



Enhanced corrosion protection of mild steel in acidic media using *p*-bromopiperazinybenzene: An EIS study

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ABSTRACT

This study proposes the new use of *p*-bromopiperazinybenzene as an inhibitor for the corrosion of mild steel immersed in 1.0 M HCl solution by means of electrochemical impedance spectroscopy (EIS). Other traditional inhibitors may not contain bromine and nitrogen atoms which makes the structure of *p*-bromopiperazinybenzene to have better adsorption characteristics and high corrosion duty. Inhibitor concentration between 0.1 and 0.5 mM was studied for 5 h at 303 K and significant enhancement in polarization resistance (R_p) and decreased values of double-layer capacitance, CPE were recorded which reached 87 % when concentration of *p*-bromopiperazinybenzene was 0.5 mM. Data support the formation of a tightly bound protective coating on the mild steel surface that restricts the infiltrations of corrosion ions and thereby lowers corrosion rate. *p*-bromopiperazinybenzene is put forward as an industrially useful corrosion inhibitor that is effective at low concentration and can withstand acidic environments thereby opening new possibilities of tackling corrosion in difficult acidic environments.

1. Introduction

A great concern in the petroleum and chemical processing and manufacturing sectors, where hydrofluoric acid (HCl) is widely employed in cleaning, descaling and pickling processes, metal corrosion in hydrochloric acid environments is a challenge [1,2]. Due to its significant mechanical characteristics and low cost, mild steel is an attractive option; however, it is easily susceptible to corrosion in these acidic environments as well which results into the deterioration of the equipment, extra expenses on maintenance and safety concerns. To avoid these issues, various anticorrosion compounds are utilized that protect the metallic surface through providing layers which reduce the metal surface and corrosive environment contacts, preventing further damage and other consequences [3]. Heteroatom-containing organic corrosion inhibitors, nitrogen, sulfur, and oxygen-containing organic corrosion inhibitors, for example, can adsorb on metal surface and generate a protective layer which inhibits corrosion. Such inhibitors have the added benefit of being efficient at low concentrations and having broad structural modification capacity to enhance corrosion protection [4]. A

strong adsorption activity on metal surfaces is particularly noted for aromatic compounds containing π -electron systems and functional groups among organic inhibitors [5,6]. Furthermore, this absorption power is enhanced if the molecules contain electron donor atoms such as nitrogen and halogens that can bond to the metal surface resulting in increased stability of the formed layer that protects the steel surface. The literature has also identified the development of corrosion inhibitors that are effective and are free of environmental and human health hazards. Chromates, phosphates and other inorganic inhibitors work, but their toxicity and their resistance to biodegradation make them environmental hazards. Other organic inhibitors and especially those that are environmentally friendly and can be decomposed easily are now more popular since they minimize possible risk for environmental pollution and risk to human health [7,8]. For instance, recent studies on quinoline derivatives and 8-hydroxyl substituted quinolines, have suggested that these inhibitors are able to offer considerable protection to mild steel materials in acidic media, with low environmental impact [9,10].

However, many effective organic inhibitors are complex and expensive to manufacture, limiting their industrial applicability. There

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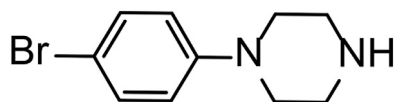


Fig. 1. Structure of tested anticorrosion compound.

