

BENZIMIDAZOLE AND ITS DERIVATIVES AS CORROSION INHIBITORS FOR MILD STEEL IN HYDROCHLORIC ACID

BENZIMIDAZOL IN NJEGOVI DERIVATI KOT ZAVIRALCI KOROZIJE MALOLEGIRANEGA JEKLA V SOLNI KISLINI

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Using potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS), the inhibition ability of benzimidazole (BI), 2-methylthio benzimidazole (2-MBI) and 2-chloromethylbenzimidazole (2-CBI) for mild steel in an HCl solution (1 mol L⁻¹) was investigated. With an increase in the concentration, 2-MBI showed the highest inhibition efficiency (IE) at 1.24×10⁻³ mol L⁻¹, while the IE of BI and 2-CBI increased continuously within the investigated concentration range. The IE increased in the order of BI < 2-MBI < 2-CBI, which was further confirmed by the morphologies of the mild-steel surfaces after their immersion in 1M HCl with or without different inhibitors. Fitted adsorption isotherm curves suggested that the adsorption of the three inhibitors onto the mild steel in 1M HCl follow the Langmuir adsorption isotherm. Considering the effects of the temperature on the adsorption behaviour of the inhibitors, the apparent activation energy (*E_a*) of the mild-steel corrosion in the HCl solution with BI, 2-MBI and 2-CBI was calculated as (42.00, 48.28 and 67.93) kJ mol⁻¹, respectively.

Keywords: mild steel, benzimidazole derivatives, inhibitor, adsorption

V članku avtorji opisujejo raziskavo sposobnosti benzimidazolovih derivatov: benzimidazola (BI), 2-metilthio benzimidazola (2-MBI) in 2-klorometilbenzimidazola (2-CBI) za zaviranje korozije malolegiranega (z nizko vsebnostjo ogljika) jekla v raztopini (1 mol L⁻¹) solne kisline. V raziskavi so za to uporabili potenciodinamične polarizacijske krivulje in elektrokemično impedančno spektroskopijo (EIS). Kot najučinkovitejši zaviralec (IE; angl.: Inhibition Efficiency) se je z naraščajočo koncentracijo pri 1,24×10⁻³ mol L⁻¹ izkazal 2-MBI, medtem ko je zaviralna učinkovitost BI in 2-CBI naraščala zvezo v preiskovanem območju koncentracij. IE je naraščala v smeri BI < 2-MBI < 2-CBI, ki so jo nadalje potrdili s preiskavami morfologije površine malolegiranega jekla po potapljanju v 1M raztopino HCl v ali brez prisotnosti izbranih zaviralcev. Zglajene adsorpcijske izotermalne krivulje kažejo na to, da izbrani zaviralci na malolegiranem jeklu v 1M HCl sledijo Langmuir-jevi adsorpcijski izoterma. Avtorji prispevka so, upoštevajoč vpliv temperature, izračunali navidezne aktivacijske energije (*E_a*) korozije malolegiranega jekla v raztopini HCl s prisotnostjo BI, 2-MBI in 2-CBI. Izračunane vrednosti *E_a* so bile (42,00, 48,28 in 67,93) kJ mol⁻¹.

Ključne besede: malolegirano jeklo, derivati benzimidazola, zaviralec, adsorpcija

1 INTRODUCTION

Corrosion behaviours of metals can be observed in different fields of industry, causing significant economic losses.¹⁻³ Using corrosion inhibitors is one of the most efficient and economical methods for the protection of metals and their alloys against corrosion, especially in acidic solutions.⁴⁻⁶ Organic compounds with π electrons and heteroatoms such as O, N, S proved to be the most effective corrosion inhibitors.⁷⁻¹⁰ The electrostatic physisorption or chemisorption ascribed to the transformation of electrons from inhibitors to the metal surface are considered to be the reasons why inhibitors can retard the corrosion behaviour. However, the relationship between the molecular structure and the inhibition efficiency (IE) has not yet been completely established.

Benzimidazole (BI) and its derivatives were used to inhibit the corrosion of metals in a corrosive medium.¹¹⁻¹⁸ J. Aljourani et al.¹¹ researched the BI, 2-methylbenzimidazole and 2-mercaptobenzimidazole as corro-

sion inhibitors for mild steel in the 1M HCl solution; they found that these inhibitors retarded both the cathodic and anodic processes and that the inhibition efficiency was increased with an inhibitor concentration in the order of 2-mercaptobenzimidazole > 2-methylbenzimidazole > BI. Recently, P. Morales-Gil et al.¹⁹ found that the IE of 2-mercaptobenzimidazole for carbon steel in the 1M hydrochloric acid is 99 %, with a concentration of 2 mM. K. F. Khaled²⁰ reported the corrosion inhibition of iron in 1.0 M HNO₃ due to some benzimidazole derivatives where the IE increased in the order of 2-methylthio benzimidazole (2-MBI) < 2-chloromethylbenzimidazole (2-CBI) < 2-aminomethylbenzimidazole (2-ABI), since 2-ABI has a higher HOMO energy and larger number of electrons transferred to the iron surface (ΔN) than that of the other two. 2-CBI was also used as the inhibitor for the carbon steel in 1M HCl, and it showed the highest IE among the involved six compounds, including imidazole, benzimidazole, pyridine and their derivatives.²¹

However, 2-MBI and 2-CBI were not directly compared as corrosion inhibitors for mild steel in HCl, which would help us to better understand the effects of the substituents on the molecular structure. In this paper, the effects of BI, 2-CBI and 2-MBI on the mild-steel corrosion in a HCl solution (1 mol L⁻¹) were studied; since the last one contains nitrogen and sulphur, it was expected to be a more efficient inhibitor than those containing only sulphur or nitrogen atoms.^{22,23} All the experiments were carried out using potentiodynamic polarization curves or electrochemical impedance spectroscopy (EIS). The standard adsorption free energy (ΔG_{ads}^0) of the inhibitors and the apparent activation energy (E_a) of the mild-steel corrosion were discussed by monitoring the IE of different inhibitors as a function of the concentration and temperature.

