



The Synthesis and Inhibitory Action of Some amido carboxylic acids on Mild Steel Corrosion Protection in Hydrochloric Acid

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Abstract

Mild steel has been utilized in a variety of applications, including reaction vessels, tanks, and other structures, however the fundamental issue with this material is that it is quickly impacted by corrosive solutions. We tried to solve this problem by producing new inhibitors. From the interaction of benzoic acid derivatives and aminoacetophenone with various quinazoline derivatives, a range of amido carboxylic acids have been produced. The corrosion inhibition capabilities of the novel compounds for mild steel corrosion in HCl solution were examined. The results of these techniques showed that increasing the concentration of inhibitor and reducing the temperature boosted inhibition efficiency. From data acquired at various temperatures, some thermodynamic parameters were derived and discussed for the examined systems. Using 1000 ppm of the newly synthesised derivative, around 94 percent inhibitory efficiency was determined. According to the polarization data, the newly synthesized compounds exhibit a mixed inhibitory effect. The Langmuir isotherm was determined to be the best fit for representing the inhibitor's adsorption behaviour.

Keywords: potentiodynamic polarization, quinazoline derivatives, nitrogen nucleophiles, steel, HCl.

1. Introduction

Hydrochloric acid is utilised in a variety of procedures, including iron pickling, chemical cleaning, boiler descaling, and oil well acidification in petroleum exploration. One of the most practical strategies for corrosion protection of metallic objects in acidic environments, as well as reducing acid consumption during corrosion, is the employment of inhibitors. Metal and alloy corrosion is a critical topic that has a significant impact on both the economics and safety. Steel is widely employed in factories, machines, and a variety of other disciplines [1]. The effectiveness of an organic compound as an inhibitor is determined by its capacity to adsorb on the metal surface by substituting water molecules [2]. In general, compounds containing heteroatoms such as O, N, S, and P have been proven to be particularly good corrosion inhibitors. The efficacy of these compounds is

determined by the electron density around the heteroatoms, the number of adsorption active centres in the molecule and their charge density, the molecule size, mode of adsorption, and the formation of metallic complexes [3-19] Furthermore, the influence of temperature on steel electrode dissolution, inhibition of steel electrode, and inhibition effectiveness of the employed compounds were investigated.

2. Experimental Techniques

2.1. Instrumentation

Polarization and potentiostatic devices were used for preliminary anticorrosive character investigations. A three-compartment containing a mild metal rod as a working electrode, a platinum counter electrode, and a saturated calomel electrode as a reference electrode was used for these studies.

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Receive Date: 17 August 2022, Revise Date: 24 May 2023, Accept Date: 29 August 2022.

DOI: [10.21608/EJCHEM.2022.156862.6802](https://doi.org/10.21608/EJCHEM.2022.156862.6802)

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The voltage was scanned from -0.6 to 0.6 Volts at a rate of 10 mVS⁻¹, and the mild steel employed as the working electrode had an exposure area of 1 cm²

before being submerged in a new sample of hydrochloric acid.

Table 1 Chemical composition of mild steel

Element	Mn	C	Cr	P	Si	S	Fe	Ni
Weight%	0.495	0.158	0.047	0.060	0.157	0.062	rest	0.006

The metal surfaces were abraded with several grades of papers (1200 - 2000), then degreased with AR-grade acetone, washed with deionized water, and immersed in the test solution, according to the tests.

Tafel curve extrapolation was used to identify parameters such as corrosion potential (*E*_{corr}) and corrosion current density (*I*_{corr}).

