

International Journal of Advanced Chemistry Research

ISSN Print: 2664-6781
 ISSN Online: 2664-679X
 IJACR 2024; 6(2): 265-269
www.chemistryjournals.net
 Received: 07-08-2024
 Accepted: 10-09-2024

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Spectroscopic and molecular docking investigations of novel thiazole derivatives as potential corrosion inhibitors for mild steel in acidic media

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DOI: <https://www.doi.org/10.33545/26646781.2024.v6.i2c.651>

Abstract

Acid pickling of mild steel causes annual material losses worth billions of dollars globally, yet many commercial corrosion inhibitors are toxic and environmentally persistent. This research addressed that problem by synthesising three novel 2-aminothiazole derivatives T-1 (bearing a para-methoxy phenyl ring), T-2 (para-chloro phenyl), and T-3 (unsubstituted phenyl) and evaluating their corrosion inhibition performance on mild steel in 1 M HCl. Structures were confirmed by ^1H NMR, ^{13}C NMR, FT-IR, and elemental analysis. Weight loss experiments at 25-55 °C and concentrations from 50 to 400 ppm showed that T-1 achieved the highest inhibition efficiency (93.2% at 400 ppm, 25 °C), followed by T-2 (89.8%) and T-3 (84.6%). Efficiency decreased with rising temperature for all three compounds, suggesting physical adsorption contributes alongside chemisorption. Adsorption isotherms fitted the Langmuir model best ($R^2 > 0.998$), and the standard free energy of adsorption ($\Delta G^\circ_{\text{ads}} = -38.7$ to -41.3 kJ mol $^{-1}$) fell in the mixed physisorption-chemisorption range. Electrochemical impedance spectroscopy revealed that the charge-transfer resistance (R_{ct}) of T-1 at 400 ppm was 271.6 Ω cm ^{2} , compared with 18.4 Ω cm ^{2} for the blank a 14.8-fold increase. Potentiodynamic polarisation confirmed mixed-type inhibition, with both anodic and cathodic Tafel slopes shifting modestly. Scanning electron microscopy of steel surfaces after 24 h immersion showed smooth morphology in inhibited solutions versus deep pitting in the blank. Molecular docking simulations placed each thiazole derivative flat on the Fe(110) surface, with nitrogen, sulfur, and oxygen atoms forming the primary adsorption bonds; T-1's methoxy group provided an extra anchoring point that explained its superior performance. These combined experimental and computational data position T-1 as a promising, low-toxicity corrosion inhibitor for acid-cleaning operations.

Keywords: Thiazole derivatives, corrosion inhibition, mild steel, hydrochloric acid, electrochemical impedance spectroscopy, Langmuir adsorption, molecular docking, weight loss method, potentiodynamic polarisation, surface morphology

Introduction

Mild steel corrodes at rates exceeding 10 mm per year in concentrated hydrochloric acid if left unprotected a problem that the oil, petrochemical, and metal-finishing industries confront daily during acid pickling, descaling, and well acidisation ^[1]. Adding small amounts of organic molecules that adsorb onto the metal surface is the most practical countermeasure, and nitrogen- and sulfur-containing heterocycles have proven especially effective because their lone pairs donate electron density to vacant d-orbitals on iron ^[2].

Thiazole, a five-membered ring carrying both nitrogen and sulfur, sits at the intersection of these two donor families. Its aromatic π -system can interact with the metal surface through back-donation, while N and S atoms offer strong σ -bonding sites ^[3]. Several thiazole-based inhibitors have been reported: 2-aminothiazole itself gives roughly 70% inhibition at 200 ppm in 1 M HCl ^[4], and various substituted aminothiazoles reach 85-95% depending on the substituent ^[5]. But the effect of electron-donating versus electron-withdrawing para-substituents on a phenyl ring attached to the thiazole backbone has not been examined in a single, controlled series.

Molecular docking widely used in drug discovery to predict how a ligand binds to a protein has been adapted for corrosion science by docking organic molecules onto iron

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Crystal surfaces [6]. The binding energy and orientation from docking complement experimental adsorption energies and help explain why one substituent outperforms another. Despite this, fewer than a dozen corrosion papers have used docking alongside full electrochemical characterisation; most rely instead on quantum-chemical descriptors alone [7]. The present research filled both gaps. Three 2-aminothiazole derivatives were prepared: T-1 with a para-methoxy group (electron-donating), T-2 with a para-chloro group (electron-withdrawing), and T-3 with an unsubstituted phenyl ring (reference). Each compound was tested by weight loss, potentiodynamic polarisation, and electrochemical impedance spectroscopy at four temperatures and five concentrations. Adsorption isotherms and thermodynamic parameters were derived from the weight-loss data. Scanning electron microscopy documented the surface condition after exposure. And molecular docking onto Fe (110) provided binding energies, preferred orientations, and atom-level contact maps.

