 75; email: youabboud@yahoo.fr
[b]*Centre d'Analyse et de Recherche, Faculté des Sciences Ben M'sik, Casablanca, Morocco*
[c]*Laboratoire de Chimie Appliquée et Environnement, Faculté des Sciences, Oujda, Morocco*
[d]*Centre Universitaire Régional d'Interface,Université Sidi Mohamed Ben Abdallah Route d'Imouzzar, BP. 2626, Fès 30000, Morocco*

Received 13 October 2009; Accepted in revised form 22 January 2010

ABSTRACT

The inhibiting properties of four diazole derivatives namely 2,2'-ethylene-bis(benzimidazole) (EBBI), 2,2'-buthylene-bis(benzimidazole) (BBBI), 2,2'-hexamethylene-bis(benzimidazole) (HBBI) and 2,2'-octamethylene-bis(benzimidazole) (OBBI), against the corrosion of mild steel in solutions of hydrochloric acid has been studied by various corrosion monitoring techniques and reported here for the first time. Preliminary screening of the inhibition efficiency was carried out using weight loss measurements. At the inhibitor concentration range of 10^{-5}–5×10^{-4} M) in 1 M HCl, the inhibitor efficiency increases with concentration of the organic substrate. Potentiodynamic polarisation studies showed that these compounds suppressed both cathodic and anodic processes of mild steel corrosion in 1 M HCl by adsorption on the metal surface according to Langmuir adsorption isotherm. The values of free energies of adsorption (ΔG^0_{ads}) suggest a mixed physisorptions and chemisorption of diazole molecules on the steel surface. The inhibition efficiency of these inhibitors increases in the order OBBI > HBBI > BBI > EBBI.

Keywords: Corrosion inhibition; Mild steel; Acidic media; Diazole derivative; Adsorption

1. Introduction

Metals are exposed to the action of acids in many different ways and for many reasons such as pickling, rescaling and cleaning process of steel surface. The use of corrosion inhibitors is usually the most appropriate way to control the corrosion of metallic materials by controlling metal dissolution and consumption. It has been shown that organic compounds contain heteroatom with high electronic density such as nitrogen, sulphur, and oxygen or those containing multiple bonds which are considered as adsorption centres, are effective acid corrosion inhibitors [1–9].

Benzotriazole (BTA) and its derivatives are proved to be highly efficient inhibitors for preventing different metals corrosion in several media [10–15]. However, environmental considerations are limiting the use of these products because they contribute to atmospheric pollution and cause health problems [16]. In addition; the toxic nature [17,18] of these inhibitors has stimulated researches for alternative corrosion inhibitors. At present, the interest in the new generation of organic inhibitors

---

* Corresponding author.

called "environmental friendly" is raising, which have been proposed to replace the toxic corrosion inhibitors. Therefore, new efficient and non-toxic inhibitors have been searched for aqueous acidic solution. Our research was aimed at making compounds with low toxicity and good inhibition efficiency against mild steel corrosion.

Benzimidazole (BI) and bis-benzimidazole (BBI) which are derivatives of imidazole, are key components in a great many bioactive compounds of both natural and synthetic origin. These ligands and their derivatives display a wide range of pharmacological activity. Various imidazole derivatives are secondary products in pharmaceutical industry and some of them have been especially synthesized for this investigation. Benzimidazole is also of interest as corrosion inhibitor for metals and alloys [19,20]. The molecular structure and anticorrosion mechanism have been studied by many authors. Otmačić and co-workers [21–23] demonstrated that some of the imidazole derivatives are efficient inhibitors for copper corrosion. Substitution by different functional groups can improve the efficiency of imidazole. Popova et al. [24,25] and Khaled [26] have investigated many diazole derivatives of benzimidazole for the corrosion inhibition of steel in hydrochloric acid by using electrochemical and weight loss methods. Their studies show that the benzimidazole derivatives have very good protective properties against corrosion of mild steel in 1 M HCl.

The object of this study is to investigate the inhibition properties of a group of some newly synthesised diazoles that acts as corrosion inhibitor for steel in acidic media and regarding less toxicity have high inhibition effect. 2,2′-aliphatic-bis(benzimidazole) is non toxic [27–30] and easy to produce with purities greater than 99%. All of the compounds investigated are reported here for the first time. The evolution of their inhibition efficiency has been studied using both weight loss and electrochemical measurements.

2. Experimental

2.1. Preparation of inhibitors

To a well stirred solution of 1,2-phenylenediamine in 4 M HCl was added the appropriate diacid. The solution was heated to reflux for 48 h and then concentrated to give a dark brown solid. The pure desired product was obtained by repeated recrystallizations from hot ethanol and characterised by elemental analysis, ^{1}HNMR, ^{13}CNMR and IR spectroscopies [31,32].

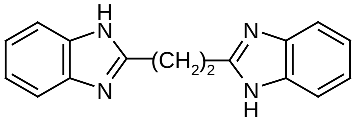
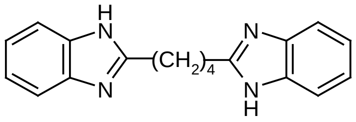
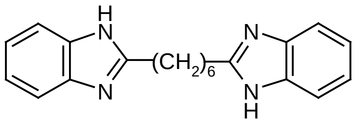
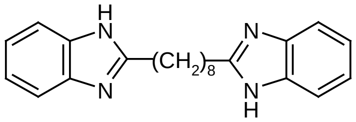
Table 1 shows the molecular structure of the obtained compounds, which have been labelled 2,2′-aliphatic-bis(benzimidazole).

2.2. Specimens

Corrosion tests were performed on a steel of the following percentage composition (wt. %): 0.21 C, 0.38 Si, 0.09 P, 0.05 Mn, 0.05 S, 0.01 Al and the remainder iron.