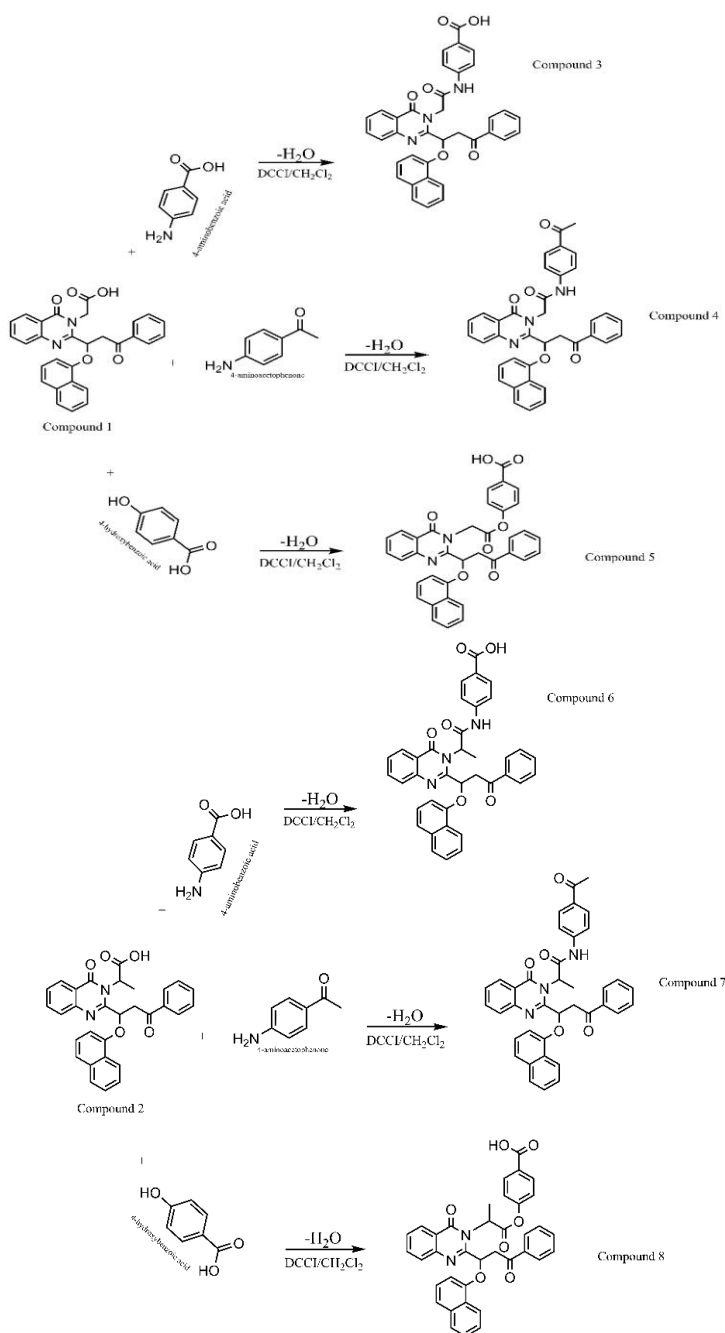
The melting points were not adjusted. A Perkin Elmer 298 spectrophotometer was used to record IR spectra in KBr. ¹HNMR spectra were collected using a Varian Gemini 200 MHz instrument with TMS as an internal reference, with chemical shifts given in ppm. The mass spectra were captured using a Shimadzu GCMS-QP 1000 EX instrument (70 eV EI mode).

2.2. Chemicals

EL Nasr co. Egypt supplied pyridine, acetic anhydride, and benzene, while BDH co. England supplied glycine, hydrazine hydrate, hydroxylamine hydrochloride, and alanine.

