



Novel Zn (II) complexes of N₁,N₂-bis(2-nitrobenzylidene) ethane-1,2-diamine as effective corrosion inhibitors for mild steel in 5M HCl solution

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Abstract: Mild steel is a common material and has found widespread use in many industries. However, its ability to corrode in aggressive environments limits its application. This study aims to study mild steel corrosion inhibition in 5.0 M HCl using Zn (II) complexes (C₃), based on N₁,N₂-bis(2-nitrobenzylidene)ethane-1,2-diamine (L₂). Measurements of electrochemical techniques, such as polarization plots and Electrochemical Impedance Spectroscopy (EIS) were used to study their behavior. Polarization plots revealed that these inhibitors are mixed type. The inhibition efficiency increases with increasing inhibitors concentrations. The impedance diagrams show that the charge transfer resistance value increases in the presence of inhibitors and the value of double layer capacity decrease. It can be interpreted by the formation of an inhibitor film on the metal surface. The surface of the steel before and after corrosion was characterized by the Scanning Electron Microscope coupled with Dispersive Energy Analysis (SEM-EDS), The obtained results show that the complex C₃ is effective for the protection of steel in 5.0 M HCl, in addition, this complex is adsorbed to the steel surface following the isotherm of Langmuir.

Keywords: inhibition, corrosion, mild steel, 5.0 M HCl, complex, isotherm.

1. Introduction

Nowadays, mild steel is extensively used in many fields such as automotive, household appliances, civil engineering, chemical engineering and shipbuilding (Behzadnasab *et al.* 2011). The use of an acid solution, in many industrial processes, for cleaning, pickling and descaling is common, especially in acidification processes (Toghan, *et al.* 2024; Salim, *et al.* 2021; Arrousse, *et al.* 2020; Zarrouk, *et al.* 2012; Zerga *et al.* 2010; Yaro & Khadom A.A. 2010). The acid solutions cause severe corrosion on metal surfaces which has a serious economic consequence in many industries.

As a consequence, it is urgent to prevent and battle against steel corrosion and it seems, to our regard, that the protection of the material against corrosion could be done by acting on the corrosive medium. The use of inhibitors is widely used because of their low cost, high efficiency and easy feasibility (El Ouafi *et al.*, 2002; Lagrenee *et al.*, 2002). In general, the use of organic complexes has been suggested in several important studies in areas chemical and biological (Gribble Jr *et al.*, 2008; A. Barakat *et al.*, 2013) and even for those in the physical field (Houslay, *et al.*, 1977). Research in this area is extensive and the bulk of studies were focused on the biological properties of complexes (Aldwayyan, *et al.*, 2013; Arjmand *et al.*, 2012). In addition, copper and zinc-based complexes show very important biological activities such as antibiotic, antifungal, antiviral, and anti-HIV agents (Sun *et al.*, 2007; Mary Ho *et al.*, 2009). In addition, the complexes have light emitting organic diode properties (Mori *et al.*, 1998).

In this study, we have oriented the application of complexes based on N₁,N₂-bis(2-nitrobenzylidene) ethane-1,2-diamine as corrosion inhibitors of mild steel in an acidic medium. The novelty of the present work is the synthesis of new organic complex based on N₁,N₂-bis(2-nitrobenzylidene) ethane-1,2-diamine. After the successful synthesis, we have examined this compound in corrosion inhibition of steel in 5.0 M HCl solution, using electrochemical (EIS, PDP) methods. The SEM-EDS technic was used to analysis the steel surface before and after corrosion with and without inhibitors.

2. Experimental details

2.1. Materials and sample preparation

The aggressive solutions of 5.0M HCl were prepared by analytical grade HCl dilution (37 wt.%) with distilled water; the acidity level of 5.0M HCl is -2.5 according to the Strehlow acidity function (Doudou Babalé *et al.*, 1990; Hammouti & Benayada 2020). It important to note that the acidity level is expressed by R_i(H) which is the generalized pH for the concentrated acid solutions. Complex inhibitors with a concentration in the range 5.10⁻⁴ to 10⁻⁶ M were used and a blank solution was prepared for comparison. Plates of mild steel with a nominal chemical composition of 0.17 wt.% C, 0.37 wt.% manganese, 0.20 wt.% SI, 0.03 wt.% S, 0.01 wt.% P and Fe were used as the samples for loss weight tests, having the dimensions of 2.00cm*1.00cm*0.20cm. For electrochemical experiments, steel samples were used with an exposed area of 1.0 cm² to the acid solution. Before use, the substrates were abraded with different grades of emery papers from 180 to 2000 grit, rinsed with distilled water, degreased with ethanol and dried with hot air. The molecular formula of the examined inhibitors is shown in Table 1.

2.2 Electrochemical cell

Electrochemical study was realized in a three-electrode electrochemical cell, composed of a mild steel plate as a working electrode, a platinum counter-electrode and an Ag/AgCl/KCl saturated reference electrode. An electrochemical measurement has been done using a potentiostat /galvanostat /PGZ100 controlled by analysis software VoltaMaster4. Electrochemical experiments were analyzed using electrochemical software ORIGIN PRO 6.1. Electrochemical parameters were, then, extracted owing to EC-Lab V10.02 and ZView software. EIS measurements were done in the range of frequency 100 kHz to 100 mHz at an Open Circuit Potential (OCP) with 10 points per decade. The amplitude of the applied alternative current signal was 10 mV.ms⁻¹. All experiments were performed after 30 min immersion of mild steel in 5.0M HCl solution with and without different concentrations of the studied inhibitors. Modelling of the impedance plots gives the charge transfer resistance (R_{ct}), the double layer

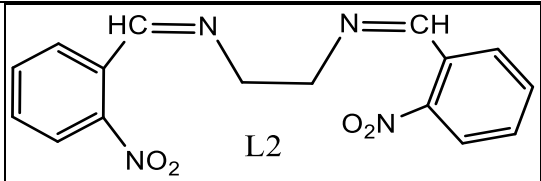
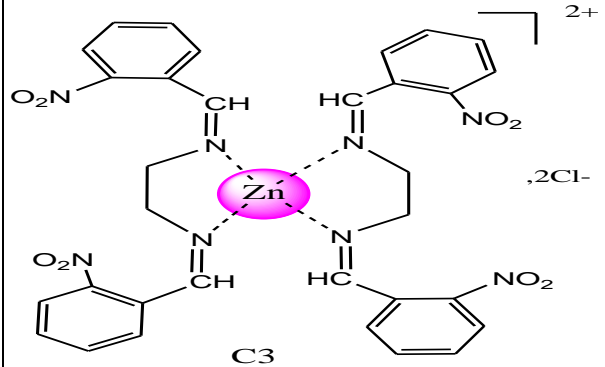
capacitance (C_{dl}) and other parameters. The inhibition efficiency ($\eta_{imp}\%$) is calculated by the following equation (Zarrok *et al.*, 2013; Hermas *et al.*, 2008):

$$\eta_{imp}\% = (R_{CT} - R_{CT}^{\circ}/R_{CT}) \times 100 \quad \text{Eqn.1}$$

$$\theta = R_{CT} - R_{CT}^{\circ}/R_{CT} \quad \text{Eqn.2}$$

Where R_{ct}° and R_{ct} are the charge transfer resistance without and with inhibitor, respectively, θ is the recovery rate.