For the gravimetric and electrochemical measurements, pre-treatment of the surface of specimens was carried out by grinding with paper of 600–1200 grit, rinsing

Table 1
Name and molecular structures of the inhibitors

S. N°	Designation	Structural formula	Abbreviation
1	2,2′-ethylene-bis(benzimidazole)		EBBI
2	2,2′-buthylene-bis(benzimidazole)		BBBI
3	2,2′-hexamethylene-bis(benzimidazole)		HBBI
4	2,2′-octamethylene-bis(benzimidazole)		OBBI

with bidistilled water, ultrasonic degreasing in ethanol, and dried at room temperature before use.

2.3. Solution

The aggressive solution used was made of AR grade HCl. Appropriate concentration of acid was prepared using bidistilled water. The concentration of the inhibitor compounds ranged from 10^{-5} to 5×10^{-4} M in 1 M HCl.

2.4. Procedures used for corrosion measurements

Different experimental techniques can be used to evaluate corrosion rate and inhibition efficiency. The simplest and most accurate method is weight loss analysis. This method is commonly used as a calibration standard for other means of corrosion monitoring, such as linear polarisation and electrical resistance.

The inhibiting efficiency, E (%) is evaluated from the gravimetric and electrochemical data by the formulas:

$$E(\%) = \frac{W_0 - W}{W_0} \times 100 \tag{1}$$

$$E(\%) = \frac{I_{corr}^{0} - I_{corr}^{inh}}{I_{corr}^{0}} \times 100 \tag{2}$$

$$E(\%) = \frac{R_p^{inh} - R_p^{0}}{R_p^{inh}} \times 100 \tag{3}$$

where W_0 and W in mg.cm^{-2}h^{-1} are the average corrosion rates in absence and in presence of an inhibitor, I_{corr}^{0}, I_{corr}^{inh}, R_p^{0} and R_p^{inh} are the corresponding corrosion current densities and polarisation resistance.

2.4.1. Weight loss study

Gravimetric experiments were carried out in a double glass cell equipped with a thermostated cooling condenser. The solution volume was 100 ml. The used steel specimens had rectangular form (length = 2 cm, width = 1 cm, thickness = 0.06 cm). Maximum duration of tests was 24 h at 30±1°C in non-deaerated solution. At the end of the tests the specimens were carefully washed in ethanol under ultrasound, and then weighed using an analytic balance (precision: ±0.1 mg). Three to six measurements were performed in each case and the mean value of the weight loss has been reported. The reproducibility of the experiment was higher than 90%. Weight loss allowed us to calculate the mean corrosion rate as expressed in mg cm^{-2}h^{-1}.

2.4.2. Electrochemical studies

Experiments were carried out in a Pyrex cell which had three compartments. A graphite rod was used as the counter electrode and a satured calomel electrode (SCE) served as a reference electrode. All potentials reported here were referred to the SCE. Measurements were obtained using a combined system containing potentiostat model Amel 551, voltage scan generator model Amel 568 and recorder type Kipp–Zonen/BD 9. All tests were performed in non-deaerated solution under continuously stirred conditions at 30±1°C. Before recording the polarisation curves, the open-circuit potential was stable within 30 min. The cathodic branch was always determined first; the open-circuit potential was then re-established and the anodic branch determined. The anodic and cathodic polarisation curves were recorded by constant sweep rate 0.5 mV/s. The polarisation resistance measurements were evaluated from the same polarisation curves in the range ±25 mV vs. E_{corr}. All plots and calculated parameters are means of three independent experiments.

3. Results and discussion

3.1. Gravimetric measurements

The values of percentage inhibition efficiency and corrosion rate obtained from weight loss method at different concentration at 30°C are summarized in Table 2, and the variation of inhibition efficiency with concentration is shown in Fig. 1. The results show that all of these compounds inhibit the corrosion of mild steel in HCl solution at all concentrations used in this study. It has been found that the inhibition efficiency for all of these inhibitors increased with the increase in concentration. It can also been observed that the optimum concentration for all inhibitors required to achieve the efficiency was 5×10^{-4} M. At the optimum concentration for each inhibitor studied, the efficiency attains 74%, 89%, 93% and 97% respectively for compounds (EBBI, BBBI, HBBI and OBBI). A further increase of inhibitors concentration does not significantly change the protective effect.

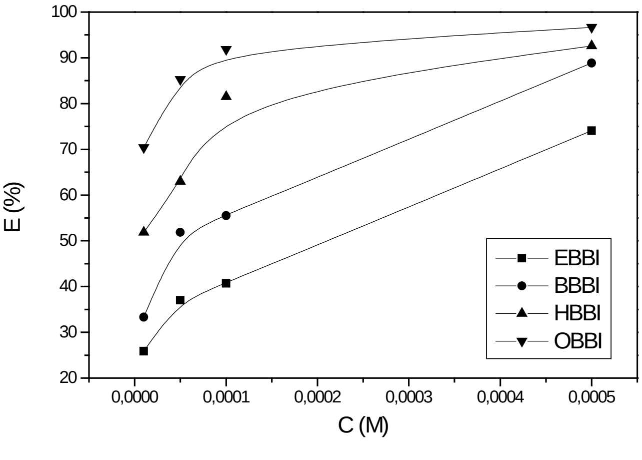


Fig. 1. Dependence of inhibitor efficiency E (%) on the concentration C (M) of the diazole derivatives (gravimetric data).

Table 2
Corrosion parameters for mild steel in 1 M HCl in the absence and presence of different concentrations of various inhibitors from weight loss measurements at 30°C for 24 h

Inhibitor concentration (10^{-5} M)		Corrosion rate (10^{-3}mg.cm^{-2}.h^{-1})	E (%)
Blank		27.0	—
EBBI	1	20.0	25.92
	5	17.0	37.03
	10	16.0	40.74
	50	7.0	74.07
BBBI	1	18.0	33.33
	5	13.0	51.85
	10	12.0	55.55
	50	3.0	88.88
HBBI	1	13.0	51.85
	5	10.0	62.96
	10	5.0	81.48
	50	2.0	92.62
OBBI	1	8.0	70.37
	5	4.0	85.25
	10	2.2	91.85
	50	0.9	96.66

Since most of organic inhibitors act by adsorption on the metal surface, the adsorption of these compounds is assumed to take place mainly through the nitrogen atoms of imidazole group (active centres). The inhibitive properties of such compounds depend on the electron densities around the active adsorption centre; the higher the electron density at the centre, the more effect is inhibitor.