2.3. Synthesis of Amido carboxylic acids

The synthesis of the compounds is performed by reaction of compounds 2-(2-(1-(naphthalen-1-yloxy)-3-oxo-3-phenylpropyl)-4-oxoquinazolin-3(4H)-yl)acetic acid (compound 1) and 2-(2-(1-(naphthalen-1-yloxy)-3-oxo-3-phenylpropyl)-4-oxoquinazolin-3(4H)-yl)propanoic acid (compound 2) with 4-aminobenzoic acid, 4-aminoacetophenone and 4-hydroxybenzoic acid in the presence of (0.01 mol) N,N-dicyclohexylcarbodiimide (DCCI) and methylene chloride (50 ml) the reactions mixture was found in ice bath and stirred for 8 hrs. The formed solid was filtrated to remove methylene chloride to give compounds (3-8)



Scheme 1 Reactions of compound 2

3. Results and Discussion

3.1. FTIR explanation

FT-IR spectrum of compound (3): 3368 cm^{-1} (N-H), 3029 cm^{-1} (aromatic C-H), 2925 cm^{-1} (aliphatic C-H), 1658 cm^{-1} (C = O of carbonyl amide).

FT-IR spectrum of compound (4): 3441 cm^{-1} (N - H), 3057 cm^{-1} (aromatic C - H), 2926 cm^{-1} (aliphatic C - H), 1657 cm^{-1} (C = O of carbonyl amide), 1628 cm^{-1} (C = O), 1442 cm^{-1} (CH_3 symmetrical bending).

FT-IR spectrum of compound (5): 3402 cm^{-1} (O - H), 3062 cm^{-1} (aromatic C - H), 2928 cm^{-1} (aliphatic C - H), 1687 cm^{-1} (C = O of carbonyl ester).

FT-IR spectrum of compound (6): 3428 cm^{-1} (N - H), 3060 cm^{-1} (aromatic C - H), 2926 cm^{-1} (aliphatic C - H), 1619 cm^{-1} (C = O of carbonyl amide).

FT-IR spectrum of compound (7): 3364 cm^{-1} (N - H), 3058 cm^{-1} (aromatic C - H), 2927 cm^{-1} (aliphatic C - H), 1627 cm^{-1} (C = O of carbonyl amide), 1592 cm^{-1} (C = O), 1444 cm^{-1} (CH_3 symmetrical bending).

FT-IR spectrum of compound (8): 3407 cm^{-1} (O - H), 3063 cm^{-1} (aromatic C - H), 2927 cm^{-1} (aliphatic C - H), 1681 cm^{-1} (C = O of carbonyl amide), 1615 cm^{-1} (C = O).

3.2. ^1H NMR explanation

Compound 4 ^1H NMR δ (ppm): 2.3 – 2.4 (s,3H,COCH₃), 2.7 – 2.8 (s,2H,CH₂CONH), 7.1 – 7.9

(m,19H aromatic protons), 8.4 (s,1H,NH). Compound 8 ^1H NMR δ (ppm): 2.3 – 2.4 (s,3H,COCH₃), 2.7 – 2.8 (s,2H,CH₂CONH), 7.1 – 8.2 (m,20H aromatic protons), 12.4 (brs,1H,COOH)

3.3. Potentiodynamic polarization

Figure 1 depicts the potentiodynamic polarization curves of mild steel in 0.1 M HCl in the absence and presence of different compound concentrations.

Potentiodynamic polarization parameters include corrosion potential (E_{corr}), anodic Tafel slopes (β_a), cathodic Tafel slopes (β_c), corrosion current density (I_{corr}), and inhibition efficiency percent (IE%)

The inhibitory effectiveness was calculated using the following equation:

$$IE \% = (1 - (I_{\text{inh}}/I_{\text{free}})) * 100$$

When I_{inh} and I_{free} are the corrosion currents of steel electrodes in the presence and absence of inhibitors. As demonstrated in table 2, the %IE increases as concentration increases.

Table 2 clearly illustrates that when the compounds are added, the change in the values β_a and β_c is small when compared to the blank solution. E_{corr} readings also remain constant and shift in E_{corr} , (≤ 11 mV).

This shows that the chitosan compounds studied are anti-corrosion of the mixed kind.

Table 2 Steel electrode corrosion characteristics in 0.1 M HCl solution with various inhibitor concentrations.