Table 1. Abbreviations, chemical structures and names of the studied complexes

Abbreviation	Chemical structure	IUPAC Name / molecular formula / Molar mass
L ₂		N ₁ ,N ₂ -bis(2-nitrobenzylidene)ethane-1,2-diamine 326,31 g/mol
C ₃ ≡(L ₂) ₂ ZnCl ₂		Complex (L ₂) ₂ ZnCl ₂ 788.90 g/mol

Potentiodynamic polarization plots were obtained by sweeping the working electrode potential from -900 mV to -100 mV with a sweep rate of 1 mV/s. All the electrochemical experiments were realized at a temperature of 298 K. Corrosion current density values (i_{corr}) and corrosion potential (E_{corr}) were obtained using the intercepts by Tafel's extrapolation method. The inhibition efficiency ($\eta_{imp}\%$) is calculated by the following equation (Ghazoui *et al.*, 2012; Liu *et al.*, 2009):

$$\eta_{imp}\% = \left[\frac{(i_{corr}^{\circ} - i_{corr})}{i_{corr}^{\circ}} \right] \times 100 \quad \text{Eqn.3}$$

i_{corr}° and i_{corr} are the corrosion current densities in the absence and presence of the inhibitor, respectively.

2.3 Surface characterization by SEM/EDX

The determination of the nature of the formed film on the metal surface, exposed to 5.0M HCl solution during 6h without and with studied inhibitors, was realized by Scanning Electron Microscopy (Quanta FEG 450) coupled with EDX analyses.

3. Results and discussion

3.1. Polarization studies

Potentiodynamic polarization plots of mild steel in 5.0M HCl solution in the absence and presence of different concentrations of L₂ and C₃ at 298 K are shown in figure 1. It was noted, from figure 1, that the nature of polarization curves with inhibitors remains the same as that without inhibitor, meanwhile, the curves shifted to a lower current density, in the presence of inhibitors. This result is in favor of an

inhibition process without modification of the recombination mechanism. Electrochemical parameters such as corrosion potential (E_{corr}), anodic Tafel slope (β_a), cathodic Tafel slope (β_c) and corrosion current density (i_{corr}) were obtained by extrapolating the anodic and cathodic Tafel intercepts with E_{corr} . $\eta_{\text{imp}}\%$ was calculated according to equation 3 and the results are shown in Table 2.

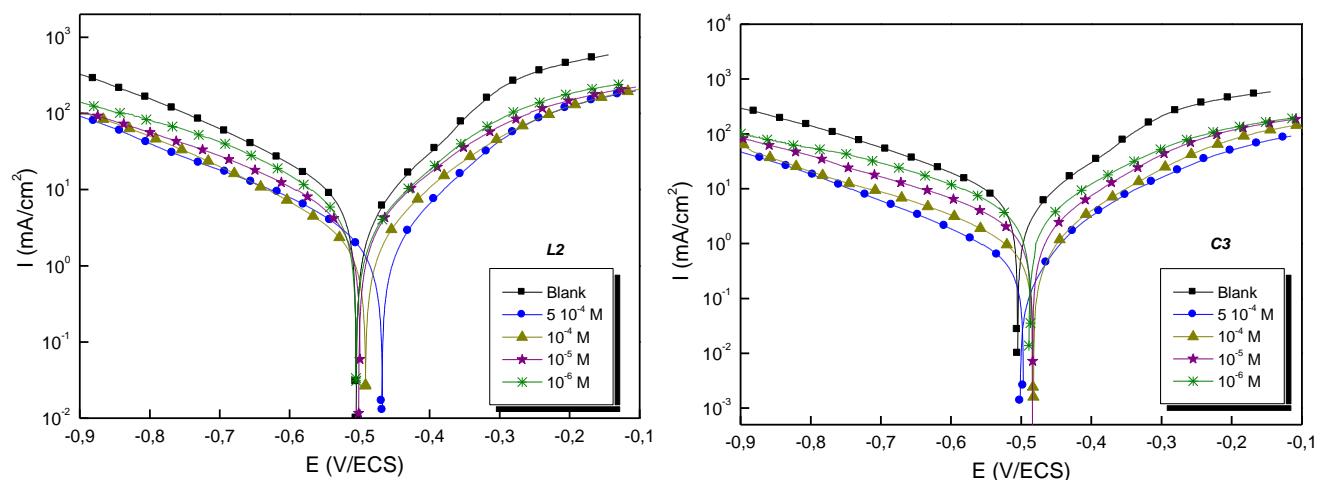


Figure 1. Polarization curves for mild steel in 5M HCl with various concentrations of L_2 and C_3 at 298 K

Table 2: Corrosion parameters obtained from Tafel polarization curves for mild steel in 5M HCl with and without different concentrations of L_2 and C_3

Compounds	Conc. M	$-E_{\text{corr}}$ mV/ECS	i_{corr} $\mu\text{A cm}^{-2}$	$-\beta_c$ mV dec $^{-1}$	β_a mV dec $^{-1}$	η_{imp} %
5.0M HCl	--	504	3417	142	138	-
C_3	10^{-6}	484	2245	137	138	34.29
	10^{-5}	483	1152	136	135	66.29
	10^{-4}	480	524	132	131	84.66
	5×10^{-4}	494	312	130	133	90.87
L_2	10^{-6}	502	2489	130	127	27.16
	10^{-5}	497	1829	131	129	46.47
	10^{-4}	488	1472	134	133	56.92
	5×10^{-4}	465	1159	138	134	66.08

The given results in Table 2 revealed that the increase in both inhibitor concentrations causes i_{corr} decrease and $\eta_{\text{imp}}\%$ increase, suggesting that inhibitors are adsorbed and form a protective film on the surface of mild steel (Wang *et al.*, 2011; Ech-chihbi *et al.*, 2020). $\eta_{\text{imp}}\%$ values of the inhibitors are in the order of $C_3 > L_2$ at 298 K. The presence of inhibitors causes a modification of E_{corr} values. If E_{corr} displacement with inhibitor is more than ± 85 mV compared to blank corrosion potential, the inhibitor can be considered as a cathodic or anodic type inhibitor (Ferreira *et al.* 2004). If E_{corr} variation is less than ± 85 mV, the corrosion inhibitor can be considered as a mixed type inhibitor (Al Hamzi *et al.*, 2013). In this study, the maximum displacement of E_{corr} is +60 mV, indicating that L_2 and C_3 are inhibitors of the mixed type, predominantly anodic.

3.2. EIS studies

Nyquist plots of submerged mild steel in acid solution with and without the addition of different concentrations of L_2 and C_3 at 298 K are indicated in Figure 2. The given impedance plots are not

perfect semicircles, it is attributed to the difference of frequency dispersion (Meryem *et al.*, 2023, Mansfeld *et al.*, 1981), due to the heterogeneity of the electrochemical system. This heterogeneity is a result of roughness, impurities, inhibitor adsorption and formation of porous layers (Galai *et al.*, 2016; Ramesh *et al.*, 2004).