On the ground of the protective effect of the investigated diazole derivatives found, it is clear that the inhibition efficiency increases with increasing the chain length "junction" between the two benzimidazole units in the order: EBBI < BBBI < HBBI < OBBI for all inhibitor concentrations (Fig. 2). The alkyl groups present between the two benzimidazole molecules have electron repulsing properties, which increase with the size of the methylene groups. These properties increase the electron density on the active adsorption centres of the molecules, which in turn increases the inhibition efficiency of the inhibitor. Thus, the increasing of the hydrocarbon chain length leads to increasing the absorbability of the inhibitor molecules on the metal surface and thereby increasing the effectiveness of the diazole derivatives as corrosion inhibitors. In other words, this means that inhibitor (OBBI) is the most efficient one.

3.2. Electrochemical measurements

3.2.1. Potentiodynamic method

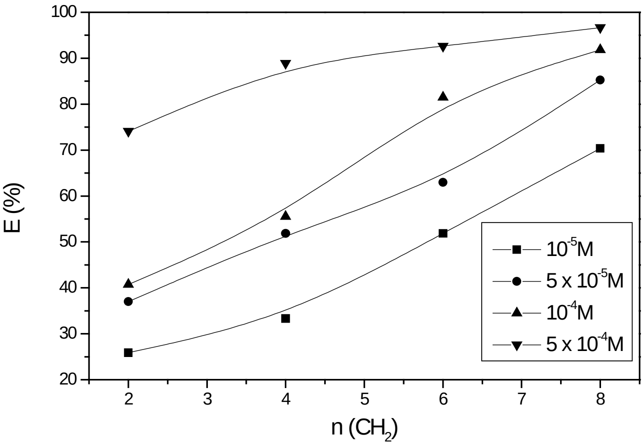


Fig. 2. Dependence of inhibitor efficiency E(%) vs. the chain length between the two benzimidazoles unit.

Fig. 3 shows the polarisation curves for the effect of different concentration of EBBI, BBBI, HBBI and OBBI on the potentiodynamic behaviour of steel in 1 M HCl solution. As would be expected both anodic and cathodic reaction of iron electrode corrosion were inhibited with the increase of diazole derivatives concentration. This result suggests that the addition of diazole derivatives reduces anodic dissolution and also retards the rate of the hydrogen evolution reaction.

The polarisation parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), cathodic (b_c) and anodic (b_a) Tafel slopes were calculated from the curves and are represented in Table 3.

From this table it can be concluded that:

- The values of cathodic and anodic Tafel slopes (b_c, b_a) are not altered significantly by addition of different inhibitors concentrations. The presence of diazole derivatives does not change the mechanism of both anodic and cathodic reactions. This may lead to the conclusions that the inhibiting action of these compounds is simple blocking of the metal surface by adsorption.
- The values of corrosion potential (E_{corr}) do not show any significantly change in the presence of various concentration of the inhibitor. This observation shows clearly that the inhibition of corrosion was under mixed control.
- The values of inhibition efficiency were found to increase with the increase in the concentration of these compounds reaching maximum values at 5×10^{-4} M.
- At one and the same inhibitors concentration the percentage of inhibition efficiency decreases in the following sequence: OBBI > HBBI > BBBI > EBBI.

The inhibiting effect of these compounds can be attributed to their parallel adsorption at the metal solution interface, and therefore impedes by merely blocking the anodic and cathodic reaction mechanism [33].