is a development of simpler, more cost-effective, fast astatine-free and environmentally friendly inhibitors. The organic compound *p*-bromopiperazinyllbenzene containing nitrogen and bromine atoms has been presented in the research as a promising candidate that may meet these needs. Its molecular structure combines a brominated aromatic ring with nitrogen atoms which improves electron concentration and enhances surface absorption along the metal spike potentially casting a thin intact layer against corrosive agents. The novelty of the research lies in the use of *p*-bromopiperazinyllbenzene with double bond groups that provide enhanced adsorption potential due to both halogen and nitrogen atoms. The bromine particle increases the electron donor content of the compound, meaning that the nitrogen atoms return to the nucleus, creating a longer corrosion inhibiting effect. Compared to other organic inhibitors, *p*-bromopiperazinyllbenzene is expected to provide high inhibition yields at relatively low concentrations, potentially reducing the environmental and economic burden associated with high dose inhibitors. Additionally, the ease of extraction of the compound supports its accessibility and predictability for advanced applications, making it a viable and sustainable alternative for corrosion testing in acidic environments. In this investigation, we employee electrochemical impedance spectroscopy (EIS) to evaluate the corrosion suppression performance of para-bromopiperazinyllbenzene (Fig. 1) along the hydrochloric acid radical. By analyzing the EIS information across different concentrations, we evaluated the inhibitor's ability to create protective layers and enhance the mild steel resistance toward the corrosion. This research adds to the current efforts to provide cost-effective, eco-friendly, and effective anticorrosion compounds for advanced usages and provides a practical radical for corrosion mitigation in acidic environments.

2. Materials and methods

2.1. Materials

Mild steel coupons with a chemical composition of Fe (99.21 %), C (0.21 %), Si (0.38 %), P (0.09 %), S (0.05 %), Mn (0.05 %), and Al (0.01 %) were used. The coupons were polished with various emery papers (grades 400, 600, 1000), cleaned with acetone, rinsed with distilled water, and dried, following ASTM G1–03 standard for surface preparation. Acidic medium was 1.0 M HCl, and *p*-bromopiperazinyllbenzene was used as the anticorrosion compound. All chemicals were analytical grade and used without further purification.

2.2. Electrochemical impedance spectroscopy (EIS)

EIS was employee to investigate the efficient of *p*-bromopiperazinyllbenzene as anticorrosion compound on mild steel in 1.0 M HCl. A three-electrode setup was employed namely, a platinum counter electrode, working electrode (metallic coupon), and a saturated calomel reference electrode (SCE). Gamry Potentiostat/Galvanostat (Ref 600), was used to conducting the measurements and impedance spectra were recorded in the frequency range of 100 to 0.1 kHz with an AC perturbation of 5 mV at open-circuit potential (OCP). The inhibitive performance (IE%) was estimated [11–13] from the values of polarization resistance (R_p) through employee Eq. (1):

$$IE\% = \frac{R_{p(\text{inh})} - R_{p(\text{uninh})}}{R_{p(\text{inh})}} \times 100 \quad (1)$$

Table 1

Electrochemical impedance parameters for mild steel in 1.0 M HCl with different concentrations of *p*-bromopiperazinyllbenzene.

Conc. (mM)	R_p ($\Omega \text{ cm}^2$)	R_s ($\Omega \text{ cm}^2$)	CPE ($\text{s}^n \Omega^{-1} \text{ cm}^2$)	IE (%)
0	52.4	1.53	548.3	–
0.1	151.6	1.61	473.5	65.4
0.2	222.1	1.65	266.5	76.5
0.3	289.6	1.66	191.4	81.9
0.4	366.5	1.69	172.3	85.7
0.5	397.7	1.71	149.5	87.0

where $R_{p(\text{inh})}$ and $R_{p(\text{uninh})}$ used in the presence and absence of the anticorrosion compound, respectively.

3. Results and discussion

3.1. Electrochemical impedance spectroscopy (EIS) techniques

Electrochemical Impedance Spectroscopy (EIS) was employed to investigate the corrosion inhibition properties of *p*-bromopiperazinyllbenzene on mild steel in a 1.0 M HCl solution. The results are presented in Table 1 and visualized in the Nyquist plots in Fig. 2a. The Nyquist plots show depressed semicircles at various concentrations of the inhibitor, with increasing diameters as the concentration of *p*-bromopiperazinyllbenzene increases, indicating enhanced corrosion inhibition [14,15].