Medium	Conc. (ppm)	β_a	$-\beta_c$	$-E_{\text{corr}}$	I_{corr}	IE%
Free		103	123.4	519.9	0.7069	-
Compound 1	200	70.96	132.78	526.8	0.4432	37.30
	400	70.85	140.34	532.8	0.03731	47.2
	600	70.21	149.4	538.4	0.2954	58.21
	800	62.89	120.4	518.2	0.2041	71.13
	1000	62.95	125	517.9	0.1882	73.40
Compound 2	200	66.2	101.1	532.1	0.3974	43.8
	400	67.4	110.9	536.3	0.3323	52.98
	600	74.7	88.29	527.7	0.1979	72
	800	70.58	126.12	518	0.1843	73.9
	1000	64.2	115	507.4	0.1492	78.9
Compound 3	200	72.83	110.9	527.2	0.3161	55.28
	400	56.11	128.9	538.4	0.2522	64.32
	600	56.33	64	526.3	0.2057	70.9
	800	69.12	102.5	533.2	0.1367	80.66
	1000	72.97	86.35	528.7	0.0982	86.11
Compound 4	200	69.02	91.84	532.3	0.2922	58.66
	400	66.69	106.84	529	0.2306	67.37
	600	69.46	92.98	515.9	0.1590	77.51
	800	86.65	103.3	521.3	0.1299	84.45
	1000	74.79	114.15	516.2	0.0673	90.48
Compound 5	200	81.63	109.63	525.5	0.2801	60.38

	400	80.43	81.4	546.3	0.2271	67.87
	600	76.76	88.74	535.4	0.1492	78.89
	800	59.35	56.59	519.1	0.1293	81.71
	1000	55.59	111.6	511.1	0.0592	91.62
Compound 6	200	64.55	88.44	514.2	0.2929	58.57
	400	79.91	111.13	525.4	0.2061	70.84
	600	69.3	105.35	518.3	0.1767	75
	800	71.39	105.97	518	0.0905	87.2
	1000	44	92.98	501.8	0.0682	90.35
Compound 7	200	75.3	93.7	523.8	0.2170	69.3
	400	82.34	86.9	505.6	0.1752	75.22
	600	69.7	92.4	517.5	0.1362	80.73
	800	57.6	90.8	505.1	0.0771	89.09
	1000	93.2	113.3	504.8	0.0556	92.13
Compound 8	200	61.5	111.45	529.1	0.1955	72.34
	400	64	115.06	522.4	0.1667	82.7
	600	67.6	75.8	523.9	0.0843	88.07
	800	67.3	79.09	520	0.0689	90.25
	1000	66.2	137.4	516.8	0.0411	94.19

3.4. Adsorption isotherm

The degree of surface coverage (θ) of steel surface by the adsorbed of compounds is calculated using the following equation.

$$\theta = 1 - (I_{inh}/I_{free})$$

The corrosion current densities in the absence and presence of the additive's components are I_{free} and I_{inh} , respectively. The degree of surface covering increased with increasing additive concentrations. A number of mathematical connections for adsorption isotherms,

including those proposed by Langmuir, Freundlich, Frumkin, and Temkin, have been proposed to suit the experimental findings in this study. The best results were achieved when the Langmuir isotherm was fitted. When C/θ is plotted against inhibitor concentration (C), straight lines with unit slopes are obtained. This indicates that the inhibitors are adsorbing in accordance with the Langmuir adsorption isotherm.