2 EXPERIMENTAL PART

The chemical composition of the involved mild-steel samples is C = 0.193 %, Si = 0.272 %, Mn = 0.436 %, P = 0.033 % and S = 0.029 %. The cylindrical mild-steel specimens with a cross-section area of 0.5 cm² and a height of 1.5 cm were welded with an insulated copper wire and sealed in PVC tubes with epoxy resin. After having been mechanically ground with 400, 600, 1000 and 1500 grit SiC abrasive papers, the epoxy-resin-sealed mild-steel samples were washed with absolute ethanol and acetone and finally stored in a moisture-free desiccator before use. BI, 2-MBI and 2-CBI were purchased from Sigma-Aldrich (Shanghai) Trading Co., Ltd., without any further treatment before their use. 1 mol L⁻¹ HCl was prepared by dissolving reagent grade hydrochloric acid in bi-distilled water. HCl solutions with different concentrations of benzimidazole and its derivatives were used as the electrolyte.

A three-electrode cell containing a mild-steel specimen as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, a platinum electrode as the counter electrode was used. All the electrochemical measurements were conducted with an AUTOLAB (AUT86742) instrument using 100 mL of the electrolyte in the stationary condition. Before every measurement, the working electrode was immersed in the corrosion cell for 30 min to achieve a stable state. The scanning scope of the polarization curves was -250 mV to 250 mV, relative to the open-circuit potential (E_{oc}) at 1 mV s⁻¹. The scanning scope of EIS was 100 KHz to 10 mHz. All the experiments were measured three times to get the average values and the representative results are displayed in the figures below.

The morphology of the mild-steel surface before and after the immersion in 1 M HCl with or without different inhibitors was determined using a scanning electron microscope (JSM-6480, JEOL). After the immersion in the HCl solution, the specimens were ultrasonically cleaned and washed with absolute ethanol and acetone.

3 RESULTS AND DISCUSSION

3.1 Effect of the inhibitor concentration

We first researched the corrosion behaviours of mild steel in 1 mol L⁻¹ HCl with different concentrations of BI, 2-MBI and 2-CBI under room temperature (298 K). The results include polarization curves and EIS curves. The relative anodic and cathodic polarization curves are shown in **Figure 1**. Electrochemical parameters, such as the corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (β_c and β_a) as well as corrosion current density (i_{corr}) were extrapolated from **Figure 1** and displayed in **Table 1**. The degree of surface coverage (θ) and the percentage of IE (η %) were calculated using the following Equations (1) and (2):^{23,24}

Table 1: Electrochemical parameters determined from the polarization curves in **Figure 1**

Inhibitor	$C \times 10^3$ (mol L ⁻¹)	$-E_{\text{corr}} \times 10^3$ (V/SCE)	$i_{\text{corr}} \times 10^3$ (A cm ⁻²)	$\beta_c \times 10^3$ (V/decade)	$\beta_a \times 10^3$ (V/decade)	θ	η
	Blank	442±2.3	661±3.1	51±0.4	135±2.3	/	/
BI	0.43	456±1.9	477±1.7	49±0.7	110±2.7	0.2788	27.88 %
	0.86	470±3.3	433±2.4	51±0.7	107±0.7	0.3457	34.57 %
	1.29	464±2.7	407±1.0	49±0.5	90±3.8	0.3842	38.42 %
	1.72	466±0.8	392±0.7	56±0.2	109±4.3	0.4070	40.70 %
	2.15	468±1.2	379±1.2	50±1.1	96±4.1	0.4266	42.66 %
2-MBI	0.31	476±3.3	377±0.9	47±2.5	101±1.0	0.4295	42.95 %
	0.62	475±0.5	346±1.1	49±1.6	104±0.4	0.4770	47.70 %
	0.93	480±0.9	314±0.8	46±0.9	96±1.2	0.5252	52.52 %
	1.24	481±1.7	298±0.3	58±3.7	128±0.7	0.5492	54.92 %
	1.55	477±2.3	338±0.5	49±4.3	103±0.4	0.4889	48.89 %
2-CBI	0.31	444±1.3	141±1.8	69±2.1	123±1.6	0.7871	78.71 %
	0.61	449±0.7	126±5.1	66±1.4	140±4.1	0.8088	80.88 %
	0.91	458±1.1	70±4.4	66±1.1	137±2.5	0.8948	89.48 %
	1.22	460±1.4	60±2.7	52±2.6	124±3.2	0.9089	90.89 %
	1.52	467±0.8	38±1.4	57±3.1	112±5.4	0.9431	94.31 %

$$\theta = \frac{i_{\text{corr}}^0 - i_{\text{corr}}}{i_{\text{corr}}^0} \quad (1)$$

$$\eta/\% = \theta \times 100\% \quad (2)$$

where i_{corr}^0 is the corrosion current density of mild steel in 1 M HCl without inhibitors.

As we can see from **Figure 1** and **Table 1**, the corrosion current density i_{corr} of mild steel in the HCl solutions containing BI or its derivatives with different concentrations are lower than that in the HCl solutions without additives (blank). For BI and 2-CBI, the i_{corr} of mild steel in 1M HCl decreases at all the inhibitor concentrations while for 2-MBI, the i_{corr} shows the minimum value at $1.24 \times 10^{-3} \text{ mol L}^{-1}$, indicating desorption at higher con-

centrations. In the report published by J. Aljourani and co-workers, the IE of BI for mild steel in 1 M HCl changed from 36.6 to 52.2 % with a concentration range from $0.43 \times 10^{-3} \text{ mol L}^{-1}$ to 2.15 mol L^{-1} and the results of our work are basically the same.¹¹ The IE of 2-methylbenzimidazole from reference¹¹ and the IE of 2-MBI found with our research are both lower than the IE of 2-mercaptobenzimidazole from reference.¹¹ Nevertheless, the IE of 2-CBI is the highest among the compounds from reference¹¹ and our research, e.g., when 2-CBI in the HCl solution is 1.52 mol L^{-1} , the IE is 94.31 %.