The equivalent circuit model used to analyze EIS data is depicted in Fig. 2b. This model includes:

- R_s (**Solution Resistance**): Solution resistance, representing the resistance of the HCl electrolyte.
- R_p (**Polarization Resistance**): Polarization resistance, which includes charge transfer resistance (R_{ct}), film resistance (R_f), and other resistive contributions at the metal/electrolyte interface.
- CPE (**Constant Phase Element**): Represents the non-ideal capacitive behavior of the double-layer capacitance, accounting for surface roughness and heterogeneity.

In this model, the diameter of the Nyquist semicircles corresponds to the overall polarization resistance (R_p), which encapsulates not only the charge transfer resistance (R_{ct}) but also other resistive components such as the film resistance (R_{pf}) formed by the adsorbed inhibitor molecules, and the resistance of the diffuse layer. This approach provides a more accurate representation of the corrosion inhibition mechanism, as the protective layer formed by the inhibitor is expected to contribute significantly to the impedance response [16–19].

As shown in Table 1, the values of R_p increase substantially with the addition of *p*-bromopiperazinyllbenzene, indicating effective corrosion inhibition. Without the inhibitor (0 mM), the polarization resistance is relatively low, suggesting rapid corrosion in the acidic solution. However, with increasing concentrations of *p*-bromopiperazinyllbenzene, R_p increases markedly, reflecting the development of a protective film that hinders the corrosion process. This increments in R_p confirms that *p*-bromopiperazinyllbenzene forms an effective barrier protect the mild steel, which restricts the interactions between the metallic surface and the corrosive ions inside the HCl solution. At the optimum inhibitor concentration (0.5 mM), the polarization resistance reaches a maximum, demonstrating that the inhibitor has effectively reduced the corrosion rate through adsorption and film formation. The significant increase in R_p with concentration supports the belief that *p*-bromopiperazinyllbenzene is rather powerful in defensive metallic surfaces in acidic media.

The decrease in constant phase element (CPE) values, demonstrated in Table 1, further supports the a protective layer formation by the tested inhibitor molecules. As the concentration of *p*-bromopiperazinyllbenzene increases, the CPE values lower, indicating

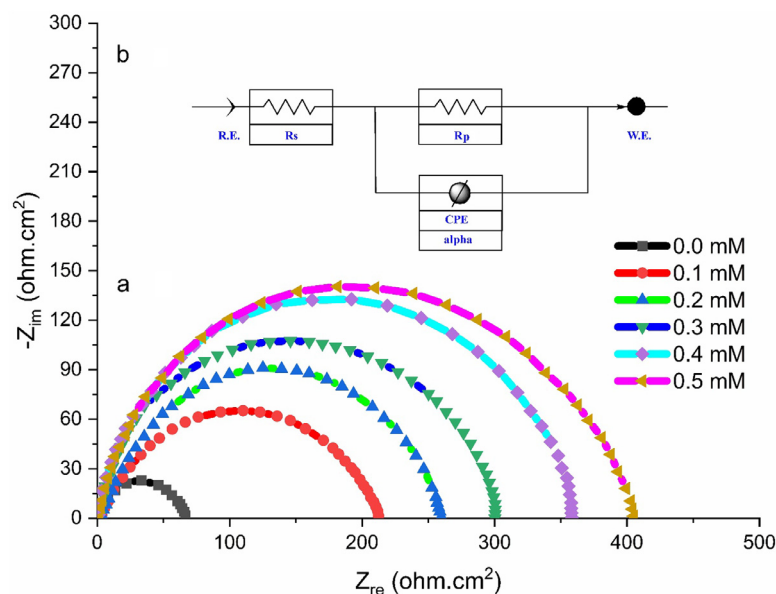


Fig. 2. Nyquist plots for mild steel in 1.0 M HCl in the absence and presence of different concentrations of *p*-bromopiperazinybenzene. (a) Nyquist plots at varying inhibitor concentrations; (b) Equivalent electrical circuit model.