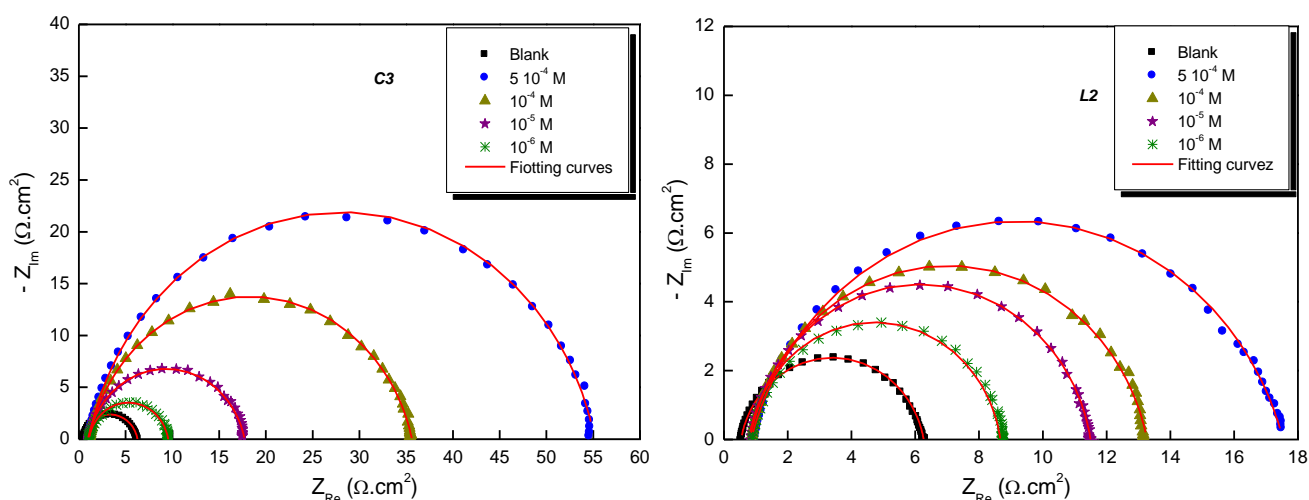


Figure 2. Impedance spectra in Nyquist plots for mild steel in 5.0M HCl containing different inhibitors: L₂ and C₃ at 298 K

In the presence of each inhibitor, the size of the capacitive loop increases with increasing inhibitor concentration. The modeling of the electrode/electrolyte interface can be modeled by the equivalent circuit shown in Figure 3. Each of the components used, connected in series or in parallel, represents a particular physical phenomenon (Ashassi *et al.*, 2005; Azgaou *et al.*, 2022). This circuit includes charge transfer resistance (R_{ct}), solution resistance (R_s) and a constant phase element (CPE). Constant phase element is represented, in the circuit, in the place of the double layer capacitance, to give a more precise adjustment because the double layer in the interface doesn't act as a perfect capacitor. Electrochemical parameters, obtained from impedance spectrums are given in Table 3.



Figure 3. Equivalent circuit for the electrochemical impedance spectra

Bode impedance curves of submerged mild steel in 5.0M HCl solution without and with different concentrations of L₂ and C₃ at 298 °K are presented in Figure 4. In Bode plots, we note the apparition of a single peak in both inhibitors and the blank sample, confirming the model of the equivalent circuit used to adjust impedance spectrums. Bode plots exhibit a single maximum phase for both inhibitors, indicating that the electrochemical process is under charge transfer control in the interface metal-solution.

The analysis of the Table 3 indicates that R_{ct} values in the presence of inhibitors are greater than those in the case of the blank sample. It can be attributed to the formation of an insulating protector film in the interface metal/solution. The value of C_{dl} decreases with increasing the concentration of both inhibitors, indicating the adsorption of both molecules on the steel surface. The increase in the concentration of inhibitors is accompanied by an increase in the thickness of the film formed.

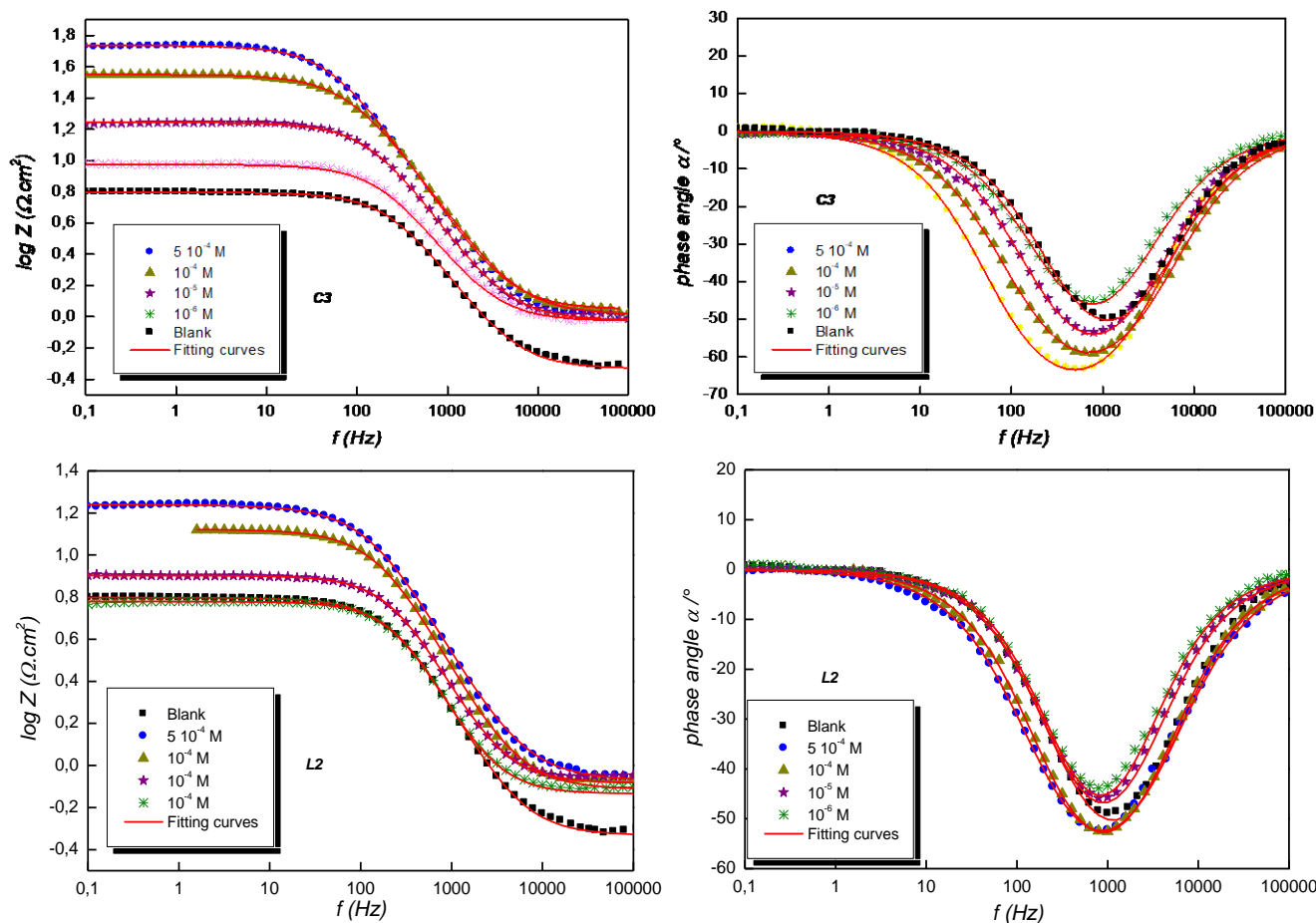


Fig. 4. Bode plots of mild steel in 5.0M HCl solution in with and without different concentrations of L_2 and C_3 at 298 K

Table 3. Impedance parameters of mild steel in 5.0M HCl solution in the presence and absence of different concentrations of L_2 and C_3 at 298 K