In addition, the results of our work are also consistent with the report published by K. F. Khaled,²⁰ in which 2-CBI also has a higher IE than 2-MBI for iron in 1M

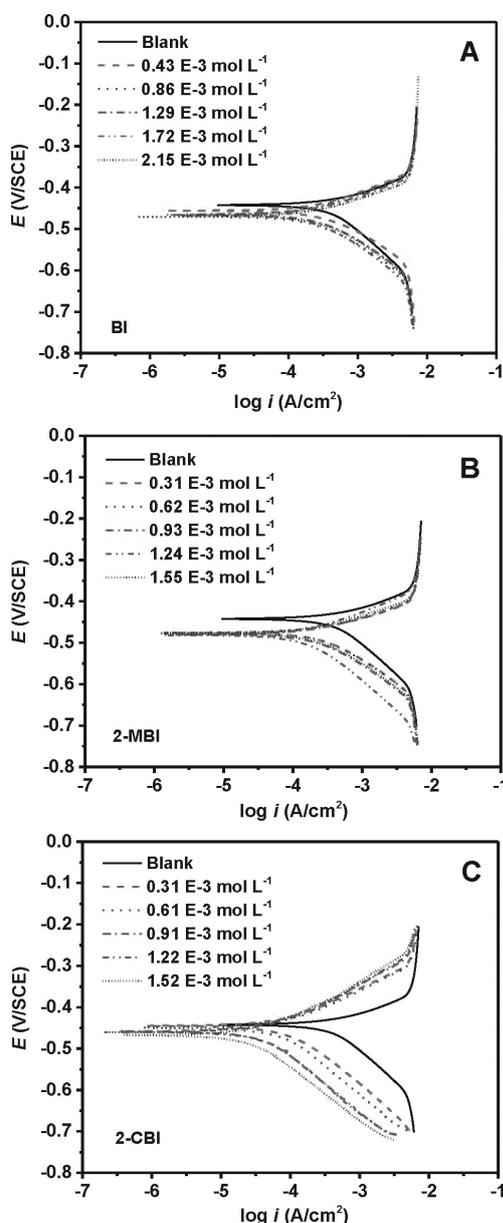


Figure 1: Polarization curves of mild steel in 1M HCl with different inhibitors at 398 K: a) benzimidazole (BI), b) 2-methylthiobenzimidazole (2-MBI) and c) 2-chloromethylbenzimidazole (2-CBI)

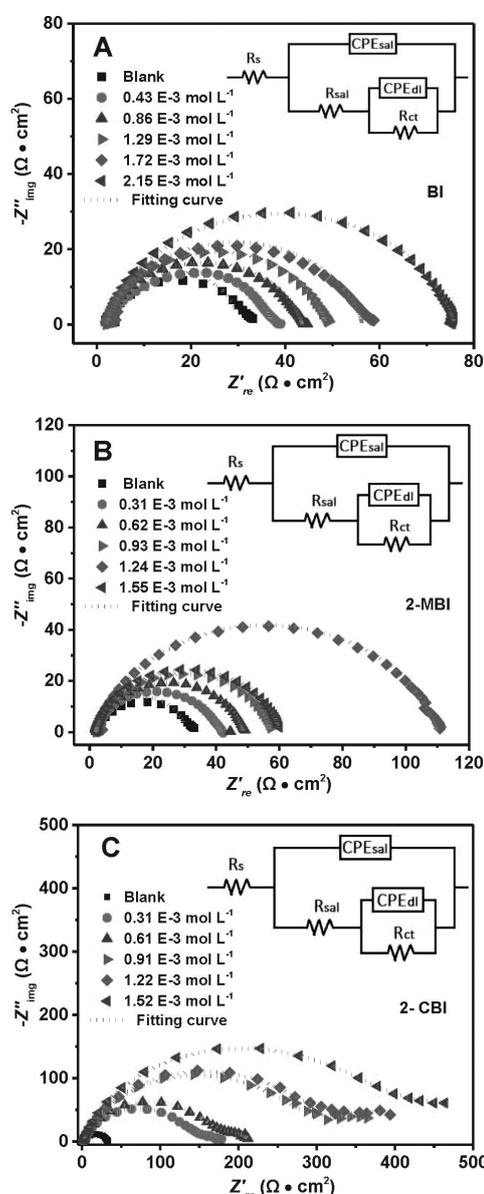


Figure 2: Nyquist plots of mild steel in 1M HCl with different concentrations of: a) benzimidazole (BI), b) 2-methylthiobenzimidazole (2-MBI) and c) 2-chloromethylbenzimidazole (2-CBI) at 303 K

HNO₃ at identical concentrations; the reasons for this were found to be a higher HOMO energy and a larger ΔN of 2-CBI. We believe that these reasons can also be used to interpret the higher IE of 2-CBI compared to 2-MBI for mild steel, found in our work. In addition, the difference between 2-CBI and 2-MBI can probably be attributed to the effects of the substituted group on the electron-cloud distribution of BI and the conformation of the inhibitor molecules. Hence, we can draw a conclusion that, just like BI, both BI derivatives can be used as inhibitors for mild steel in an HCl solution. The IE of the three inhibitors increases in the order of BI < 2-MBI < 2-CBI.

In order to verify the phenomena presented in **Figure 1**, we conducted EIS measurements of the mild steel in 1 M HCl with the three inhibitors. The electrical equivalent circuit inserted in **Figure 2** A, B and C was used to fit the EIS data and the results are shown in **Figure 2** and **Table 2**. They reveal that the Nyquist plots contain a depressed semi-circle, with the centre below the real X axis, which means that the corrosion is mainly a charge-transfer process.²⁵ Also, the total resistance, R_{tot} , which represents the corrosion-protection ability of the layers, as well the percentage of inhibition efficiency (η %) were evaluated with the following Equations (3) and (4):¹⁷

$$R_{tot} = R_{sal} + R_{ct} \quad (3)$$

$$\eta/\% = \frac{R_{tot} - R_0}{R_{tot}} \times 100 \quad (4)$$

where R_{sal} is the resistance of electrons or ions through the inhibitor layer, R_{ct} is the charge-transfer resistance, and R_0 is the charge-transfer resistance without the inhibitor.