a decrease within the effective double-layer capacitance (C_{dl}). This decrease is attributed to the replacement of water molecules and other ions at the metal surface by means of the inhibitor molecules, efficiently growing the thickness of the double layer and reducing the surface area to be had for electrochemical reactions. The decrease CPE values at higher inhibitor concentrations propose that the inhibitor forms a stable dense adsorbed film, which prevents competitive chloride ions from gaining access to the metallic surface. This film not just blocks active corrosion sites however also modifies the metal/electrolyte interface properties, contributing to the increased polarization resistance (R_p) located inside the Nyquist plots [20–24].

The elongations observed at low frequencies in the Nyquist plots indicate accumulations that are characteristic of the adsorption behavior of inhibitors on the metal surface. These elongates refer to the presence of more resistive parameters that go after the transfer of simple charging, such as the resistance of the protecting film and the resistance inside the diffuse layer. The function of those factors is significant in information about the inhibitor's protective mechanism, as they highlight the complex, multilayered nature of the barrier formed by using *p*-bromopiperazinybenzene.

The Inhibition efficacy is increased in the presence of *p*-bromopiperazinybenzene as corrosion inhibitor, estimated on the basis of R_p , with concentration. The inhibitive efficacy at inhibitor concentration 0.1 mM, was 65.4 % which indicated great protection even with low concentrations. As concentration increases, efficiency reaches 87.0 % at 0.5 mM. This concentration-dependent behavior confirms that *p*-bromopiperazinybenzene adsorbs onto the steel surface at low concentrations and improves protection as more molecules cover the surface.

The EIS data indicates that *p*-bromopiperazinybenzene acts as an effective corrosion inhibitor by forming a stable, adsorbed protective film on the mild steel surface. The detected increase in R_p value and decrease in CPE with increasing inhibitor concentration underscore the inhibitor's functionality to reduce corrosion through blocking energetic sites and proscribing the penetration of corrosive ions. This complex mechanism of protection indicates that *p*-bromopiperazinybenzene is a promising inhibitor for acidic media, providing efficient and stable corrosion resistance for metals.

3.2. Adsorption isotherm and thermodynamic analysis

To understand the adsorption behavior of *p*-bromopiperazinybenzene on the mild steel surface, the Langmuir

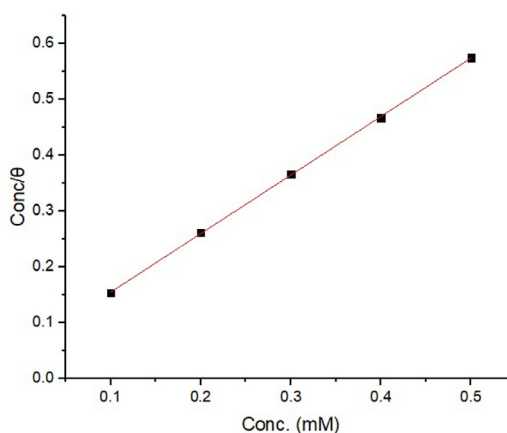


Fig. 3. Plot of Langmuir adsorption isotherm tested anticorrosion compound on steel surface in 1.0 M HCl solution.

adsorption isotherm was applied. The Langmuir isotherm assumes monolayer adsorption on a homogeneous surface without interactions between adsorbed species. The isotherm is represented by the following Eq. (2):

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (2)$$

where: C is the concentration of the inhibitor in the solution (mM), θ is the surface coverage of the inhibitor, and K is the adsorption equilibrium constant, representing the affinity of the inhibitor for the metal surface.