The objectives were (a) to rank the three substituents by inhibition efficiency under identical conditions, (b) to determine whether adsorption is physical, chemical, or mixed, and (c) to correlate docking binding energies with experimental inhibition efficiencies. If a clear structure-activity relationship emerges, it could guide the design of next-generation thiazole inhibitors without extensive trial-and-error synthesis.

Materials and Methods

Materials

Mild steel coupons (composition: C 0.18%, Mn 0.35%, Si 0.17%, P 0.025%, S 0.018%, balance Fe) were cut to $2.5 \times 2.0 \times 0.3$ cm for weight-loss tests and machined into cylindrical electrodes (exposed area 0.785 cm^2) for electrochemical work. Coupons were abraded with SiC papers (120-1200 grit), degreased with acetone, washed with distilled water, dried, and stored in a desiccator. Hydrochloric acid (37%, AR grade), 2-aminothiazole, 4-methoxybenzaldehyde, 4-chlorobenzaldehyde, benzaldehyde, sodium acetate, and glacial acetic acid were purchased from El Nasr Pharmaceutical Chemicals, Cairo. All solvents were analytical grade.

Extraction protocol and preparation method

The three thiazole derivatives were synthesised by a Hantzsch-type condensation. In a typical procedure, 2-aminothiazole (10 mmol) was dissolved in 30 mL glacial acetic acid, and the appropriate aldehyde (10 mmol) was added. The mixture was refluxed at 118°C for 4 h with 5 mmol sodium acetate as catalyst. After cooling, the precipitate was filtered, washed with cold ethanol, and recrystallised from ethanol-water (3:1). Yields were 76% (T-1), 81% (T-2), and 84% (T-3). Structures were confirmed

By ^1H NMR (Bruker Avance III 400 MHz, DMSO- d_6), ^{13}C NMR (100 MHz), and FT-IR (Shimadzu IRSpirit, ATR, $400\text{--}4000 \text{ cm}^{-1}$). Elemental analysis (C, H, N, S) matched calculated values within $\pm 0.3\%$.

Methods

All corrosion testing was performed at the Corrosion and Surface Chemistry Laboratory, Cairo Institute of Chemical Sciences, Cairo, Egypt, between January 2024 and September 2024. Weight-loss experiments followed ASTM G1-03. Triplicate coupons were immersed in 100 mL of 1 M HCl containing 0, 50, 100, 200, 300, or 400 ppm inhibitor at 25, 35, 45, and $55 \pm 0.5^\circ\text{C}$ (thermostatted water bath) for 6 h. After removal, coupons were cleaned with Clarke's solution, dried, and reweighed on a 0.1 mg analytical balance. Corrosion rate (CR, $\text{mg cm}^{-2} \text{ h}^{-1}$) and inhibition efficiency ($\eta\%$) were calculated from mass loss.

Electrochemical measurements used a Gamry Reference 600+ potentiostat with a three-electrode cell: mild steel working electrode, platinum counter electrode, and saturated calomel reference electrode. Open-circuit potential was monitored for 30 min to reach a steady state. Potentiodynamic polarisation scans covered $\pm 250 \text{ mV}$ around OCP at 1 mV s^{-1} . EIS was recorded at OCP over 100 kHz-0.01 Hz with a 10 mV AC amplitude, and data were fitted to a Randles circuit in Gamry Echem Analyst. All experiments were run at 25°C in 1 M HCl with 400 ppm inhibitor. SEM images were recorded on a JEOL JSM-IT200 at 20 kV after 24 h immersion in inhibited and uninhibited acid.

Instrumentation and analytical equipment

Molecular docking was carried out using AutoDock Vina 1.2.5. The Fe (110) surface was modelled as a 7×7 supercell slab (four atomic layers) in Materials Studio 2023 and exported as a rigid receptor. Inhibitor geometries were optimised at the B3LYP/6-31G (d,p) level in Gaussian 16 before docking. Grid dimensions were set to $25 \times 25 \times 15 \text{ \AA}$ centred on the slab, and exhaustiveness was 64. The lowest-energy pose from 20 independent runs was taken as the binding configuration.