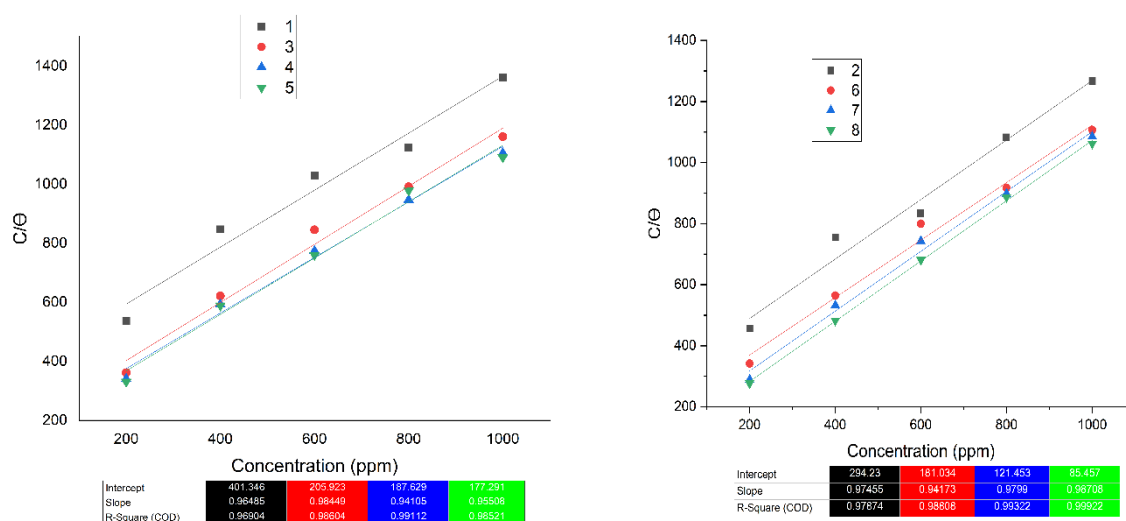


Figure 1 Langmuir adsorption isotherm of the adsorption of compounds on the mild steel in 0.1M HCl at 25°C.