	C (M)	R_s ($\Omega \text{ cm}^2$)	R_{ct} ($\Omega \text{ cm}^2$)	C_{dl} ($\mu\text{F cm}^{-2}$)	n_{dl}	Q ($\mu\text{F.S}^{n-1}$)	θ	η_{imp} %(R_{ct})	η_{imp} %(C_{dl})
HCl	--	0.5	5.7	180.9	0.881	361.0	-	-	-
L_2	10^{-6}	0.7	7.8	118.3	0.906	235.5	0.269	26.9	
	10^{-5}	0.9	10.6	90.4	0.892	198.7	0.462	46.2	50.0
	10^{-4}	0.8	12.5	74.1	0.866	187.8	0.544	54.4	59.0
	$5 \cdot 10^{-4}$	0.8	16.7	68.5	0.827	220.2	0.658	65.9	62.0
C_3	10^{-6}	1.0	8.5	92.2	0.882	213.5	0.329	32.9	49.0
	10^{-5}	0.9	16.7	64.7	0.867	160.5	0.658	65.9	64.2
	10^{-4}	1.0	34.6	34.2	0.855	129.8	0.835	83.5	81.1
	$5 \cdot 10^{-4}$	1.0	54.1	25.1	0.866	121.6	0.894	89.5	86.1

Based on survey literature, the efficiency can be estimated using capacitance (C_{dl}) which values are in good agreement with those obtained using R_{ct} . According to Cao, (1996), if the shift of E_{corr} due to addition of inhibitor is negligible, the inhibition is most probably caused by a geometric blocking effect of the adsorbed inhibitive species on the surface of the corroding metal. In other words, geometric blocking is defined as the diminution of surface area where electrochemical reactions can occur due to the adsorption of non-reactive species (Cao, 1996; Vracar & Drazic D. 2002). The surface

coverage limits the metal surface area at which corrosion reactions can occur, and then, the mechanisms of these reactions are unaffected since the adsorbed inhibitor does not participate/alter the rate determining steps. Consequently, the Tafel slopes (β_c & β_a) remain unchanged. In this case the inhibition efficiency (η_{imp}) equals the coverage (θ) of the adsorbed species and can be estimated by polarization resistance (R_p) measurements.

4. Adsorption isotherm

Important information about the interaction between the inhibitor and mild steel surface can be provided by the adsorption isotherm. From the above results, it can be concluded that the surface coverage θ increases with the inhibitor concentration; this may be attributed to more adsorption of inhibitor molecules onto the steel surface. As it is known, the adsorption of inhibitor is always a displacement reaction involving removal of adsorbed water molecules from the metal surface (Belghiti *et al.*, 2020; Kalman *et al.*, 1994), eq. following:



Where $org_{(sol)}$ and $org_{(ads)}$ are the organic molecules in the aqueous solution and adsorbed on the steel surface, respectively. $H_2O_{(ads)}$ is the water molecule on the steel surface and x reflects the size ratio representing the number of water molecules replaced by one unit of inhibitor.

the literature reports a several isotherms to evaluate the adsorption of inhibitors on the metal surface (Table 4). Among the most frequently used isotherms are Langmuir, Temkin, Freundlich, Flory-Huggins, Frumkin and El Awady (Abdel-Gaber *et al.*, 2006; Duong Do .1998). All these isotherms obey a common general expression given by the following equation (Ech-chihbi *et al.*, 2019):

$$f(\theta, x)e^{(-2a\theta)} = K_{ads} C_{inh} \quad \text{Eqn.5}$$

Or $f(\theta, x)$ is the correspondence factor that depends on the physical model and the assumptions underlying the derivation of the isotherm and a is the molecular interaction parameter as a function of the molecular interactions in the adsorption layer and the degree heterogeneity of the surface, C_{inh} is the concentration of inhibitor, θ is the surface coverage degree, and K_{ads} is the adsorptive equilibrium constant. The value of θ was obtained experimentally from EIS.

Table 4 List of adsorption isotherms

Isotherms	Linear form	Curves	Réf
Langmuir	$k_{ads}c_{inh} = \frac{\theta}{1-\theta}$	$\frac{C_{inh}}{\theta}$ vs C_{inh}	(Langmuir 1916)
Temkin	$e^{-2f\theta} = k_{ads}C_{inh}$	θ vs $\ln(C_{inh})$	(Temkin <i>et al.</i> , 1940)
Freundlich	$\theta = k_{ads}C_{inh}^n$	$\ln(\theta)$ vs $\ln(C_{inh})$	(Freundlich 1906)
Frumkin	$\frac{\theta}{1-\theta}e^{-2f\theta} = k_{ads}C_{inh}$	$\ln\left(C_{inh}\frac{1-\theta}{\theta}\right)$ vs θ	(Frumkin 1925)

In this study, the isotherms were fitted presented in Figure 5. Their corresponding fitting curves results are shown in Table 5. It is noted that the inhibitors were adsorbed by mild steel surface according to Langmuir isotherm model with an excellent adjustment of the experimental values by slopes and correlation factors close to unity for the three inhibitors studied. The Langmuir model seems to be the most suitable to describe the adsorption of the compounds studied.

In the present study, we have tried to look for other models taking into account the non-ideal nature of the adsorption process. Thus, the isotherms Temkin, Frumkin and Freundlich, were undertaken. Firstly, the values of the correlation factors were very close to unity, which prompted us to go further into the investigation. On the other hand, the fact that the adsorption process of the tested inhibitors follows as well Temkin and Frumkin isotherms is an indication of the existence of molecular interaction in the adsorbed layer, which is not entirely ideal as suggested by the intermolecular interaction between the adsorbed molecules on the metal surface “ f^{Frum} ” and “ f^{Temk} ”, of Frumkin’s isotherm and Temkin’s isotherm, respectively, indicating lateral interactions in the adsorbed layer.