By plotting C/θ versus C , a straight line was obtained, as shown in Fig. 3. The linear relationship with an R^2 value of 0.9997 confirms that the adsorption of *p*-bromopiperazinybenzene on mild steel follows the Langmuir adsorption isotherm model. The Gibbs free energy of adsorption (ΔG_{ads}^0) was calculated to understand the spontaneity and nature of the adsorption process. Eq. (3) was used:

$$\Delta G_{ads}^0 = -RT \ln (55.5 \times K) \quad (3)$$

where: R is the gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), T is the temperature in Kelvin (303 K), and 55.5 is the concentration of water in mol/L, representing the solvent effect.

The negative value of ΔG_{ads}^0 indicates that the adsorption of *p*-bromopiperazinybenzene onto the mild steel surface is spontaneous. Since the value is around -20 kJ/mol , this suggests that the adsorp-

tion mechanism likely involves physisorption with some degree of chemisorption, supporting the formation of a stable protective film that enhances corrosion resistance. The adsorption study confirms that *p*-bromopiperazinylbenzene strongly and spontaneously adsorbs onto the mild steel surface, following a Langmuir adsorption isotherm. The high *K* value and negative ΔG_{ads}^0 suggest that *p*-bromopiperazinylbenzene forms an effective protective layer on the steel surface, making it a suitable corrosion inhibitor for acidic environments

4. Conclusion

In conclusion, the current investigation shows that the *p*-bromopiperazinylbenzene is an efficient inhibitor for steel in a 1.0 M HCl medium. Employee the analysis of the electrochemical impedance (EIS), the performance of the barrier has been assessed through different inhibitor concentrations, showing its ability to increase the corrosion resistance significantly. Protective film formations on the metallic surface, as it becomes clear from the increased polarization resistance (RP) and the decrease in CPE, plays a decisive role in its inhibition mechanism. It is worth noting that the *p*-bromopiperazinylbenzene provides great protection from corrosion even in low concentrations, which highlights its capabilities for industrial applications where reducing the use of the barrier is desirable in it. The following points summarize the main results:

- *p*-Bromopiperazinylbenzene showed high inhibition efficiency, reaching 87.0 % at a concentration of 0.5 mM in 1.0 M HCl solution.
- EIS analysis revealed an increase in R_p and a decrease in CPE indicating the formation of a protective film that effectively blocks corrosive ions.
- The inhibitor provided effective corrosion protection even at lower concentrations, achieving 65.4 % efficiency at 0.1 mM.
- The concentration-dependent inhibition efficiency suggests that *p*-bromopiperazinylbenzene can be a cost-effective option for corrosion control.
- With its high efficiency at relatively low concentrations, *p*-bromopiperazinylbenzene is a promising candidate for industrial applications in acidic environments.

CRediT authorship contribution statement

Mohanad Muzahem Khalaf: Formal analysis, Data curation, Conceptualization. **Muzher Taha Mohamed:** Methodology, Investigation, Funding acquisition. **M.M. Hanoon:** Resources, Supervision, Validation. **A.A. Khadom:** Software, Investigation, Formal analysis, Data curation. **F.F. Sayyid:** Methodology, Funding acquisition, Conceptualization. **A.M. Mustafa:** Visualization, Validation, Project administration, Methodology. **Ahmed A. Al-Amiery:** Writing – review & editing, Supervision.

Conflict of interest

Ahmed A. Al-Amiery reports financial support was provided by Al-Ayen University. Ahmed A. Al-Amiery also reports a relationship with Al-Ayen University that includes funding grants. Additionally, Ahmed A. Al-Amiery has a grant code registered under AUIQ-RFP2024-CI. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Clinical trial declaration

No clinical trial was conducted as part of this manuscript.

Data availability

The data supporting the findings of this study are available within the manuscript. Additional data may be available upon request from the corresponding author.

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Declaration of interests

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Ahmed A. Al-Amiery reports financial support was provided by Al-Ayen University. Ahmed A. Al-Amiery also reports a relationship with Al-Ayen University that includes funding grants. Additionally, Ahmed A. Al-Amiery has a grant code registered under AUIQ-RFP2024-CI. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. AAlamiery-664

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