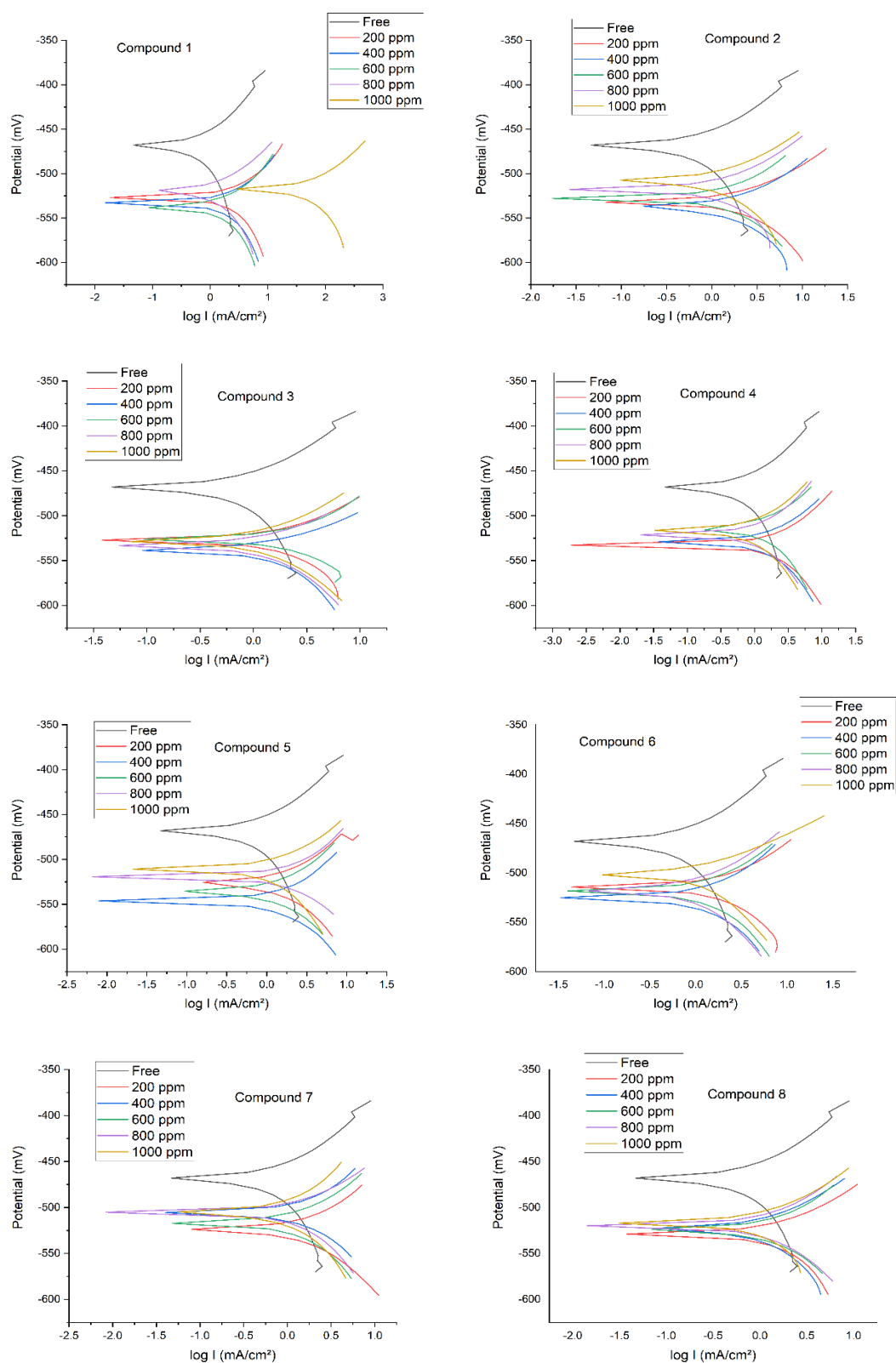


Figure 2 anodic and cathodic polarization curves of steel electrode in 0.1 M HCl solution containing different concentration of Compounds at 25°C

3.5. Effect of temperature

The effect of temperature on corrosion metrics such as I_{corr} , E_{corr} , and %IE was studied in a 0.1 M HCl solution containing 1000 ppm of inhibitors at temperatures ranging from 25 to 65 °C. The findings demonstrated that temperature variation had no effect on the shape of the polarization curves. According to the results in Table 3, E_{corr} became less negative as

the temperature rose, whereas I_{corr} values increased. This illustrates that increasing the temperature has a faster effect on the corrosion reaction. Increased temperature, on the other hand, diminishes inhibition efficiency. This is because higher temperatures hasten the desorption process.

Table 3 The influence of temperature on steel electrode corrosion characteristics in 0.1 M HCl and (0.1M HCl + 1000ppm) inhibitor.

Compound	T(K)	- E_{corr}	I_{corr}	IE%
0.1 M HCl	298	519.9	0.7069	0
	308	560	0.7345	0
	318	517.8	0.8009	0
	328	532	0.8335	0
	338	525.8	0.9658	0
Compound 1	298	540.8	0.1882	73.4
	308	524.3	0.3241	55.9
	318	506.6	0.3857	51.8
	328	491.8	0.4516	45.8
	338	485.1	0.5536	42.7
Compound 2	298	507.4	0.1492	78.9
	308	495.7	0.2067	71.9
	318	487	0.2971	62.9
	328	503	0.3449	58.6
	338	508	0.4551	52.9
Compound 3	298	528.7	0.0982	86.11
	308	522.7	0.2197	70.09
	318	522.9	0.2806	64.96
	328	549.5	0.3467	58.4
	338	528	0.4133	57.21
Compound 4	298	516.2	0.0673	90.48
	308	515.9	0.1698	76.88
	318	507.6	0.1790	76.40
	328	494.7	0.1886	75.99
	338	503.6	0.2172	73.62
Compound 5	298	511	0.0592	91.62
	308	523.4	0.2342	68.11
	318	513.5	0.3156	60.59
	328	528.5	0.3356	60.09
	338	519.9	0.3725	59.38
Compound 6	298	501.8	0.0682	90.35
	308	507.2	0.1392	81.04
	318	511.2	0.1637	79.56
	328	518.3	0.1989	76.14
	338	508.8	0.2066	75.50
Compound 7	298	504.8	0.0556	92.13
	308	511.7	0.1234	81.84
	318	516	0.1410	81.39
	328	511	0.1697	79.64
	338	518	0.2024	79.04
Compound 8	298	516.8	0.0411	94.19
	308	501	0.1491	79.70
	318	512.6	0.1739	78.29
	328	517.9	0.1847	77.84
	338	528	0.1996	76.23