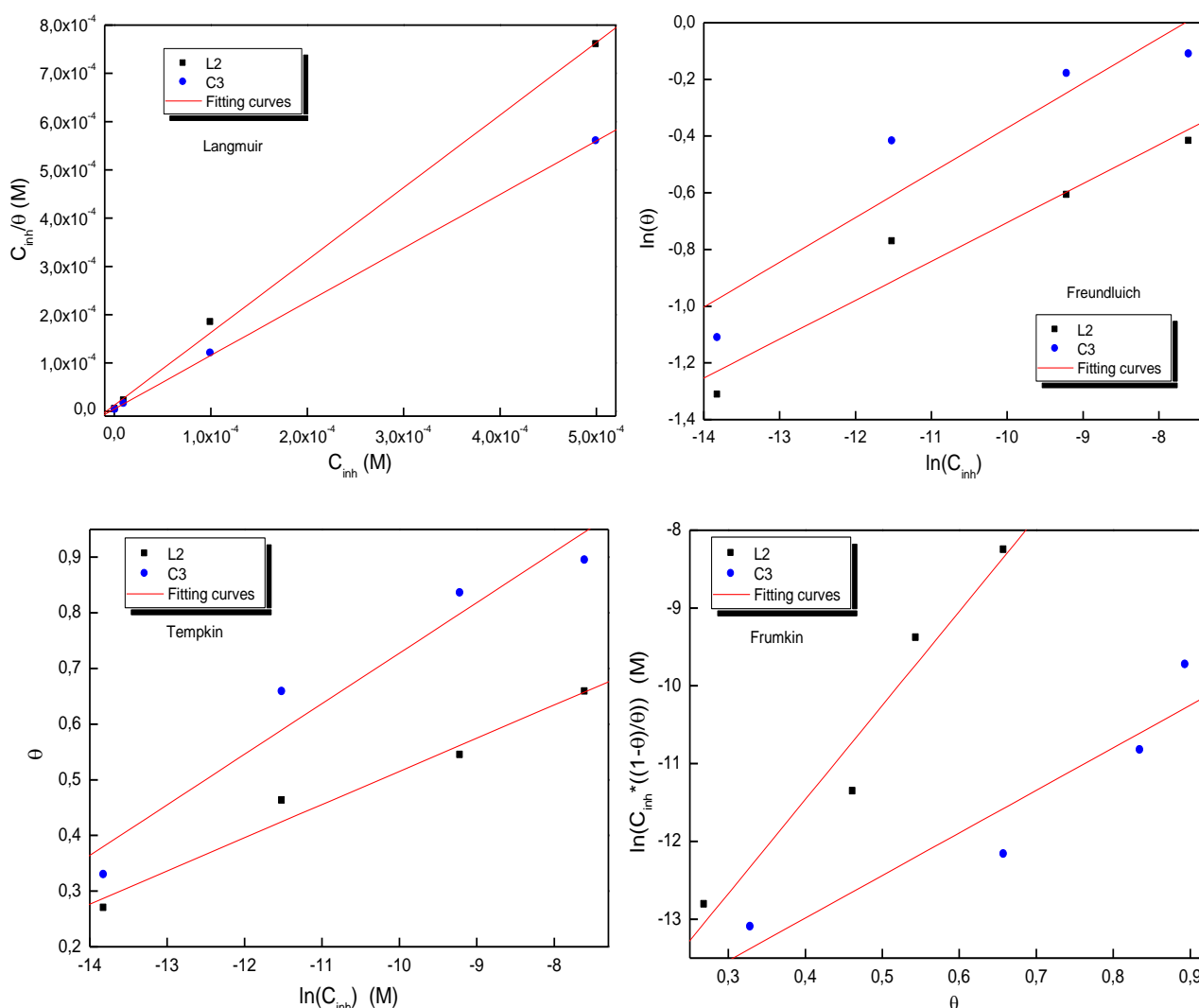


Figure 5. Different adsorption isotherm plots for the adsorption of L2 and C3 on mild steel corrosion surface in 5.0 M hydrochloric acid

There is a good correlation between the equilibrium constant of the adsorption (K_{ads}) and the standard free adsorption energy (ΔG_{ads}) which is:

$$K_{ads} = \frac{1}{55.5} e^{-\frac{\Delta G_{ads}}{RT}} \quad \text{Eqn.6}$$

$$\Delta G_{ads} = -RT \ln (55.5 K_{ads}) \quad \text{Eqn.7}$$

Where, R is universal gas constant and the absolute temperature is denoted by T. The molar concentration of water is expressed in mol/L and in solution its value is 55.5 (Flis *et al.*, 1996).

As seen in Table 5, it is clear that the value of K_{ads} obtained from different isotherms is high, except in the case of the isothermal model of Freundlich, indicating a strong adsorption of inhibitors studied on the metal surface. Nevertheless, the values of K_{ads} and ΔG_{ads} obtained by the Freundlich adsorption isotherm are very weak, calling into question the applicability of this isotherm to the system. Indeed, the value " n^{Freun} " of the Freundlich isotherm is far from the typical value of 0.6 (Khadom *et al.*, 2010), which means that the studied process of adsorption couldn't, rationally, be simulated by the Freundlich isotherm, even though obtained value of R^2 , from the corresponding plot, seems to be good.

Table 5. Thermodynamic parameters of adsorption values for mild steel in 5.0M HCl at different concentrations of L_2 and C_3

Isotherms	Thermodynamic Parameters	L_2	C_3
<i>Langmuir</i>	R^2	0.9992	0.99994
	K_{ads} ($L mol^{-1}$)	$78.06 \cdot 10^3$	$215.8 \cdot 10^3$
	Slope	1.5	1.11
	ΔG_{ads} (kJ/mol)	-37.8	-40.4
<i>Freundlich</i>	R^2	0.967	0.93863
	K_{ads} ($L mol^{-1}$)	1.95	3.35
	Slope (n)	0.14	0.16
	ΔG_{ads} (kJ/mol)	-11.6	-12.9
<i>Temkin</i>	R^2	0.98718	0.97054
	K_{ads} ($L mol^{-1}$)	$123.1 \cdot 10^6$	$65.5 \cdot 10^6$
	Pente ($-1/2f$)	0.05963	0.09085
	F	-8.38	-5.50
	ΔG_{ads} (kJ/mol)	-56.1	-54.5
<i>Frumkin</i>	R^2	0.97577	0.93891
	K_{ads} ($L mol^{-1}$)	$119.7 \cdot 10^5$	$38.95 \cdot 10^5$
	Pente ($-2f$)	12.09117	5.47331
	F	-6.04	-2.74
	ΔG_{ads} (kJ/mol)	-50.33	-47.54

Generally, values of ΔG_{ads} around or less than $-20 kJ \cdot mol^{-1}$ suggested that the adsorption process is related with the electrostatic interaction between charged inhibitor molecules and the charged surface of the metal, which is termed as "physisorption" (Boumhara *et al.*, 2015; Halambek 2010); while values around or higher than $-40 kJ mol^{-1}$ are associated with sharing of charge or transfer from the inhibitor molecules to the metal surface to form a coordinate type of metal bond termed as "chemisorption" (Behpour *et al.*, 2010; Eteram *et al.*, 2008). In the Langmuir model, the isotherm values approach $-40 kJ mol^{-1}$, which argues in favor of a process of chemisorption. Thus, simply based on these criteria, it is not easy to make the distinction between physisorption and chemisorption,

especially when charged species are adsorbed. The possibility of Colomb interactions between the adsorbed anions and the cations, specifically adsorbed, may increase Gibbs's energy, even though no chemical bond appears (Singh *et al.*, 2011). The inhibition process, in a real system, remains complex and not very known, which means that one or all the above-mentioned mechanisms may act.

5. Surface analysis

In order to confirm the obtained results with electrochemical measurements. Qualitative microscopic analyses of MEB coupled with quantitative analyses EDS have been done (Figure 6).