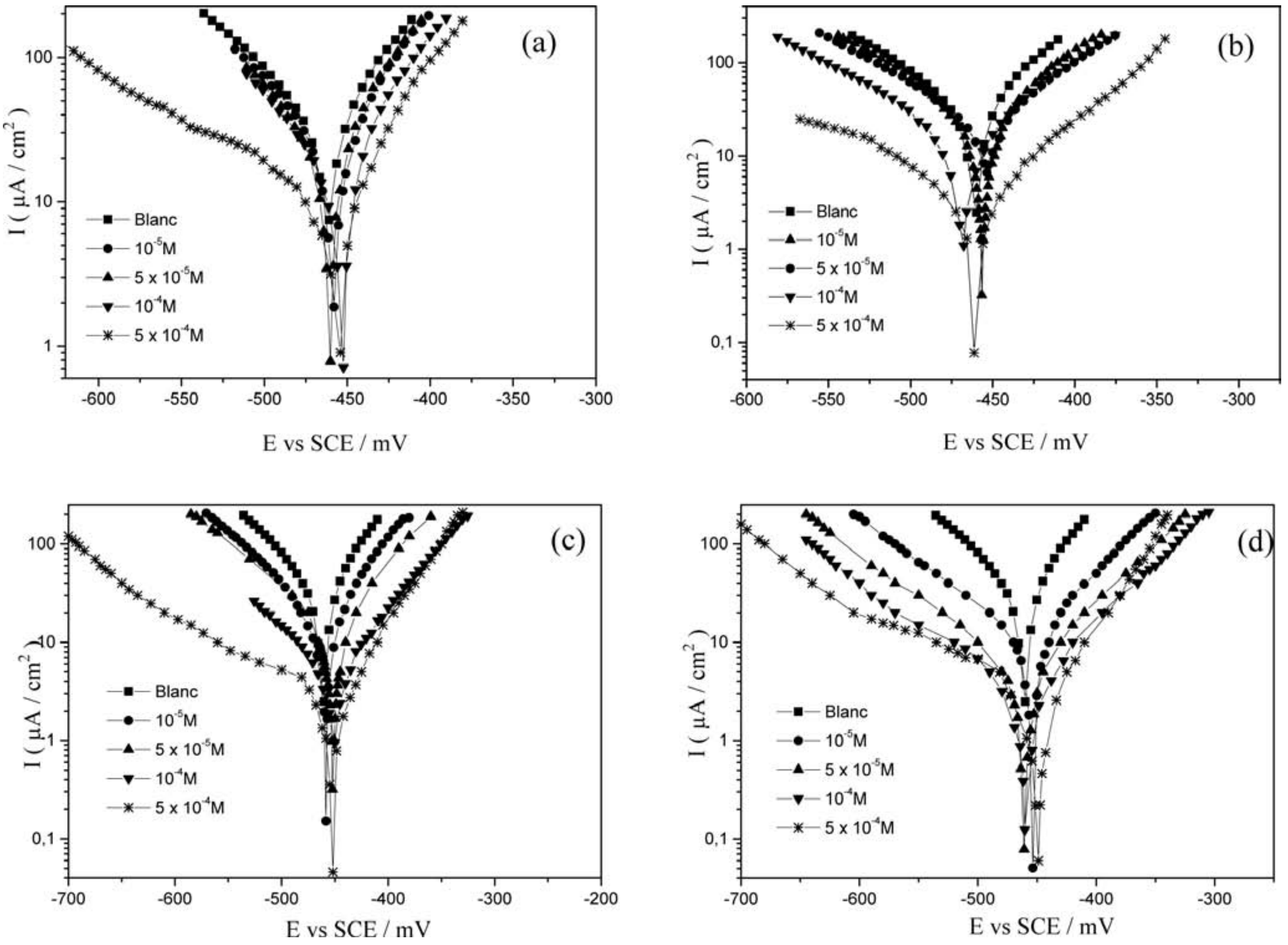


Fig. 3. Polarisation curves for the effect of different concentration of studied diazole derivatives on the potentiodynamic behaviour of mild steel in 1 M HCl solution: (a) EBBI, (b) BBBI, (c) HBBI and (d) OBBI.

3.2.2. *Linear polarisation method*

Linear polarisation curves for mild steel in 1 M HCl containing different concentrations of the organic compounds tested are made and the deduced parameters are given in Table 4. The corrosion current density was calculated using the Stern–Geary equation:

$$I_{corr} = \frac{b_c \cdot b_a}{2.3\left(b_c + b_a\right) R_p} \qquad (4)$$

These data showed that, as was expected, R_p values were higher at the optimum concentration for all inhibitors investigated. In addition, the variation of E (%) with molecular structure was identical to that observed from the Tafel-extrapolation method.

The polarisation resistance values increase from 370.1 Ω cm^{-2} of the blank acid to 1344.5 Ω cm^{-2}, 4222.5 Ω cm^{-2}, 5507.1 Ω cm^{-2} and 6027.7 Ω cm^{-2}, respectively, for the highest concentrations of 2,2′-ethylene, 2,2′-buthylene, 2,2′-hexamethylene and 2,2′-octamethylene-bis(benzimidazole).

The inhibiting efficiency of investigated diazole derivatives, as determined through polarisation resistance measurements, follows at all concentrations a trend quite similar to that obtained by Tafel extrapolation method. There was excellent agreement between E (%) values obtained from Tafel extrapolation method (Table 3) and their linear polarisation measurements (Table 4).

3.3. *Adsorption isotherms*

One of the most ways of expressing adsorption quantitatively is by applying an adsorption isotherm that gives the relationship between the coverage of an interface with an adsorbed species (the amount adsorbed) and the concentration of the species in solution. This allows the inhibition efficiency to be expressed as a function of inhibitor concentration at a constant temperature. The

Table 3
Electrochemical parameters for mild steel in 1 M HCl containing different concentrations of diazole derivatives calculated by Tafel extrapolation method

Compound	C (10^{-5} M)	I_{corr} (μAcm^{-2})	$-E_{corr}$ (mV)	$-b_c$ (mVdec^{-1})	b_a (mVdec^{-1})	E (%)
Blank	—	35.41	461	100.30	67.98	—
EBBI	1	25.41	458	80.06	67.70	28.24
	5	23.65	460	77.57	61.70	33.21
	10	18.37	452	77.82	65.61	48.12
	50	9.91	454	132.62	65.74	72.00
BBBI	1	20.70	457	97.75	74.46	41.54
	5	17.64	454	103.62	81.90	50.18
	10	12.36	467	105.93	82.57	65.14
	50	3.62	461	136.88	63.53	89.77
HBBI	1	14.51	458	105.93	73.47	59.02
	5	10.50	452	118.76	93.45	70.34
	10	4.81	450	100.70	78.67	86.41
	50	1.56	451	105.48	63.17	95.64
OBBI	1	9.85	454	113.76	80.84	72.23
	5	3.77	461	106.15	85.83	89.35
	10	2.22	460	99.70	80.84	93.73
	50	1.21	449	104.53	52.44	96.58

Table 4
Electrochemical parameters for mild steel in 1 M HCl containing different concentrations of diazole derivatives on the basis of polarisation resistance method

Compound	C (10^{-5} M)	I_{corr} (μAcm^{-2})	R_p (Ω cm^{-2})	E (%)
Blank	—	47.53	370.10	—
EBBI	1	31.50	505.80	26.82
	5	28.82	518.80	28.66
	10	20.65	748.50	50.55
	50	14.24	1344.50	72.47
BBBI	1	28.84	636.27	41.83
	5	28.10	707.10	47.65
	10	18.71	1076.90	65.63
	50	4.46	4222.50	91.23
HBBI	1	20.64	912.50	59.43
	5	18.44	1231.10	69.93
	10	6.67	2874.23	87.12
	50	3.11	5507.07	93.28
OBBI	1	14.54	1411.38	73.77
	5	5.87	3554.72	89.58
	10	3.37	5752.46	93.56
	50	2.51	6027.68	93.86

inhibition efficiency of the studied inhibitors is related to their adsorption on the surface. To investigate the adsorption isotherm, the degree of surface coverage determined from the different measurements was evaluated graphically for fitting a suitable adsorption isotherm.