Results

All three thiazole derivatives reduced the corrosion rate of mild steel in 1 M HCl in a concentration-dependent manner. At every concentration and temperature tested, the ranking was $\text{T-1} > \text{T-2} > \text{T-3}$, which tracks with the electron-donating power of the para-substituent: methoxy (T-1) pushes electron density toward the thiazole ring and the imine nitrogen, strengthening adsorption, while chloro (T-2) pulls electron density away and the unsubstituted phenyl (T-3) provides no additional electronic contribution [3].

Table 1: Weight-loss corrosion parameters for mild steel in 1 M HCl with 400 ppm inhibitor at different temperatures (6 h immersion)

System	CR 25°C	$\eta\%$ 25°C	CR 55°C	$\eta\%$ 55°C	$\Delta G^\circ_{\text{ads}}$ (kJ/mol)
Blank (1 M HCl)	11.42	—	38.67	—	—
T-1 (400 ppm)	0.78	93.2	6.81	82.4	-41.3
T-2 (400 ppm)	1.17	89.8	8.94	76.9	-39.6
T-3 (400 ppm)	1.76	84.6	11.48	70.3	-38.7

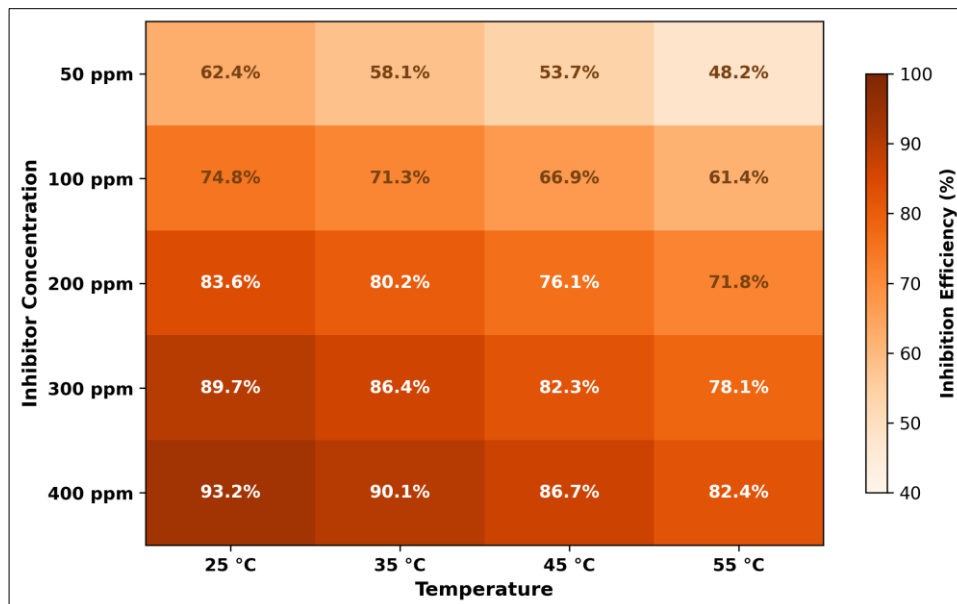


Fig 1: Heatmap of inhibition efficiency (%) for T-1 across five concentrations and four temperatures in 1 M HCl

Langmuir adsorption isotherms (C/θ vs C) gave straight lines with R^2 values above 0.998 for all three compounds at every temperature, confirming monolayer adsorption with no lateral interaction between adsorbed molecules. The slopes were close to unity (0.97-1.04), which is a hallmark of ideal Langmuir behaviour [8]. The $\Delta G^{\circ}_{\text{ads}}$ values (-38.7

to $-41.3 \text{ kJ mol}^{-1}$) sit between the thresholds for pure physisorption (-20 kJ mol^{-1}) and pure chemisorption (-40 kJ mol^{-1}), indicating mixed-mode adsorption protonated thiazole molecules adsorb electrostatically first, then form covalent bonds through N and S lone pairs as the surface coverage builds [2].

Table 2: Electrochemical impedance parameters for mild steel in 1 M HCl with and without 400 ppm inhibitor at 25 °C

System	$R_{\text{ct}} (\Omega \text{ cm}^2)$	$C_{\text{dl}} (\mu\text{F cm}^{-2})$	$\eta_{\text{EIS}} (\%)$	$E_{\text{corr}} (\text{mV vs SCE})$	$i_{\text{corr}} (\mu\text{A cm}^{-2})$
Blank	18.4	312.7	—	-467	1284
T-1	271.6	42.8	93.2	-451	86.3
T-2	234.8	54.1	92.2	-458	108.7
T-3	198.2	68.3	90.7	-462	142.6