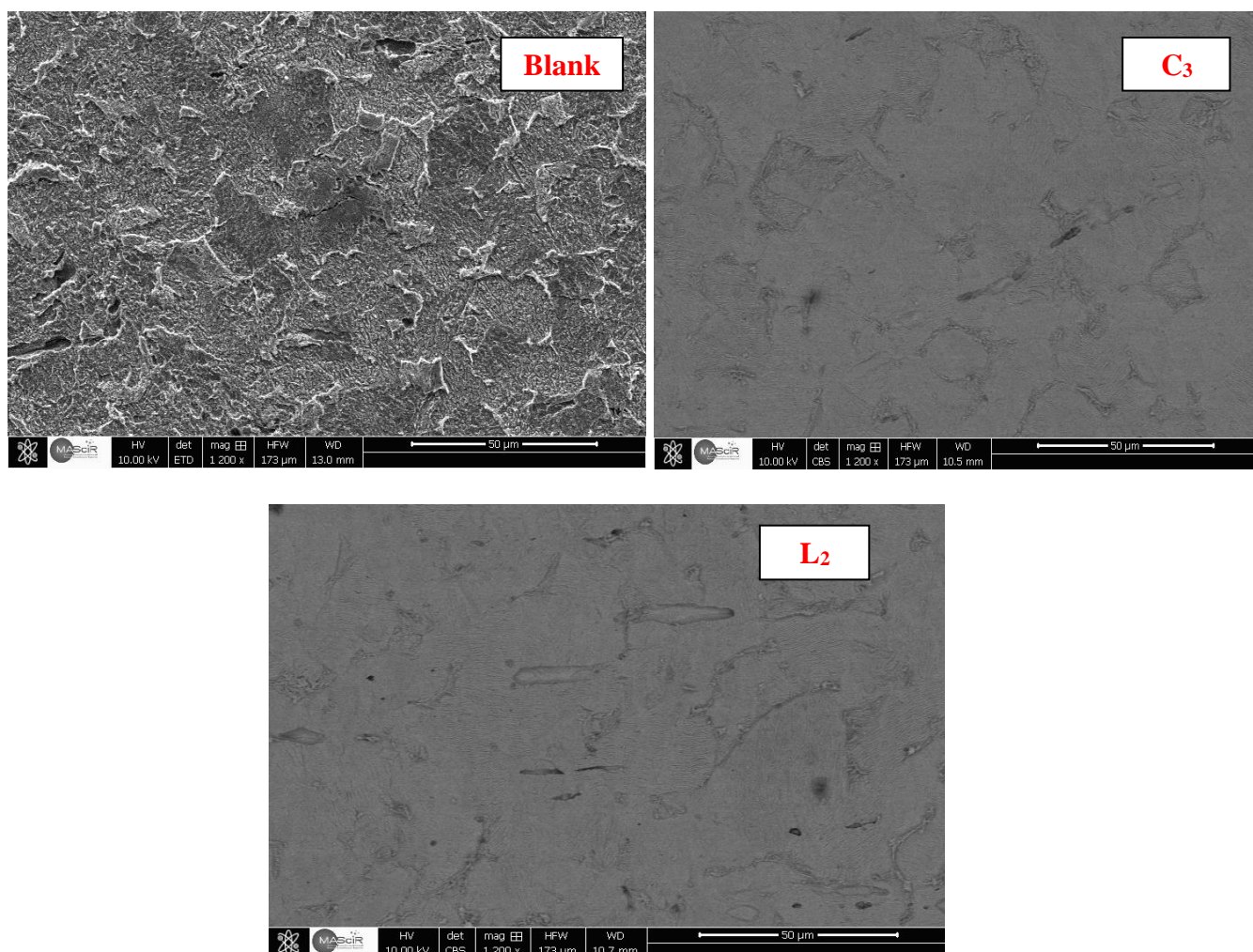


Figure 6. SEM image of mild steel after 6 h of immersion in 5.0 M HCl solution without and with 5.10^{-4} M of inhibitors: L₂ and C₃

The analysis of the Figure 6 shows that the morphology of the exposed surface to 5M HCl exhibits a heterogeneous layer of corrosion products. The surface is free from any corrosion products in the presence of inhibitor L₂ and C₃ and reveals the formation of a protective layer (Yadav *et al.*, 2015). The EDS analysis (Figure 7), show a decrease in the peaks of O atoms and apparition of peaks of Nitrogen N, indicating that the molecules of the products L₂ and C₃ are strongly adsorbed on the metal surface (Suzuki *et al.*, 1996). As a consequence, these results confirm those obtained with electrochemical measurements.

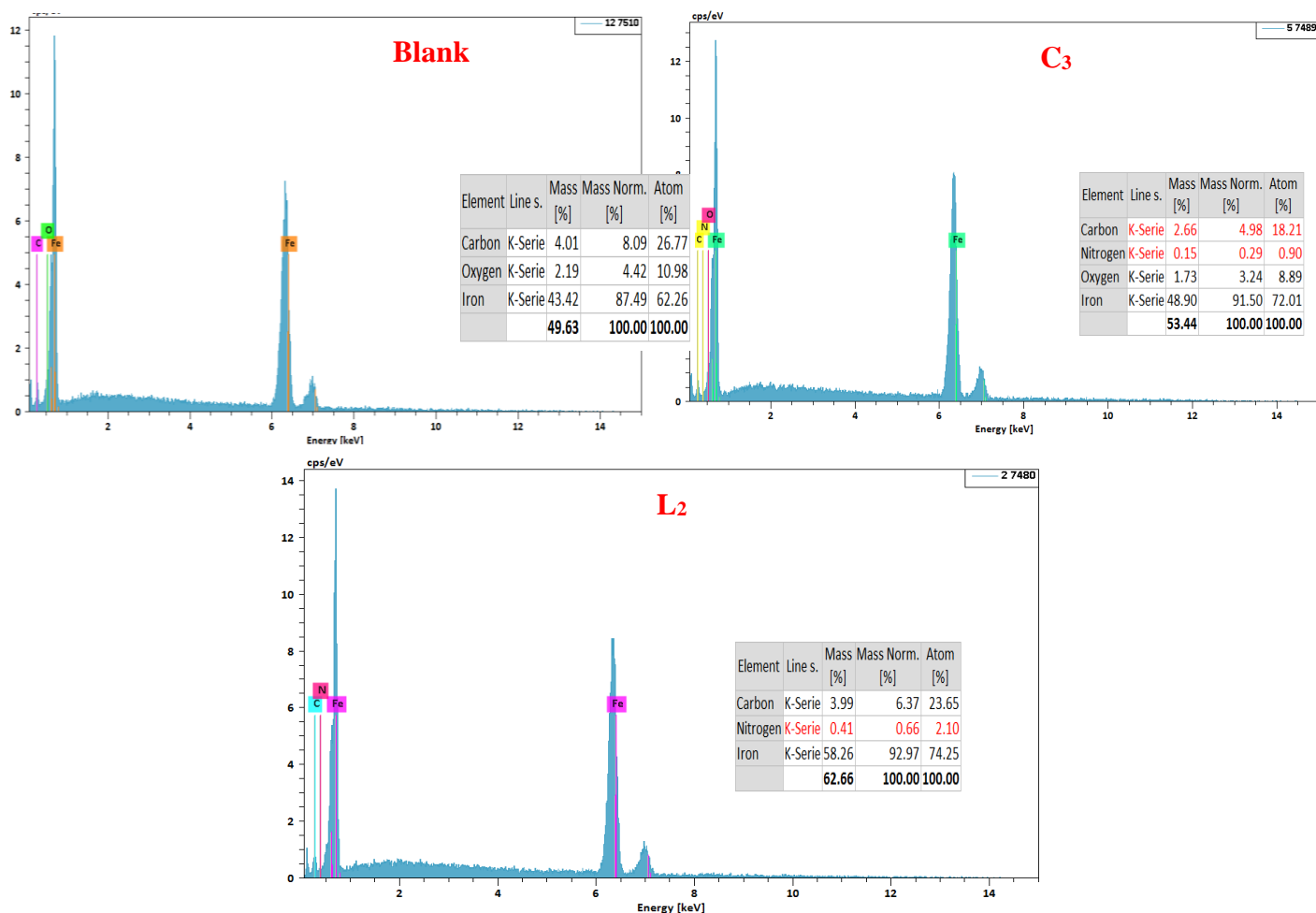


Figure 7. Qualitative and quantitative EDS analysis of the corroded surface after 6h of immersion in 5.0 M HCl solution without and with 5.10^{-4} M of inhibitors: L_2 and C_3

Conclusion

On the basis of the results presented on mild Steel in 5M HCl solution, in the presence of Novel Zn (II) complexes of N_1, N_2 -bis(2-nitrobenzylidene) ethane-1,2-diamine, the following conclusions could be drawn:

- C_3 is an excellent corrosion inhibitor for mild steel in a high concentration 5.0M HCl solution. C_3 is more efficient than L_2 .
- Polarization plots indicate that the studied inhibitors inhibit both the anodic dissolution of the metal, as well as the evolution reactions of the cathodic hydrogen.
- Electrochemical impedance results show that the obtained Nyquist diagrams exhibit one single capacitive loop, indicating that mild steel corrosion is essentially under charge transfer control, leading to the formation of a protective layer on the metal surface, which limits the steel corrosion.
- Adsorption of complexes C_3 on mild steel in 5.0M HCl follows Langmuir isotherm adsorption with a correlation coefficient of one.
- SEM images also confirm the inhibitor adsorption process and reduction in the surface damage of mild steel due to corrosion.
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References