The simplest, being the Langmuir isotherm, is based on the assumption that all adsorption sites are equivalent and the particle binding occurs independently from nearby sites being occupied or not. Under those circumstances, the proportionality between surface coverage (θ) and concentration (C) of the adsorbing compound is as follows [34]:

$$KC = \frac{\theta}{1-\theta} \tag{5}$$

It is convenient to rearrange Eq. (5) yielding

$$\frac{C}{\theta} = \frac{1}{k} + C \tag{6}$$

So that a linear relationship is observed when C/θ is plotted as a function of C, with a slope of ideal unity. If simple adsorptive behaviour is assumed for the diazole derivatives in the present study, the surface coverage θ can readily be calculated from of Eqs. (1), (2) or (3), as in the case it is numerically identical to the value of the inhibition efficiency [35].

$$\theta = \frac{E(\%)}{100} \tag{7}$$

In the following, θ was evaluated from the gravimetric data because it is assumed that the adsorption equilibrium is completely reached with 24 h.

In Fig. 4, the proposed relation is plotted for the in-

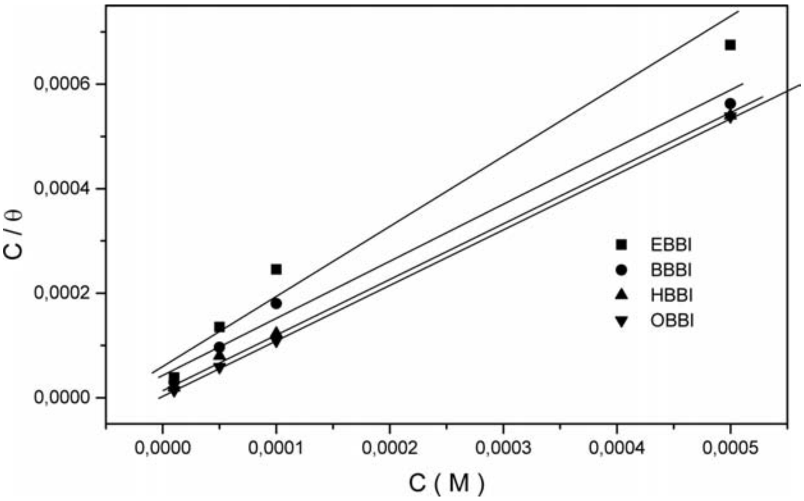


Fig. 4. Adsorption isotherms for investigated inhibitors on the mild steel in 1 M HCl obtained at 30°C for EBBI, BBBI, HBBI and OBBI.

vestigated diazole derivatives. The expected linear relationship is well approximated for all of these inhibitors, which indicates that the adsorption of inhibitors onto steel surface accords with the Langmuir adsorption isotherm.

The free energy of adsorption, (ΔG_{ads}) was calculated from the equation [36]:

$$K = \frac{1}{55.5} \exp\left(\frac{-\Delta G^0_{ads}}{RT}\right) \tag{8}$$

where K is the equilibrium constant, θ is the degree of coverage on the metal surface, R the universal gas constant, T the thermodynamic temperature and 55.5 the concentration of water in the solution in mol l^{-1}. The values of K and ΔG_{ads} are given in Table 5. The largest negative values of free energy of adsorption (ΔG_{ads}) indicate that the inhibitor molecules are spontaneously adsorbed onto the steel surface [37,38], and also suggest that the inhibitor molecules are strongly adsorbed on the metal surface [39,40]. Generally, the standard free energy of adsorption values around -20 kJmol^{-1} or lower are associated with an electrostatic interaction between charged molecules and charged metal surface, physisorption, while those around -40 kJmol^{-1} or higher involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate covalent bond, chimisorption [41–43]. In the present case, the calculated values of ΔG^0_{ads} (Table 5) range from -34.23 to -40.43 kJmol^{-1}; probably mean that both physical and chemical adsorption would take place [44–46].

Table 5
Equilibrium constant (K) and free energy of adsorption (ΔG_{ads}) for different diazole derivatives

	EBBI	BBBI	HBBI	OBBI
K, M^{-1}	14088.5	22522.5	56328.8	168707.5
$-\Delta G$, kJmol^{-1}	34.23	35.36	37.68	40.43

3.4. Effect of temperature

The effect of the temperature on the corrosion of steel in free and inhibited 1 M HCl solutions was studied using gravimetric measurements in the range of temperature 30°C–50°C. The acid solutions were inhibited by addition of 5×10^{-4} M of inhibitors. The corresponding data are shown in Table 6. Inspection of Table 6 reveals that the inhibition efficiencies of all the compounds decrease with increasing temperature from 30 to 50°C. This is attributed to decrease in the protective nature of the inhibitive film formed on the metal surface which may be explained with desorption of adsorbed inhibitor molecules from the metal surface at higher temperature [47]. Therefore, a physical adsorption process may be proposed [48].

Plotting ln W vs. $1/T$ gives straight lines, as revealed by Fig. 5, and the calculated values of the effective activation energy E_a of the corrosion process obtained from Arrhenius equation [49], are 76.07, 57.20, 78.18, 58.32 and 26.81 kJmol^{-1} for OBBI, HBBI, BBBI, EBBI and free acid, respectively. The obtained results suggest that the diazole derivatives inhibit the corrosion reaction by increasing its activation energy. This could be doing to the physical character of the adsorption.