For BI and 2-CBI, the radius of the semi-circle and R_{tot} increase with the inhibitor concentration. On the other hand, for 2-MBI, the radius of the semi-circle and R_{tot} increase with the concentration increase to 1.24×10^{-3}

mol L⁻¹, and then they decrease when the concentration is 1.55×10^{-3} mol L⁻¹, which indicates the desorption of 2-MBI at a higher concentration. For BI and 2-MBI, R_{tot} is mostly derived from R_{ct} , while for 2-CBI, R_{tot} is much bigger than that of the other two, and R_{sal} is comparable to R_{ct} . This phenomenon may be interpreted as the BI and 2-MBI layer being able to change the structure of the double electric layer, but with a lower resistance. However, not only R_{ct} , but also R_{sal} increased sharply when 2-CBI was used as the inhibitor. This means that in addition to increasing the resistance of the double electric layer, 2-CBI can also form a dense molecular layer with a higher resistance. Whatever, the IE values we calculated from the EIS curves (**Table 2**) are the same, with the tendency of the anodic and cathodic polarization curves shown in **Figure 1** and **Table 1**.

3.2 Morphological characterization

The surface morphologies of the mild-steel specimens immersed in 1 M HCl for 7 days with or without different inhibitors are presented in **Figure 3**. **Figure 3B** reveals that the surface morphology of the mild steel immersed in the HCl solution without an inhibitor is rough and porous, which means that the specimen was seriously corroded by the HCL solution. **Figures 3C–D** show the surface morphologies of the mild steel immersed in the HCl solution with BI, 2-MBI and 2-CBI, respectively. In contrast, the surfaces of these mild-steel specimens were protected by the three compounds, which proves that they can be used as inhibitors for mild steel in HCl. It should be emphasized that the surface morphology of the specimen with 2-CBI as the inhibitor is nearly the same as the freshly polished mild steel (**Figure 3A**). Moreover, the smoothness of the mild-steel surface increases in the order of BI < 2-MBI < 2-CBI, which also supports the results obtained from the polarization curves and EIS.

Table 2: Electrochemical parameters determined from the Nyquist plots in **Figure 2**

Inhibitor	$C \times 10^3$ (mol L ⁻¹)	R_{ct} (Ω cm ²)	R_{sal} (Ω cm ²)	R_{tot} (Ω cm ²)	η	θ
BI	Blank	27.5±1.7	0.08±0.02	27.5	/	/
	0.43	34.5±0.8	0.92±0.06	35.4	22.33 %	0.2233
	0.86	40.8±1.8	1.43±0.11	42.2	34.86 %	0.3486
	1.29	45.8±3.2	1.22±0.15	47.0	41.49 %	0.4149
	1.72	52.1±2.2	4.14±0.21	56.2	51.08 %	0.5108
	2.15	74.0±1.9	0.35±0.12	74.4	63.00 %	0.6300
2-MBI	0.31	38.0±1.5	1.78±0.49	39.8	30.84 %	0.3084
	0.62	45.8±2.2	1.18±0.37	47.0	41.44 %	0.4144
	0.93	53.7±4.3	1.81±0.61	55.5	50.44 %	0.5044
	1.24	89.8±3.6	2.19±0.83	92.0	70.09 %	0.7099
	1.55	58.1±6.8	1.91±0.66	60.0	54.16 %	0.5416
2-CBI	0.31	139.7±11.8	35.1±7.7	174.8	84.26 %	0.8426
	0.61	164.8±17.7	49.5±7.1	214.3	87.16 %	0.8716
	0.91	281.8±16.5	139.8±5.3	421.6	93.47 %	0.9347
	1.22	290.3±21.1	207.6±10.8	497.9	94.47 %	0.9447
	1.52	362.9±27.5	307.5±16.5	670.4	95.90 %	0.9590

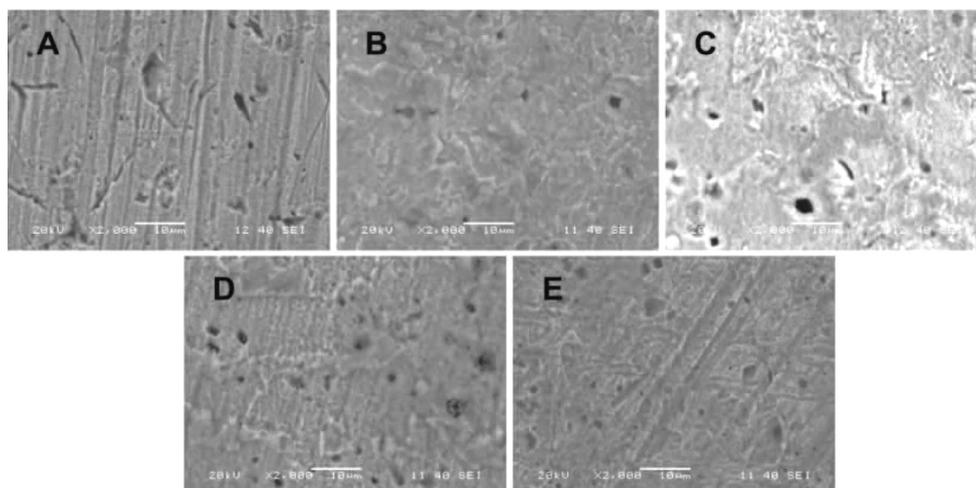


Figure 3: a) Morphology of the freshly polished mild-steel surface after the immersion in the 1 M HCl solution for 7 d without the inhibitor, b) with $0.43 \times 10^{-3} \text{ mol L}^{-1}$ benzimidazole (BI), c) with $1.24 \times 10^{-3} \text{ mol L}^{-1}$ 2-methylthiobenzimidazole (2-MBI), d) with $1.22 \times 10^{-3} \text{ mol L}^{-1}$ 2-chloromethylbenzimidazole (2-CBI) (E)