- Abdel-Gaber A. M., Abd-El-Nabey B.A., Sidahmed I.M., El-Zayady A.M., M.Saadawy Inhibitive action of some plant extracts on the corrosion of steel in acidic media , *Corros. Sci* 48 (9) (2006) 2765–2779.
- Aldwayyan A.S., Al-Jekhedab F.M., Al-Noaimi M., Hammouti B., Hadda T. B., Suleiman M., Warad I., Synthesis and Characterization of CdO Nanoparticles Starting from Organometallic Dmphen-CdI₂ complex, *Int. J. Electrochem. Sci.*, 8 (2013), 10506 – 10514.
- Al Hamzi A. H., Zarrok H., Zarrouk A., *et al.* (2013), The Role of Acridin-9(10H)-one in the Inhibition of Carbon Steel Corrosion: Thermodynamic, Electrochemical and DFT Studies , *Inter. J. Electrochemical Science*, 8, 2586-2605.
- Arjmand F., Parveen S., Afzal M., Shahid M. (2012), Synthesis, characterization, biological studies (DNA binding, cleavage, antibacterial and topoisomerase I) and molecular docking of copper (II) benzimidazole complexes, *J. Photochem. Photobiol. B* 114, 15–26.
- Arrousse, N., Salim, R., Houari, G.A. *et al.* (2020) Experimental and theoretical insights on the adsorption and inhibition mechanism of (2E)-2-(acetylamino)-3-(4-nitrophenyl)prop-2-enoic acid and 4-nitrobenzaldehyde on mild steel corrosion. *J. Chem. Sci.*, 132, 112. <https://doi.org/10.1007/s12039-020-01818-w>
- Ashassi-Sorkhabi H., Shaabani B., Seifzadeh D. (2005), Corrosion inhibition of mild steel by some schiff base compounds in hydrochloric acid, *Appl. Surf. Sci.* 239, 154–164.
- Azgaou K., Damej M., El Hajjaji S., Sebbar NK. , Elmsellem H., El Ibrahim B., Benmassoud M. (2022), Synthesis and characterization of N-(2-aminophenyl)- 2-(5-methyl-1H-pyrazol-3-yl) acetamide (AMPA) and its use as a corrosion inhibitor for C38 steel in 1 M HCl. Experimental and theoretical study, *Journal of Molecular Structure* , 1266, 133451
- Barakat A., Mousa A., Suleiman M., *et al.* (2013), One Step Synthesis of NiO Nanoparticles via Solid-State Thermal Decomposition at Low-Temperature of Novel Aqua(2,9-dimethyl-1,10-phenanthroline)NiCl₂ Complex, *Int. J. Mol. Sci.*, 14, 23941-23954,
- Behzadnasab M., Mirabedini S.M., Kabiri K., jamali S. Corrosion performance of epoxy coatings containing silane treated ZrO₂ nanoparticles on mild steel in 3.5% NaCl solution. *Corrosion Science* 53 (2011) 89-98.
- Behpour M., Ghoreishi SM, Mohammadi N, Soltani N, Salavati-Niasari M. (2010), Investigation of some Schiff base compounds containing disulfide bond as HCl corrosion inhibitors for mild steel, *Corrosion Science*, 52, 4046-4057.
- Belghiti M. E., Bouazama S., Echihi S., *et al.* (2020), Understanding the adsorption of newly Benzyldene-aniline derivatives as a corrosion inhibitor for carbon steel in hydrochloric acid solution: Experimental, DFT and molecular dynamic simulation studies, *Arabian Journal of Chemistry*, 13, 1499-1519, <https://doi.org/10.1016/j.arabjc.2017.12.003>
- Boumhara K., Tabyaoui M., Jama C., Bentiss F. (2015), Artemisia Mesatlantica essential oil as green inhibitor for carbon steel corrosion in 1 M HCl solution: Electrochemical and XPS investigations, *Journal of Industrial and Engineering Chemistry*, (29), 146-155.
- Cao C. (1996), On electrochemical techniques for interface inhibitor research, *Corrosion Science*, 38(12), 2073-2082, ISSN0010-938X, [https://doi.org/10.1016/S0010-938X\(96\)00034-0](https://doi.org/10.1016/S0010-938X(96)00034-0)
- Do D. D., Adsorption Analysis: Equilibria and Kinetics, *Imperial College Press*. ISBN-13, 978-1860941375 (1998).
- Doudou Babale D., Wandji R., Bessiere J. (1990), Concentrated hydrochloric acid media: acid-base, oxidation-reduction, and solvation properties, *J. Chem. Eng. Data*, 35(3), 345–347, <https://doi.org/10.1021/je00061a033>
- Ech-chihbi E., Nahlé A., Salim R., *et al.* (2019), An investigation into quantum chemistry and experimental evaluation of imidazopyridine derivatives as corrosion inhibitors for C-Steel in acidic media, *Journal of Bio- and Tribo-Corrosion*, 5, article number 24, <https://doi.org/10.1007/s40735-019-0217-9>
- Ech-Chihbi E., Nahlé A., Salim R., *et al.*, (2020), Journal of Alloys and Computational, MD simulation, SEM/EDX and experimental studies for understanding adsorption of benzimidazole derivatives as corrosion inhibitors in 1.0 M HCl, *Journal of Alloys and Compounds*, 844, 155842
- El Ouafi A., Hammouti B., Oudda H., Kertit S., Touzani R., Ramdani A. (2002), New bipyrazole derivatives as effective inhibitors for the corrosion of mild steel in 1M HCl medium, *Anti-Corrosion Methods and Materials* , 49, 199-204.