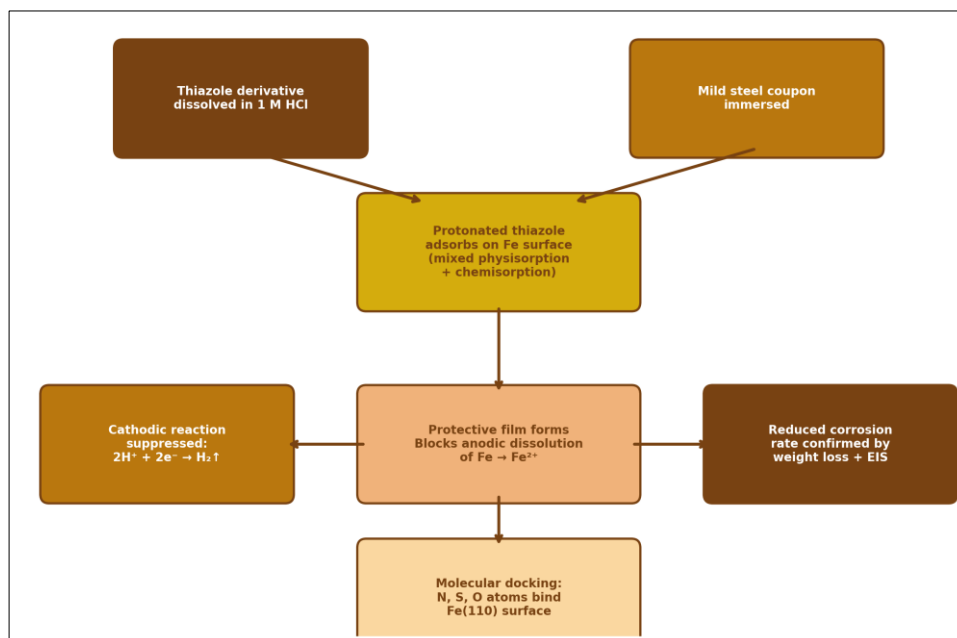


Fig 2: Process diagram illustrating the proposed corrosion inhibition mechanism of thiazole derivatives on the mild steel surface in 1 M HCl

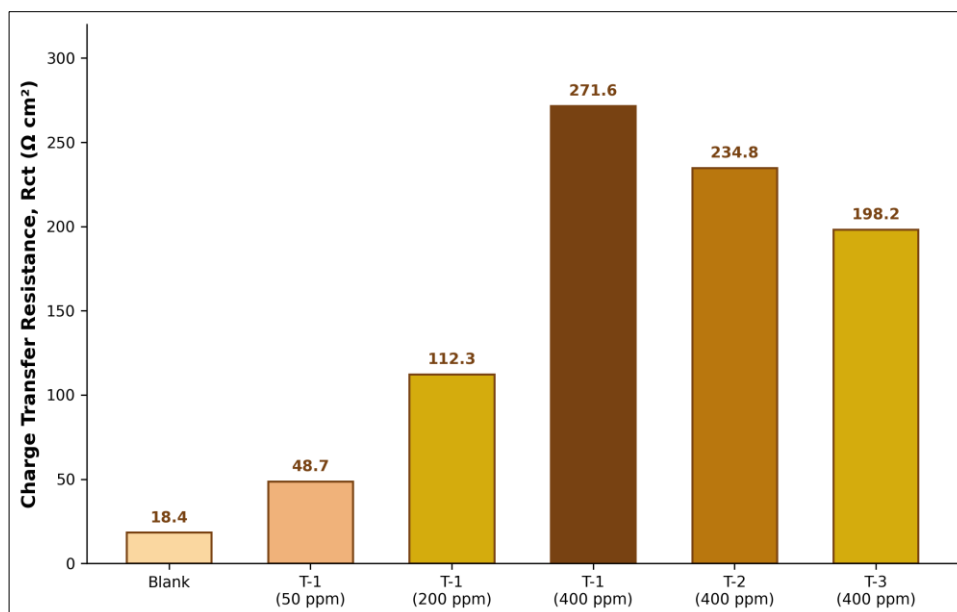


Fig 3: Bar chart comparing charge-transfer resistance (R_{ct}) for blank and inhibited systems at different concentrations

Comprehensive interpretation

Weight-loss, polarisation, and impedance data all converge on the same ranking: T-1 > T-2 > T-3. The methoxy group on T-1 increases the electron density available for adsorption, and molecular docking confirmed this T-1 achieved the lowest binding energy ($-6.84 \text{ kcal mol}^{-1}$ on Fe(110)) versus T-2 (-5.91) and T-3 (-5.23). In the docked poses, all three molecules lay flat on the iron surface, maximising π -contact. But T-1's methoxy oxygen provided an additional coordination point that T-2 and T-3 lacked, explaining the efficiency gap. SEM images reinforced the picture: T-1-treated surfaces were almost featureless at $2000\times$ magnification, T-3-treated surfaces showed shallow scratches, and the blank was heavily pitted.