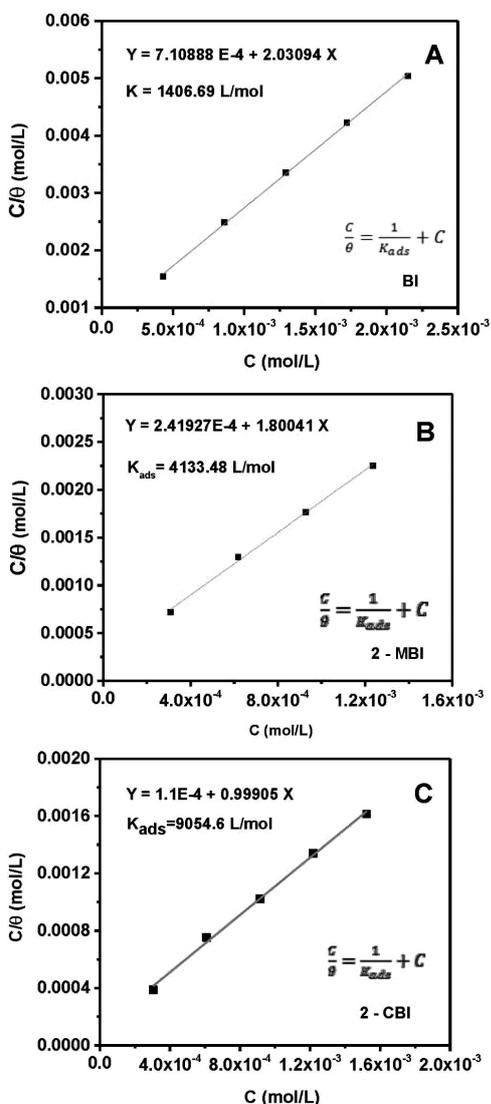


Figure 4: Adsorption-isotherm fitting curves of the three inhibitors on the mild steel in 1 M HCl at 398 K: a) benzimidazole (BI), b) 2-methylthiobenzimidazole (2-MBI), c) 2-chloromethylbenzimidazole (2-CBI)

3.3 Adsorption isotherms

Furthermore, the adsorption isotherms of BI and its derivatives used on the mild-steel surface in the HCl solution were investigated in this research, and the results are shown in **Figure 4** and **Table 3**. Different adsorption models mainly include Langmuir,²⁶ Brunauer-Emmett-Teller (BET),²⁷ Temkin,²⁸ Multisite Langmuir,²⁹ Flory-Huggins³⁰ and Frumkin.³¹ It was found that the adsorption of all three inhibitors onto the mild steel in the HCl solution can be effectively described with the Langmuir adsorption isotherm, in which C/θ can be represented as:³²

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (5)$$

Where K_{ads} is the adsorption equilibrium constant; the K_{ads} of BI, 2-MBI and 2-CBI adsorbed onto the mild-steel surface was calculated as (1406.69, 4133.48 and 9054.6) L mol^{-1} , respectively.

Table 3: Adsorption thermodynamic parameters of different inhibitors on the mild steel in 1M HCl and the subsequent apparent activation energy of mild steel

	K_{ads} L/mol	ΔG_{ads}^0 KJ/mol	E_a KJ/mol
Blank	—	—	33.74
BI	1.41×10^3	-27.91	42.00
2-MBI	4.13×10^3	-30.58	48.28
2-CBI	9.05×10^3	-32.52	67.93

Based on the K_{ads} values for different inhibitors, the standard free energy of adsorption ΔG_{ads}^0 can be calculated with the following Equation (6):³³⁻³⁵

$$\Delta G_{ads}^0 = -RT \ln(55.5 K_{ads}) \quad (6)$$

where R is the gas constant and T is the absolute temperature. The value of 55.5 is the concentration of water in the solution in mol L^{-1} . The ΔG_{ads}^0 values of the

three inhibitors are presented in **Table 3**. A larger K_{ads} is preferable for the inhibitors adsorbed onto the mild-steel surface, and the negative ΔG^0_{ads} means that the adsorption is spontaneous.^{36–38} Table 3 reveals that the K_{ads} increased in the order of BI < 2-MBI < 2-CBI, and the respective ΔG^0_{ads} values are (-27.91, -30.58 and -32.52) kJ mol⁻¹. The interaction between the inhibitors and the mild-steel surface is reflected by the absolute value of ΔG^0_{ads} : if it is not more than 20 kJ mol⁻¹, the interaction is an electrostatic force (physisorption); if it is not less than 40 kJ mol⁻¹, the interaction involves sharing and a transfer of electrons from the inhibitors to the metal surface (chemisorption).³⁹ In this research, all the absolute values of ΔG^0_{ads} are around 30 kJ mol⁻¹, indicating that the interaction between the three inhibitors and mild steel may be a mix of physisorption and chemisorption.

3.4 Effects of the temperature

The effects of the temperature on the corrosion current density of mild steel can be used to determine the apparent activation energy (E_a) of mild-steel corrosion in the HCl solution with or without inhibitors. The effects of the temperature on the polarization curves are presented in **Figure 5**; the i_{corr} values of the mild steel in 1 M HCl with different inhibitors (fixed concentrations) were extrapolated from these polarization curves, and the results are recorded in **Table 4**. We used the following Equation (7):⁴⁰

$$\ln i_{corr} = \ln A - \frac{E_a}{RT} \quad (7)$$

Where A is the Arrhenius pre-exponential constant. The relative electrochemical parameters are listed in **Table 4**, and the fitted straight lines of $\ln i_{corr}$ as a function of the reciprocal of temperature are displayed in