3.5. Chemical structure and corrosion inhibition

Benzimidazole and its derivatives are organic bases as a result of the presence of the lone electron pair above the N atom in the five-member ring and in the presence of a strong acid they can be transformed to cationic form. Since the aggressive medium used in the present work

Table 6
Corrosion parameters for mild steel in 1 M HCl in the absence and presence of 5×10^{-4} M of diazole derivatives at different temperatures obtained from weight loss measurements

Inhibitor	Temperature (K)	Corrosion rate (10^{-3} mg. cm^{-2}. h^{-1})	Surface coverage, θ	Inhibition efficiency, *E* (%)
Blank	303	27.0	—	—
	313	31.5	—	—
	323	52.4	—	—
EBBI	303	7.0	0.7407	74.07
	313	13.6	0.5682	56.82
	323	29.4	0.4435	44.35
BBBI	303	3.0	0.8888	88.88
	313	7.3	0.7701	77.01
	323	20.5	0.6090	60.90
HBBI	303	2.0	0.9262	92.62
	313	3.3	0.8971	89.71
	323	8.2	0.8436	84.36
OBBI	303	0.9	0.9666	96.66
	313	3.2	0.9000	90.00
	323	5.8	0.8893	88.93

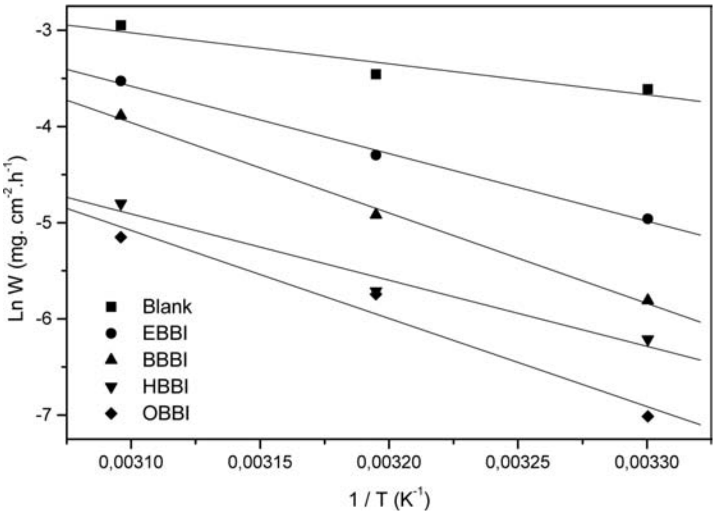


Fig. 5. Arrhenius plots of the corrosion rates of steel in 1 M HCl + 5×10^{-4} M of various inhibitors.

is 1 M HCl, formation of the protonated form can be expected. So both protonated and nonprotonated forms should be taken in consideration when discussing the inhibitor efficiencies of these compounds [50,51]. Generally, two modes of adsorption could be considered. The neutral molecule may be adsorbed on the metal surface via the chemisorption mechanism, involving the displacement of water molecules from the metal surface and sharing electrons between the nitrogen atoms and iron. The diazole derivatives can be also adsorbed on the metal surface on the basis of donor–acceptor interaction between π-electrons of the benzene ring and vacant d-orbitals of iron. In another hand, Cl$^-$ could adsorb on the metal surface and the protonated form of these compounds may adsorb in the cationic form through electrostatic interaction between the positively charged part (ammonium–N$^+$) and already adsorbed chloride ions.

A schematic representation of adsorption model of benzimidazole nucleus is shown in Fig. 6.

4. Conclusion

The following was concluded on the basis of the results obtained.

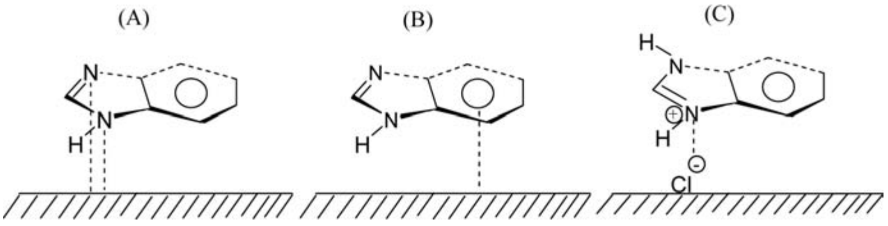


Fig. 6. Schematic representation of adsorption model of benzimidazole nucleus: (A), (B) neutral form, (C) cationic form.

1. All investigated diazole derivatives have shown good inhibiting properties for mild steel corrosion in hydrochloric acid.
2. The structure and composition of all four diazole studied influence their inhibiting efficiency.
3. Both gravimetric and electrochemical measurements showed that the inhibition efficiency increased with increasing inhibitor concentration. The efficiencies agreed for all the methods applied.
4. The inhibiting efficiency increases with increasing the length of the aliphatic chain linking the two benzimidazole nuclei.
5. Results obtained from electrochemical polarisation measurements indicated that the diazole derivatives are mixed-type inhibitors.
6. The adsorption of all investigated compounds is well described by the Langmuir isotherm, involving both physical and chemical process.