- Eteram A. N., Aisha A H. (2008), Thermodynamic study of metal corrosion and inhibitor adsorption processes in mild steel/1-methyl-4 [40 (-X)-styryl pyridinium iodides/hydrochloric acid Mater. Chem. Phys, 110, 145-154, <https://doi.org/10.1016/j.matchemphys.2008.01.028>
- Ferreira E.S., Giancomlli C., Giacomlli F. C. (2004), Spinelli A., Evaluation of the inhibitor effect of l-ascorbic acid on the corrosion of mild steel Mater. Chem. Phys. 83, 129–134. <http://dx.doi.org/10.1016/j.matchemphys.2003.09.020>
- Flis J., Zakroczymski T. (1996), Impedance Study of Reinforcing Steel in Simulated Pore Solution with Tannin, *J. Electrochem. Soc* 143, 2458.
- Freundlich HMF. (1906), Over the adsorption in solution, *J. Phys. Chem.* 57, 385-471.
- Frumkin A. Z. - Zeitschrift fur physikalische Chemie (Leipzig), On the adsorption properties of surface-chemically pure aqueous solutions of n-alkyl-dimethyl and n-alkyl-diethyl phosphine oxides (1925).
- Galai M., El Gouri M., Dagdag O., El Kacimi Y., Elharfi A., Ebn Touhami M. (2016), New hexa propylene glycol cyclotriphosphazene as efficient organic inhibitor of carbon steel corrosion in hydrochloric acid medium, *J. Mater. Environ. Sci.* 7, 1562-1575.
- Ghazoui A., Saddik R., Benchat N., Guenbour M., Hammouti B., Al-Deyab S.S., Zarrouk A. (2012), Comparative Study of Pyridine and Pyrimidine Derivatives as Corrosion Inhibitors of C38 Steel in Molar HCl, *Inter. J. of Electrochemical Science*, 7, 7080-7097
- Gribble Jr M.W., Ellman J.A., Bergman R.G., Synthesis of a benzodiazepine-derived rhodium NHC complex by C–H bond activation, *Organomet* 27 (10) (2008), 2152–2155.
- Halambek J., Berkovic K., Vorkapic-Furac J., (2010), The influence of Lavandula angustifolia L. oil on corrosion of Al-3Mg alloy, *Corrosion Science* 52, 3978-3983.
- Hammouti B., Benayada A. (2020) Electrochemical sensor in situ control of acidity level of concentrated HCl solutions *Moroccan Journal of Chemistry* 8 (3), 573-580
- Hammouti B., H. Oudda, A. Benayada, A. ElMaslout, Bessière J. (1997), In situ determination of acidity level in concentrated phosphoric acid solutions by potentiometric method at imposed current intensity, *Ber. Bunsenges. Phys. Chem.*, 101, 65-69
- Hermas A.A., Morad MS. (2008), A comparative study on the corrosion behaviour of 304 austenitic stainless steel in sulfamic and sulfuric acid solutions, *Corros. Sci.* 50 (9), 2710-2717.
- Houslay M.D., Ellory J.C., Smith G.A., Hesketh T.R., Stein J.M., Warren G.B., Metcalfe J.C. (1977), Exchange of partners in glucagon receptor-adenylate cyclase complexes. Physical evidence for the independent, mobile receptor model, *Biochim. Biophys.* 467 (2), 208–219.
- Kalman E., Varhegi B., Bako. I, Felhosi I., Karman F.H, Shaban A. (1994), Corrosion inhibition by 1-hydroxyethane-1,1-diphosphonic acid: an electrochemical impedance spectroscopy study, *J. Electrochem. Soc.* 141, 3357.
- Khadom A. A., Yaro A.S; Abdul A.H., Adsorption mechanism of benzotriazole for corrosion inhibition of copper-Nickel alloy in hydrochloric acid, *Journal of the Chilean Chemical Society* 55, (2010) 150-152.
- Lagrene M., Mernari B., Bouanis M., Traisnel M., Bentiss F. (2002), Study of the mechanism and inhibiting efficiency of 3,5-bis(4-methylthiophenyl)-4H-1,2,4-triazole on mild steel corrosion in acidic media, *Corros. Sci.* 44, 573–588.
- Langmuir I. (1916), The constitution and fundamental properties of solids and liquids. parti. Solids, *Journal of the American Chemical Society*, 38 (11), 2221-2295.
- Liu FG., Du M., Zhang J., Qiu M., Electrochemical behavior of Q235 steel in saltwater saturated with carbon dioxide based on new imidazoline derivative inhibitor, *J. Corros. Sci.* 51 (1) (2009), 102-109.
- Mansfeld F., Kending M.W., Tsai S. (1981), Recording and Analysis of AC Impedance Data for Corrosion Studies, *J. Corrosion*, 37, 301-307.
- Mary X. Ho, Hudson B.P., Das K., Arnold E., Ebright R.H. (2009), Structures of RNA polymerase–antibiotic complexes, *Curr. Opin. Struct. Biol.* 19 (6), 715–723.
- Merimi C., Hammouti B., Zaidi K., et al. (2023) Acetylsalicylic acid as an environmentally friendly corrosion inhibitor for carbon steel XC48 in chloride environment, *Journal of Molecular structure*, 1278, 134883.
- Mori T., Fujikawa H., Tokito S., Taga Y. (1998), Electronic structure of 8-hydroxyquinoline aluminum/LiF/Al interface for organic electroluminescent device studied by ultraviolet photoelectron spectroscopy, *Appl. Phys. Lett.* 73 (19), 2763–2765.
- Ramesh S., Rajeswari S. (2004), Corrosion inhibition of mild steel in neutral aqueous solution by new triazole derivatives, *Electrochim. Acta* 49, 811–820.

- Salim, R., Nahlé, A., El-Hajjaji, F. *et al.* (2021). Experimental, density functional theory, and dynamic molecular studies of imidazopyridine derivatives as corrosion inhibitors for mild steel in hydrochloric Acid. *Surf. Engin. Appl. Electrochem.* 57, 233–254, <https://doi.org/10.3103/S1068375521020083>
- Singh A. K., Quraishi M.A. (2011), Investigation of the effect of disulfiram on corrosion of mild steel in hydrochloric acid solution, *Corrosion Science*, 53, 1288-1297.
- Sun R.W.Y., Ma D.L., Wong E.L.M., Che C.M. (2007), Some uses of transition metal complexes as anti-cancer and anti-HIV agents, *Dalton Trans.* (43), 4884–4892, <https://doi.org/10.1039/b705079h>
- Suzuki T., Nishihara H., Aramaki K. (1996), The synergistic inhibition effect of octylmercaptopropionate and 8-quinolinol on the corrosion of iron in an aerated 0.5 M Na₂SO₄ solution, *Corros. Sci.* 38, 1223-1234.
- Temkin M.I. (1940), Kinetics of ammonia synthesis on promoted iron catalysts, *Acta Physiochim. URSS* (12), 327-356.
- Toghan A., Alduaij O.K., Fawzy A., Mostafa A.M., Eldesoky A.M., Farag A.A. (2024) Effect of Adsorption and Interactions of New Triazole-Thione-Schiff Bases on the Corrosion Rate of Carbon Steel in 1 M HCl Solution: Theoretical and Experimental Evaluation. *ACS Omega*, 9(6), 6761-6772. doi: [10.1021/acsomega.3c08127](https://doi.org/10.1021/acsomega.3c08127)
- Vračar D.M. & Dražić D. (2002), Adsorption and corrosion inhibitive properties of some organic molecules on iron electrode in sulfuric acid, *Corrosion Science*, 44, 1669–1680, [https://doi.org/10.1016/S0010-938X\(01\)00166-4](https://doi.org/10.1016/S0010-938X(01)00166-4)
- Yaro A.S., Khadom A.A. (2010) Polarisation resistance behaviour of corrosion inhibition of low carbon steel in H₃PO₄ acid, *International Journal of Surface Science and Engineering* 4 (4-6), 429-438, <http://dx.doi.org/10.1504/IJSURFSE.2010.035145>
- Wang X., Yang H., Wang F. (2011), An investigation of benzimidazole derivative as corrosion inhibitor for mild steel in different concentration HCl solutions, *J. Corros. Sci.* 53, 113–121. <http://dx.doi.org/10.1016/j.corsci.2010.09.029>
- Yadav M., Kumar S., Sinha R.R., Bahadur I., Ebenso E.E., New pyrimidine derivatives as efficient organic inhibitors on mild steel corrosion in acidic medium: Electrochemical, SEM, EDX, AFM and DFT studies, *J. Mol. Liq.* 211 (2015), 135-145. <https://doi.org/10.1016/j.molliq.2015.06.063>
- Zarrouk A., Hammouti B., Zarrok H., *et al.* (2012), Corrosion inhibition of copper in nitric acid solutions using a new triazole derivative, *Int. J. Electrochem. Sci.* 7, 89–105.
- Zarrok H., Zarrouk A., Salghi R., *et al.* (2013), Inhibitive properties and thermodynamic characterization of quinoxaline derivative on carbon steel corrosion in acidic medium, *Der Pharmacia Lettre*, 5(2), 43-53.
- Zerga B., Attayibat A., Sfaira M., Taleb M., Hammouti B., Ebn Touhami M., Radi S., Rais Z. (2010). Effect of some tripodal bipyrazolic compounds on C38 steel corrosion in hydrochloric acid solution, *Journal of Applied Electrochemistry*, 40, 1575–1582, <http://dx.doi.org/10.1007/s10800-010-0164-0>

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