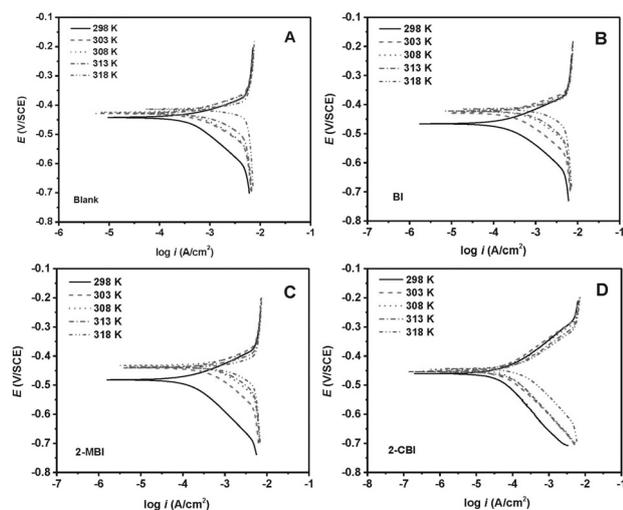


Figure 5: Polarization curves of mild steel in 1M HCl with or without inhibitors at different temperatures: a) blank, b) benzimidazole (BI), c) 2-methylthiobenzimidazole (2-MBI), d) 2-chloromethylbenzimidazole (2-CBI)

Figure 6. Based on the slopes of the straight lines ($-E_a/RT$), the apparent activation energy of the mild steel in HCl with different inhibitors is recorded in **Table 3**.

Table 4: Electrochemical parameters extrapolated from the polarization curves in **Figure 5**

Inhibitor	T (K)	$-E_{corr} \times 10^3$ (V/SCE)	$i_{corr} \times 10^6$ (A cm ⁻²)	θ	η
Blank	298K	442±2.3	661±3.1	–	–
	303K	428±0.5	825±2.9	–	–
	308K	424±0.6	1010±2.2	–	–
	313K	428±1.0	1290±6.8	–	–
	318K	414±0.3	1541±9.7	–	–
BI	298K	466±0.8	392±0.7	0.4070	40.70 %
	303K	428±2.3	521±3.1	0.3686	36.86 %
	308K	422±1.8	663±2.5	0.3434	34.34 %
	313K	422±1.6	895±5.3	0.3060	30.60 %
	318K	413±0.9	1130±5.8	0.2668	26.68 %
2-MBI	298K	481±1.7	298±0.3	0.5492	54.92 %
	303K	440±2.7	409±7.6	0.5041	50.41 %
	308K	432±1.5	545±1.8	0.4629	46.29 %
	313K	437±2.9	769±8.8	0.4036	40.36 %
	318K	439±2.5	1006±6.6	0.3473	34.73 %
2-CBI	298K	460±1.4	60±2.7	0.9089	90.89 %
	303K	451±3.4	936±2.9	0.8878	88.78 %
	308K	446±6.7	141±6.1	0.8608	86.08 %
	313K	454±3.7	228±4.7	0.8229	82.29 %
	318K	443±3.2	330±10.5	0.7861	78.61 %

It is not surprising that with various inhibitors, E_a of the mild-steel corrosion in 1 M HCl increased in the order of BI (42.00 kJ mol⁻¹) < 2-MBI (48.28 kJ mol⁻¹) < 2-CBI (67.93 kJ mol⁻¹); all its values are higher than the one obtained without the inhibitor (33.74 kJ mol⁻¹). Thus, this tendency is consistent with that of IE.

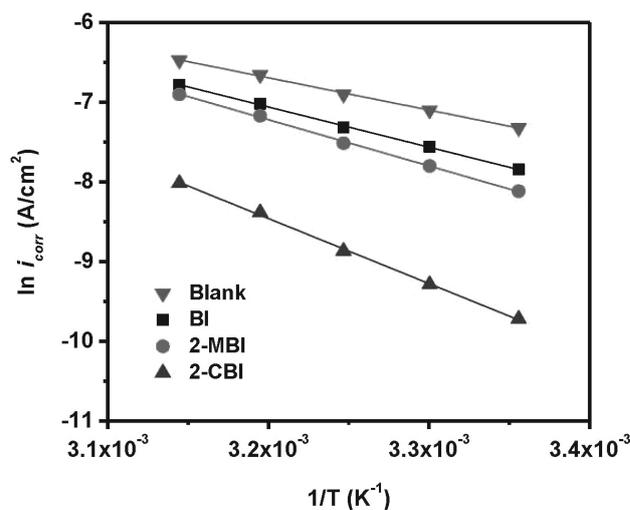


Figure 6: $\ln i_{corr}$ as a function of $1/T$ for mild steel in 1 M HCl in the absence or presence of 0.43×10^{-3} mol L⁻¹ benzimidazole (BI), 1.24×10^{-3} mol L⁻¹ 2-methylthiobenzimidazole (2-MBI) and 1.22×10^{-3} mol L⁻¹ 2-chloromethylbenzimidazole (2-CBI)

4 CONCLUSIONS

So far, we have come to the following conclusions by measuring electrochemical behaviours of mild steel in 1 M HCl with or without benzimidazole and its derivatives:

1. Benzimidazole (BI), 2-methylthiobenzimidazole (2-MBI) and 2-chloromethylbenzimidazole (2-CBI) can be used as corrosion inhibitors for mild steel in 1 M HCl. For BI and 2-CBI, the inhibition efficiency (IE) increased with the increasing concentration. However, the IE of 2-MBI decreased when the concentration reached 1.24×10^{-3} mol L⁻¹ due to the desorption process. Under the same condition, IE improved the most for BI, followed by 2-MBI and 2-CBI.
2. In this research, the adsorption of BI, 2-MBI and 2-CBI onto the mild steel in 1 M HCl was found to obey the Langmuir adsorption isotherm. The adsorption equilibrium constant (K_{ads}) of the inhibitors adsorbed onto the mild steel in 1 M HCl also improved in the same order as IE.
3. With an increase in the temperature, the corrosion current density increased as well. The values for the apparent activation energy (E_a) of mild-steel corrosion in the HCl solution with the inhibitors are all higher than the one obtained without the inhibitor. Moreover, the variation in E_a is in accordance with the IE values for the three inhibitors.