References

[1] S.M.A. Hosseini, M. Salari, E. Jamalizadeh, S. Khezripoor and M. Seifi, Inhibition of mild steel corrosion in sulfuric acid by some newly synthesized organic compounds, Mater. Chem. Phys., 119 (2010) 100.
[2] P. Lowmunkhong, D. Ungthararak and P. Sutthivaiyakit, Tryptamine as a corrosion inhibitor of mild steel in hydrochloric acid solution, Corros. Sci., 52 (2010) 30.
[3] R. Rosliza and W.B. Wan Nik, Improvement of corrosion resistance of AA6061 alloy by tapioca starch in seawater, Current Appl. Phys., 10 (2010) 221.
[4] K. Stanly Jacob and G. Parameswaran, Corrosion inhibition of mild steel in hydrochloric acid solution by Schiff base furoin thiosemicarbazone, Corros. Sci., 52 (2010) 224.
[5] Y. Abboud, A. Abourriche, T. Saffaj, M. Berrada, M. Charrouf, A. Bennamara, N. Ahimidi and H. Hannache, 2,3-quinoxalinedione as a novel corrosion inhibitor for mild steel in 1 M HCl, Mater. Chem. Phys., 105 (2007) 1.
[6] Y. Abboud, A. Abourriche, T. Saffaj, M. Berrada, M. Charrouf, A. Bennamara and H. Hannache, A novel azo dye, 8-quinolinol-5-azoantipyrine as corrosion inhibitor for mild steel in acidic media, Desalination, 237 (2009) 175.
[7] L.G. Da Trindade and R.S. Gonçalves, Evidence of caffeine adsorption on a low-carbon steel surface in ethanol, Corros. Sci., 51 (2009) 1578.
[8] D.Q. Zhang, Q.R. Cai, X.M. He, L.X. Gao and G.S. Kim, The corrosion inhibition of copper in hydrochloric acid solutions by a tripeptide compound, Corros. Sci., 51 (2009) 2349.
[9] B.V. Appa Rao, M.Y. Iqbal and B. Sreedhar, Electrochemical and surface analytical studies of the self-assembled monolayer of 5-methoxy-2-(octadecylthio)benzimidazole in corrosion protection of copper, Electrochim. Acta, 55 (2010) 620.
[10] M.M. Antonijeveć and S.M. Milić, Electrochemical behaviour of $Cu_{24}Zn_5Al$ alloy in alkaline medium in the presence of chloride ions and benzotriazole, Mater. Chem. Phys., 118 (2009) 385.
[11] X. Xuejun, H. Jie, L. Ke and P. Ling, Study on the synergistic inhibitive effect of an imidazole derivative and BTA on copper in deionised water, Anti-Corros. Methods Mater., 56 (2009) 271.
[12] D. Gopi, K.M. Govindaraju, V. Collins, A. Prakash, V. Manivannan and L. Kavitha, Inhibition of mild steel corrosion in groundwater by pyrrole and thienylcarbonyl benzotriazoles, J. Appl. Electrochem., 39 (2009) 269.
[13] K.F. Khaled, S.A. Fadl-Allah and B. Hamouti, Some benzotriazole derivatives as corrosion inhibitors for copper in acidic medium: Experimental and quantum chemical molecular dynamics approach, Mater. Chem. Phys., 117 (2009) 148.
[14] S.M. Milić and M.M. Antonijević,Some aspects of copper corrosion in presence of benzotriazole and chloride ions, Corros. Sci., 51 (2009) 28.
[15] K.F. Khaled, Experimental and atomistic simulation studies of corrosion inhibition of copper by a new benzotriazole derivative in acid medium, Electrochim. Acta, 54 (2009) 4345.
[16] D.A. Pillard, Comparative toxicity of formulated glycol deicers and pure ethylene and propylene glycol to *Ceriodaphnia dubia* and *Pimephales promelas*, Environ. Toxicol. Chem., 14 (1995) 311.
[17] D.A. Pillard, J.S. Cornell, D.L. Dufresne, D.L. Dufresne and M.T. Hernandez, Toxicity of benzotriazole and benzotriazole derivatives to three aquatic species, Wat. Res., 35 (2001) 557.
[18] N.I. Sax, Dangerous Properties of Industrial Materials, Reinhold Publishing, New York, 1957.
[19] Y. Abboud, A. Abourriche, T. Saffaj, M. Berrada, M. Charrouf, A. Bennamara, A. Cherquaoui and D. Takky, The inhibition of mild steel corrosion in acidic medium by 2,2′-bis(benzimidazole), Appl. Surf. Sci., 252 (2006) 8178.
[20] J. Aljourani, K. Raeissi and M.A. Golozar, Copper corrosion inhibitors in near neutral media, Corros. Sci., 51 (2009) 1836.
[21] H. Otmačić and E. Stupnišek-Lisac, Benzimidazole and its derivatives as corrosion inhibitors for mild steel in 1 M HCl solution, Electrochim. Acta, 48 (2003) 985.
[22] H. Otmačić, T. Brajdić, K. Tadić and E. Stupnišek-Lisac, Synergistic effect of KI and azole compunds on copper corrosion in hydrochloric acid, 10th European Symposium on Corrosion and Scale Inhibitors, Ferrara, Centro Stampe Universita Ferrara, Italy, 2005, p. 785.
[23] H. Otmačić, J. Telegdi and E. Stupnišek-Lisac, Evaluation of protective properties of an inhibitor layer formed in copper in neutral chloride solution, 203rd ECS Meeting Abstracts, Pennington, SAD, The Electrochemical Society, 2003, p. 1.
[24] A. Popova, E. Sokolova, S. Raicheva and M. Christov, AC and DC study of the temperature effect on mild steel corrosion in acid media in the presence of benzimidazole derivatives, Corros. Sci., 45 (2003) 33.
[25] A. Popova, M. Christov, S. Raicheva and E. Sokolova, Adsorption and inhibitive properties of benzimidazole derivatives in acid mild steel corrosion, Corros. Sci., 46 (2004) 1333.

[26] K.F. Khaled, The inhibition of benzimidazole derivatives on corrosion of iron in 1 M HCl solutions, Electrochim. Acta, 48 (2003) 2493.

[27] M. Castelli, M. Malagoli, L. Lupo, T. Riccomi, C. Casolari, C. Cermelli, A. Zanca and G. Baggio, Antiviral and antiproliferative activity in vitro of some new benzimidazole derivatives, Pharmacol. Toxicol., 88 (2004) 67.

[28] L. Garuti, M. Roberti, M. Malagoli, T. Rossi and M. Castelli, Synthesis and antiprolifrative activity of some benzimidazole-4,7-dione derivatives, Bioorg. Med. Chem. Lett., 17 (2000) 2193.