The corrosion reaction is regarded as a rate process which is given by Arrhenius equation.

$$\log(I_{corr}) = \log(A) - Ea/2.303RT$$

Where I_{corr} represents the rate of corrosion reaction.

A is Arrhenius factor and E_a is the apparent activation energy of the corrosion reaction. Plotting the $\log(I_{corr})$ versus $(1/T)$ gave straight lines in Fig (3).

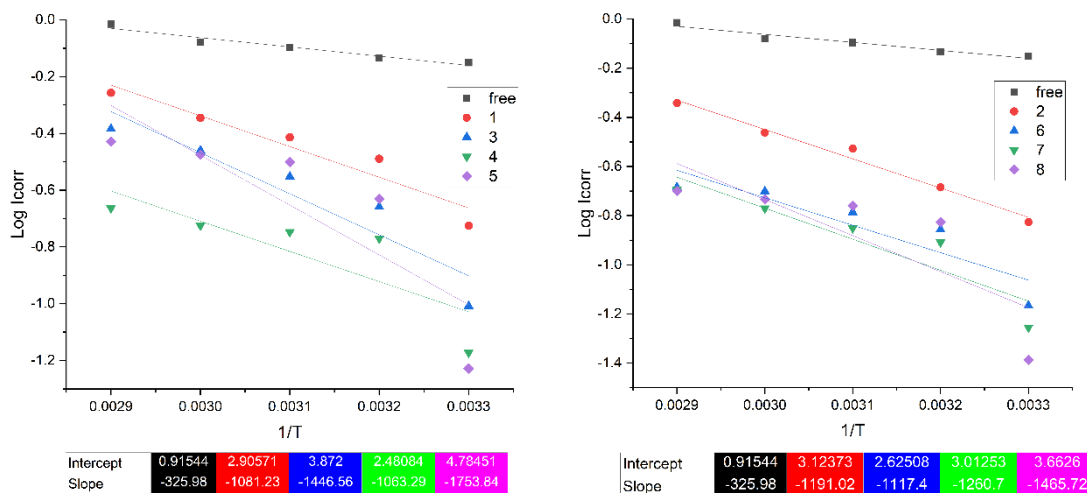


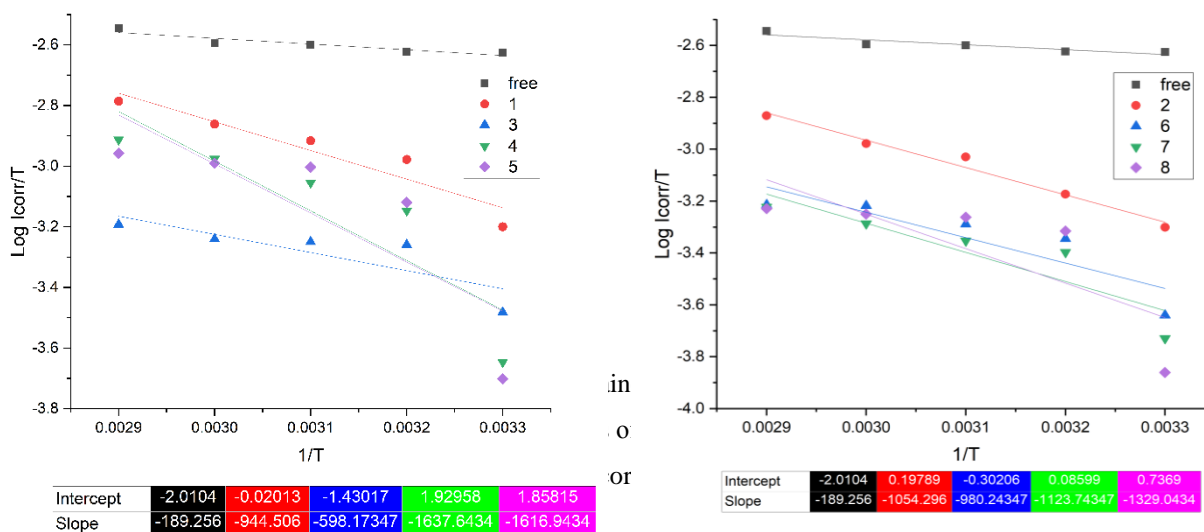
Figure 3 Arrhenius plots of steel corrosion rate in 0.1 M HCl in absence and presence of 1000 ppm of inhibitors.