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5 REFERENCES

- ¹ C. B. Zheng, X. Chen, ZrMoN films on 304 stainless steel as bipolar plates for PEMFCs using physical-vapor-deposition (PVD) technology, *Mater. Technol.*, 51 (2017) 4, 699–705, doi:10.17222/mit.2016.316
- ² X. Y. Lu, X. G. Feng, Y. Zuo, P. Zhang, C. B. Zheng, Improvement of protection performance of Mg-rich epoxy coating on AZ91D magnesium alloy by DC anodic oxidation, *Progress in Organic Coatings*, 104 (2017), 188–198, doi:10.1016/j.porgcoat.2016.11.001
- ³ Z. B. Wang, H. X. Hu, Y. G. Zheng, W. Ke, Y. X. Qiao, Comparison of the corrosion behavior of pure titanium and its alloys in fluoride-containing sulfuric, *Corrosion Science*, 103 (2016), 50–65, doi:10.1016/j.corsci.2015.11.003
- ⁴ G. TrabANELLI, 1991 Whitney Award Lecture: Inhibitors – An Old Remedy for a New Challenge, *Corrosion*, 47 (1991) 6, 410–419, doi:10.5006/1.3585271
- ⁵ Y. Qiang, S. Zhang, L. Guo, X. Zheng, B. Xiang, S. Chen, Experimental and theoretical studies of four allyl imidazolium-based ionic liquids as green inhibitors for copper corrosion in sulfuric acid, *Corrosion Science*, 119 (2017), 68–78, doi:10.1016/j.corsci.2017.02.021
- ⁶ C. B. Zheng, L. Cai, Z. J. Tang, X. L. Shen, The inhibition effect of the molybdate on hydrogen permeation of 2205 duplex stainless steel, *Surface and Coatings Technology*, 287 (2016), 153–159, doi:10.1016/j.surfcoat.2015.12.077
- ⁷ M. Hosseini, S. F. L. Mertens, M. Ghorbani, M. R. Arshadi, Asymmetrical Schiff bases as inhibitors of mild steel corrosion in sulphuric acid media, *Materials Chemistry and Physics*, 78 (2003) 3, 800–808, doi:10.1016/S0254-0584(02)00390-5
- ⁸ M. Hosseini, S. F. L. Mertens, M. R. Arshadi, Synergism and antagonism in mild steel corrosion inhibition by sodium dodecylbenzenesulphonate and hexamethylenetetramine, *Corrosion Science*, 45 (2003) 7, 1473–1489, doi:10.1016/S0010-938X(02)00246-9
- ⁹ K. C. Emregül, M. Hayvali, Studies on the effect of vanillin and protocatechualdehyde on the corrosion of steel in hydrochloric acid, *Materials Chemistry and Physics*, 83 (2004) 2–3, 209–216, doi:10.1016/j.matchemphys.2003.08.030
- ¹⁰ M. Lebrini, M. Lagrenée, H. Vezin, L. Gengembre, F. Bentiss, Electrochemical and quantum chemical studies of new thiazole derivatives adsorption on mild steel in normal hydrochloric acid medium, *Corrosion Science*, 47 (2005) 2, 485–505, doi:10.1016/j.corsci.2004.06.001
- ¹¹ J. Aljourani, K. Raeissi, M. A. Golozar, Benzimidazole and its derivatives as corrosion inhibitors for mild steel in 1 M HCl solution, *Corrosion Science*, 51 (2009) 8, 1836–1843, doi:10.1016/j.corsci.2009.05.011
- ¹² M. Mahdavian, S. Ashhari, Corrosion inhibition performance of 2-mercaptobenzimidazole and 2-mercaptobenzoxazole compounds for protection of mild steel in hydrochloric acid solution, *Electrochimica Acta*, 55 (2010) 5, 1720–1724, doi:10.1016/j.electacta.2009.10.055
- ¹³ S. Sun, Y. Geng, L. Tian, S. Chen, Y. Yan, S. Hu, Density functional theory study of imidazole, benzimidazole and 2-mercaptobenzimidazole adsorption onto clean Cu(111) surface, *Corrosion Science*, 63 (2012), 140–147, doi:10.1016/j.corsci.2012.05.024
- ¹⁴ M. E. Olvera-Martinez, J. Mendoza-Flores, F. J. Rodriguez-Gomez, M. E. Palomar-Pardave, J. Genesca, Effects of turbulent flow on the corrosion inhibition properties of 2-mercaptobenzimidazole, *Materials and Corrosion*, 64 (2013) 6, 522–529, doi:10.1002/maco.201106323
- ¹⁵ M. Yadav, D. Behera, S. Kumar, R. R. Sinha, Experimental and quantum chemical studies on the corrosion inhibition performance of benzimidazole derivatives for mild steel in HCl, *Industrial & Engineering Chemistry Research*, 52 (2013) 19, 6318–6328, doi:10.1021/ie400099q
- ¹⁶ P. Morales-Gil, M. S. Walczak, C. Ruiz Camargo, R. A. Cottis, J. M. Romero, R. Lindsay, Corrosion inhibition of carbon-steel with 2-mercaptobenzimidazole in hydrochloric acid, *Corrosion Science*, 101 (2015), 47–55, doi:10.1016/j.corsci.2015.08.032
- ¹⁷ G. Žerjav, I. Milošev, Corrosion protection of brasses and zinc in simulated urban rain. Part II. The combination of inhibitors benzotriazole and 2-mercaptobenzimidazole with stearic acid, *Materials and Corrosion*, 67 (2016) 1, 92–103, doi:10.1002/maco.201508384
- ¹⁸ K. F. Khaled, The inhibition of benzimidazole derivatives on corrosion of iron in 1 M HCl solutions, *Electrochimica Acta*, 48 (2003) 17, 2493–2503, doi:10.1016/S0013-4686(03)00291-3
- ¹⁹ P. Morales-Gil, M. S. Walczak, R. A. Cottis, J. M. Romero, R. Lindsay, Corrosion inhibitor binding in an acidic medium: Interaction of 2-mercaptobenzimidazole with carbon-steel in hydrochloric acid, *Corrosion Science*, 85 (2014), 109–114, doi:10.1016/j.corsci.2014.04.003
- ²⁰ K. F. Khaled, Experimental and computational investigations of corrosion and corrosion inhibition of iron in acid solutions, *Journal of Applied Electrochemistry*, 41 (2011) 3, 277–287, doi:10.1016/j.japsusc.2007.01.075