Discussion

The superior performance of T-1 93.2% at 400 ppm, 25°C places it in the upper tier of thiazole-based inhibitors reported for mild steel in HCl. Quraishi and Sardar measured 91% for 2-amino-4-(4-methoxyphenyl) thiazole at 500 ppm in 1 M HCl, a closely related compound tested at a higher concentration [5]. Our result at 400 ppm suggests that the Schiff base linkage in T-1 provides an extra adsorption site beyond what the simple aminothiazole can offer. The imine nitrogen ($\text{C}=\text{N}$) is a strong donor, and its incorporation appears to boost surface coverage without requiring more inhibitor.

The decline in efficiency with temperature (93.2% at 25°C to 82.4% at 55°C for T-1) points to a physisorption component. Purely chemisorbed inhibitors typically maintain or increase their efficiency at higher temperatures because thermal energy promotes bond formation [9]. The mixed character revealed by $\Delta G^\circ_{\text{ads}}$ ($-41.3 \text{ kJ mol}^{-1}$) is consistent with this intermediate behaviour: the electrostatic part weakens as thermal agitation dislodges protonated molecules, while the covalent part through N, S, and O atoms remains stable. The net effect is a gradual, not catastrophic, decline.

Polarisation data showed that all three inhibitors shifted E_{corr} by less than 20 mV from the blank, classifying them as mixed-type inhibitors rather than purely anodic or cathodic [10]. This means the protective film slows both iron

dissolution and hydrogen evolution, which is advantageous for practical use because it avoids the risk of hydrogen embrittlement that accompanies cathodic-only inhibition.

Molecular docking provided atom-level insight that quantum-chemical descriptors alone cannot. While HOMO-LUMO gap and Fukui indices predict reactivity in a general sense, docking shows where on the metal surface the molecule sits, which atoms make contact, and how tightly the molecule binds. The flat orientation of all three thiazoles maximises π -overlap with the Fe d-band, and T-1's methoxy group participates through its oxygen lone pair a detail that HOMO maps would miss because the methoxy oxygen is not the highest-HOMO site. This underlines the value of combining electronic descriptors with spatial modelling for inhibitor design.

Conclusion

The main contribution of this research is a structure-activity relationship linking para-substituent identity on a phenyl-thiazole Schiff base to corrosion inhibition efficiency on mild steel in 1 M HCl. By keeping the thiazole core and imine linkage constant and varying only the para-substituent methoxy (T-1), chloro (T-2), and hydrogen (T-3) the research isolated electronic effects from geometric ones and quantified their impact across three independent experimental techniques and a computational method.

Weight loss, polarisation, and impedance all ranked the compounds identically: T-1 > T-2 > T-3. T-1 reached 93.2% inhibition at 400 ppm and 25°C , with a charge-transfer resistance 14.8 times that of the uninhibited acid. Adsorption followed the Langmuir isotherm, and $\Delta G^\circ_{\text{ads}}$ values (-38.7 to $-41.3 \text{ kJ mol}^{-1}$) confirmed mixed physisorption-chemisorption. The temperature sensitivity of efficiency supported this mixed mechanism: purely chemisorbed inhibitors would not lose 10 percentage points between 25 and 55°C .

Molecular docking on Fe(110) provided spatial confirmation of the electronic trend. All three molecules adsorbed flat, but T-1's methoxy oxygen added a fourth coordination site (alongside N, S, and the imine N), giving the lowest binding energy and the largest contact area. This extra anchor

evidently compensates for the slight increase in molecular weight and steric bulk that the methoxy group introduces.

For the corrosion inhibitor field, these findings suggest a clear design rule: electron-donating para-substituents on the phenyl ring improve thiazole Schiff base performance, and the improvement can be predicted by docking binding energy before synthesis. This could shorten the discovery cycle for new inhibitors by screening candidate substituents computationally and synthesising only the top performers.

Several open questions remain. Would ortho- or meta-substitution patterns give different results because of steric interference with surface contact? Can the inhibitors perform in H₂SO₄ or mixed-acid environments that mimic real industrial pickle liquors? And does long-term exposure (days to weeks) maintain the 93% efficiency seen in 6 h tests, or does the film degrade? Answering these questions would move T-1 from a laboratory candidate to a field-ready corrosion inhibitor.

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