[29] D.L. Garner, Hoechst 33342: The dye that enabled differentiation of living X-and Y-chromosome bearing mammalian sperm, Theriogenology, 71 (2009) 11.

[30] V.A. Anisimova, A.A. Spasov, V.A. Kosolapov, I.E. Tolpygin, V.I. Porotikov, A.F. Kucheryavenko, V.A. Sysoeva, E.V. Tibir'kova and L.V. El'tsova, Synthesis and pharmacological activity of 3-(2,2,2-trichloro-1-hydroxyethyl)imidazo [1,2-a]benzimidazole dihydrochlorides, Pharm. Chem. J., 43 (2009) 491.

[31] Y. Abboud, Synthèse et caractérisation de nouveaux alcaloïdes d'intérêt biologique et leur application dans l'inhibition de la corrosion de l'acier en milieu acide chlorhydrique. PhD thesis, University Hassan II-Mohammedia, Casablanca, Morocco, 2004.

[32] Y. Abboud, A. Abourriche, H. Mouho, T. Seffaj, M. Berrada, M. Charrouf and A. Bennamara, Synthesis of bis-benzimidazoles, Proc. 8th Meeting on Supercritical Fluids, April 14–17, 2002, 1 (2002) 227.

[33] N.S. Patel, S. Jauhari and G.N. Mehta, 1,7'dimethyl 1-2' propy1-1H,3H'-2,5' bibenzo[d]imidazole as corrosion inhibitor of mild steel in 1 M HCl, Chem. Pap., 64 (2010) 51.

[34] M.M. Solomon, S.A. Umoren, I.I. Udosoro and A.P. Udoh , Inhibitive and adsorption behaviour of carboxymethyl cellulose on mild steel corrosion in sulphuric acid solution, Corros. Sci., 52 (2010) 1317–1325.

[35] I.B. Obot and N.O. Obi-Egbedi, Adsorption properties and inhibition of mild steel corrosion in sulphuric acid solution by ketoconazole: Experimental and theoretical investigation, Corros. Sci., 52 (2010) 198.

[36] P.C. Okafor, X. Liu and Y.G. Zheng, Corrosion inhibition of mild steel by ethylamino imidazoline derivative in CO_2-saturated solution, Corros. Sci., 51 (2009) 761.

[37] O. Benali, L. Larabi, M. Traisnel, L. Gengembre and Y. Harek, Electrochemical, theoretical and XPS studies of 2-mercapto-1-methylimidazole adsorption on carbon steel in 1 M HClO4, Appl. Surf. Sci., 253 (2007) 6130.

[38] R. Solmaz, G. Kardaş, M. Çulha, B. Yazici and M. Erbil, Investigation of adsorption and inhibitive effect of 2-mercaptothiazoline on corrosion of mild steel in hydrochloric acid media, Electrochim. Acta, 53 (2008) 5941.

[39] S.A. Umoren and E.E. Ebenso, The synergistic effect of polyacrylamide and iodide ions on the corrosion inhibition of mild steel in H_2SO_4, Mater. Chem. Phys., 106 (2007) 387.

[40] H. Ashassi-Sorkhabi, B. Shaabani and D. Seifzadeh, Corrosion inhibition of mild steel by some schiff base compounds in hydrochloric acid, Appl. Surf. Sci., 239 (2005) 154.

[41] M. Ehteshamzadeh, T. Shahrabi and M. Hosseini, Innovation in acid pickling treatments of copper by characterizations of a new series of Schiff bases as corrosion inhibitors, Anti-Corros. Anti-Corros. Method Mater., 53 (2006) 296.

[42] R. Fuchs-Godec, CMC determination and corrosion inhibition of some N-alkyl quaternary ammonium salts on carbon steel surface in 2 M H_2SO_4,Colloids. Surf., A Physicochem. Eng. Aspects, 280 (2006) 130.

[43] M.A. Quraishi, J. Rawat and M. Ajmal, Dithiobiurets: a novel class of acid corrosion inhibitors for mild steel, J. Appl. Electrochem., 30 (2000) 745.

[44] K.F. Khalid and M.M. Al-Qahtani, The inhibitive effect of some tetrazole derivatives towards Al corrosion in acid solution: Chemical, electrochemical and theoretical studies, Mater. Chem. Phys., 113 (2009) 150.

[45] A.K. Singh and M.A. Quaraishi, Effect of cefazolin on the corrosion of mild steel in HCl solution, Corros. Sci., 52 (2010) 152.

[46] X. Li, S. Deng, H. Fu and G. Mu, Inhibition effect of 6-benzylaminopurine on the corrosion of cold rolled steel in H_2SO_4 solution, Corros. Sci., 51 (2009) 620.

[47] Q. Zhang and Y. Hua, Corrosion inhibition of aluminum in hydrochloric acid solution by alkylimidazolium ionic liquids, Mater. Chem. Phys., 119 (2010)57.

[48] I.B. Obot, N.O. Obi-Egbedi and S.A. Umoren, The synergistic inhibitive effect and some quantum chemical parameters of 2,3-diaminonaphthalene and iodide ions on the hydrochloric acid corrosion of aluminium, Corros. Sci., 51 (2009) 276.

[49] A. Fiala, A. Chibani, A. Darchen, A. Boulkamh and K. Djebbar, Investigations of the inhibition of copper corrosion in nitric acid solutions by ketene dithioacetal derivatives, Mater. Lett., 61 (2007) 3276.

[50] A. Popova, M. Christov and A. Zwetanova, Effect of the molecular structure on the inhibitor properties of azoles on mild steel corrosion in 1 M hydrochloric acid, Corros. Sci., 49 (2007) 2131.

[51] A. Popova, M. Christov and T. Deligeorgiev, Influence of the molecular structure on the inhibitor properties of benzimidazole derivatives on mild steel corrosion in 1 M hydrochloric acid, Corrosion, 59 (2003) 756.