- ²¹ R. L. Camachomendoza, E. Gutiérrezmoreno, E. Guzmánper-cástegui, E. Aquinotorres, J. Cruzborbolla, J. A. Rodríguezávila, J. G. Alvaradorodríguez, O. Olveraneria, P. Thangarasu, J. L. Medina-Franco, DFT and electrochemical studies: Structure-efficiency relationship on corrosion inhibition, *J. Chem. Inf. Model.*, 267 (2015) 9, 6081–6085, doi:10.1021/acs.jcim.5b00385
- ²² O. Benali, L. Larabi, M. Traisnel, L. Gengembre, Y. Harek, Electrochemical, theoretical and XPS studies of 2-mercapto-1-methylimidazole adsorption on carbon steel in 1M HClO₄, *Applied Surface Science*, 253 (2007) 14, 6130–6139, doi:10.1016/j.apsusc.2007.01.075
- ²³ F. Bentiss, M. Lagrenee, M. Traisnel, Thermodynamic characterization of metal dissolution and inhibitor adsorption processes in mild steel/2,5-bis(n-thienyl)-1,3,4-thiadiazoles/hydrochloric acid system, *Corrosion Science*, 47 (2005) 12, 2915–2931, doi:10.1016/j.corsci.2005.05.034
- ²⁴ M. A. Migahed, I. F. Nassar, Corrosion inhibition of tubing steel during acidization of oil and gas wells, *Electrochimica Acta*, 53 (2008) 6, 2877–2882, doi:10.1016/j.electacta.2007.10.070
- ²⁵ F. Bentiss, M. Lagrenee, M. Traisnel, J. C. Hornez, The corrosion inhibition of mild steel in acidic media by a new triazole derivative, *Corrosion Science*, 41 (1999) 4, 789–803, doi:10.1016/S0010-938X(98)00153-X
- ²⁶ E. A. Flood, *The solid-gas interface*, Marcel Dekker, New York 1967, 1690
- ²⁷ S. Brunauer, P. H. Emmett, E. Teller, Adsorption of gases in multimolecular layers, *Journal of the American Chemical Society*, 60 (1938) 2, 309–319, doi:10.1021/ja01269a023
- ²⁸ B. B. Damaskin, O. A. Petrii, V. V. Batrakov, *Adsorption of Organic Compounds on Electrodes*, Plenum Press, New York 1971, 500
- ²⁹ P. Loganathan, R. G. Burau, Sorption of heavy metal ions by a hydrous manganese oxide, *Geochim. Geochimica et Cosmochimica Acta*, 37 (1973) 5, 1277–1293, doi:10.1016/0016-7037(73)90061-6
- ³⁰ R. Parsons, The electrical variable and the form of the isotherm for the adsorption of organic compounds at electrodes, *Journal of Electroanalytical Chemistry*, 8 (1964) 2, 93–98, doi:10.1016/0022-0728(64)87002-9
- ³¹ A. N. Frumkin, Electrocapillary curve of higher aliphatic acids and the state equation of the surface layer, *International Journal of Research in Physical Chemistry and Chemical Physics*, 116 (1925), 466–488
- ³² X. Li, S. Deng, G. Mu, H. Fu, F. Yang, Inhibition effect of nonionic surfactant on the corrosion of cold rolled steel in hydrochloric acid, *Corrosion Science*, 50 (2008) 2, 420–430, doi:10.1016/j.corsci.2007.08.014
- ³³ K. F. Khaled, M. M. Al-Qahtani, The inhibitive effect of some tetrazole derivatives towards Al corrosion in acid solution: Chemical, electrochemical and theoretical studies, *Materials Chemistry and Physics*, 113 (2009) 1, 150–158, doi:10.1016/j.matchemphys.2008.07.060
- ³⁴ Y. Qiang, S. Zhang, S. Xu, W. Li, Experimental and theoretical studies on the corrosion inhibition of copper by two indazole derivatives in 3.0 % NaCl solution, *Journal of Colloid and Interface Science*, 472 (2016), 52–59, doi:10.1016/j.jcis.2016.03.023
- ³⁵ H. H. Abdel-Rahman, A. M. Hafez, A. A. Helmy, Physicochemical study on the effectiveness of eco-friendly anti-corrosion agent on the corrosion of steel in H₃PO₄ solution, *Electrochemistry*, 83 (2015) 6, 440–444, doi:10.5796/electrochemistry.83.440
- ³⁶ F. M. Donahue, K. Nobe, Theory of organic corrosion inhibitors: Adsorption and linear free energy relationships, *Journal of The Electrochemical Society*, 112 (1965) 9, 886–891, doi:10.1149/1.2423723
- ³⁷ F. Touhami, A. Aouniti, Y. Abed, Hammouti, B. S. Kertit, A. Ramdani, K. Elkacemi, Corrosion inhibition of armco iron in 1 M HCl media by new bipyrazolic derivatives, *Corrosion Science*, 42 (2000) 6, 929–940, doi:10.1016/S0010-938X(99)00123-7
- ³⁸ M. H. Wahdan, A. A. Hermas, M. S. Morad, Corrosion inhibition of carbon-steels by propargyltriphenylphosphonium bromide in H₂SO₄ solution, *Materials Chemistry and Physics*, 76 (2002) 2, 111–118, doi:10.1016/S0254-0584(01)00526-0
- ³⁹ E. Khamis, F. Bellucci, R. Latanision, E. El-Ashry, Acid corrosion inhibition of nickel by 2-(triphenosporanylidene) succinic anhydride, *Corrosion*, 47 (1991) 9, 677–686, doi:10.5006/1.3585307
- ⁴⁰ S. Li, S. Chen, S. Lei, H. Ma, R. Yu, D. Liu, Investigation on some Schiff bases as HCl corrosion inhibitors for copper, *Corrosion Science*, 41 (1999) 7, 1273–1287, doi:10.1016/S0010-938X(98)00183-8