A is Arrhenius factor and E_a is the apparent activation energy of the corrosion reaction. Plotting the $\log(I_{corr})$ versus $(1/T)$ gave straight lines in Fig (3).

The other activation parameters were calculated using the transition state equation:

$$\log\left(\frac{I_{corr}}{T}\right) = (\log(R/hn)) + \left(\frac{\Delta S^*}{2.303R}\right) - \left(\frac{\Delta H^*}{2.303RT}\right)$$

Where, R is the universal gas constant (8.314 J / mol.k), n is the Avogadro's number (6.02×10^{23}), h is the plank's constant ($6.62 \times 10^{-34} \text{ m}^2\text{kg/s}$) where ΔS^* and ΔH^* are the entropy and the enthalpy change, respectively. plotting $\log(I_{corr}/T)$ versus $(1/T)$ gives straight lines Fig (4).



$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$$

Figure 4 The relation between $\log(I_{corr}/T)$ and $1/T$ for steel electrode in 0.1 M HCl in absence and presence of 1000 ppm of compounds

The obtained ΔG^* values were also listed in Table (4).

Table 4 Activation parameters of the dissolution reaction of steel electrode in 0.1 M HCl solution in absence and presence of 1000 ppm of compounds.

Compound	Ea K.J/mol	ΔH^* K.J/mol	$-\Delta S^*$ K.J/mol	ΔG^* K.J/mol. K
Free HCl	6.241	3.623	0.23608	73.975
Compound 1	20.702	18.084	0.198	77.088
Compound 2	22.804	20.186	0.194	77.998
Compound 3	27.697	11.453	0.225	78.503
Compound 4	20.358	31.356	0.161	79.334
Compound 5	33.581	30.959	0.162	79.235
Compound 6	21.395	18.768	0.203	79.262
Compound 7	24.138	21.516	0.196	79.924
Compound 8	28.064	25.447	0.183	79.981

The activation energy clearly increases in the presence of the inhibitor due to the inhibitor's adsorption on the metal's surface. The growth of an adhering coating on the mild steel surface causes an increase in E_a values. These findings indicate the physical adsorption of compounds on the surface of mild steel.

The positive sign of ΔH^* expresses the endothermic system of the process, and the elevated values of E_a^* comparable to the values of ΔH^* indicate the gaseous nature of the corrosion process, which can be easily explained by the evolution of hydrogen gas, which is accompanied by the volume decrease of the reaction.

4. Conclusion

According to this study, using electrochemical tests, freshly produced compound derivatives had a better corrosion prevention effect for mild steel in 0.1M HCl than the original compound.

Potentiodynamic polarization curve data in 0.1 M HCl at 298 K indicated that compounds coated substrates exhibited greater corrosion inhibition activity than bare mild steel. The inhibitory effectiveness (IE) in 0.1M HCl solution was found to be 94%.

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