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IMPACT OF ZNCL$_2$ ON MILD STEEL CORROSION IN MANUFACTURING TECHNOLOGIES UNDER PH VARIATIONS

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Abstract: This study investigates the efficacy of $ZnCl_2$ as a corrosion inhibitor for mild steel across varied pH environments (3.5, 7, and 10). Findings highlight a significant reduction in corrosion rates with increasing $ZnCl_2$ concentrations, pinpointing optimal levels at 350 ppm (pH 3.5), 575 ppm (pH 7), and 325 ppm (pH 10). Through comprehensive experimental analyses, the study robustly validates the protective capacity of the inhibitor, shedding light on its practical application in safeguarding metallic materials amidst varying pH conditions. $ZnCl_2$ will be applied as a solution, forming a protective layer on the surface of mild steel, thereby acting as a barrier against corrosive agents. The study's originality lies in its specific exploration of $ZnCl_2$ efficiency under varied pH conditions, emphasizing its substantial contribution to corrosion protection in different environmental settings.

Key words: Corrosion, inhibition, $ZnCl_2$, mild Steel, pH Levels

1. INTRODUCTION

The corrosion, a natural process, alters metals exposed to harsh environments. It involves a chemical reaction between the metal material and its environment, often exacerbated by water or corrosive agents. Protection against corrosion aims to prevent or slow down this destructive process. Corrosion inhibitors, such as $ZnCl_2$, are used to form protective layers on the metal surface, thereby reducing the corrosion rate. Other methods include applying special coatings or using sacrificial anodes to divert corrosive attacks. Understanding corrosion mechanisms and protection techniques is essential for extending the lifespan of metallic materials in various industrial and everyday applications [1].

The utilization of $ZnCl_2$ as a corrosion inhibitor is crucial in combating the detrimental effects of corrosion. Corrosion inhibitors, like $ZnCl_2$, provide complete protection against metal deterioration in various environments. Studies such as those conducted by Bensaada et al. [2] highlighted the impact of chlorides on steel reinforcement corrosion, while Lafont et al. [3] examined phosphonate-derived compounds with zinc salts for cooling water treatment, demonstrating increased efficacy with concentration. Additionally, Duprat et al. [4] showed that surface chelate formation was crucial in the effectiveness of 2-ethylamino-ethanol as an inhibitor. Morris et al. [5] assessed the effectiveness of a surface-applied corrosion inhibitor (MCI) on concrete with steel bars, highlighting its limitations in marine environments. Xhanari et al. [6] explored the inhibitory effects of eight amines on C15 mild steel, noting reduced corrosion and improved performance at different temperatures. Lee et al. [7] examined the action of lithium nitrite and amino alcohol inhibitors on reinforcement steel in chloride-rich environments. Abouchane et al. [8] conducted research on the effectiveness of triazole compounds as inhibitors for mild steel in phosphoric acid, highlighting enhanced efficacy through collaboration with KI. Ashassi-Sorkhabi et al. [9] discovered that four percent ethylenediamine showcased remarkable inhibitive properties when used with carbon steel in water-petroleum blends. Bastidas et al. [10] investigated the influence of tributylamine on the corrosion of mild steel in “Hcl” acid, observing an adsorption orientation based on the projected molecular area. Noor et al. [11] investigated the efficacy of quaternary N-heterocyclic compounds in “H_3PO_4”, demonstrating their role as effective mixed inhibitors.

This work use $ZnCl_2$ as a corrosion inhibitor complements prior studies. While earlier research demonstrated the inhibitors' effects in various environments, this study specifically focuses on determining the optimal concentrations of $ZnCl_2$ to protect mild steel submerged in a sodium chloride solution at pH 3.5, 7, and 10. It fills gaps by providing specific data on $ZnCl_2$ efficacy in environments with different pH levels, an area insufficiently explored in previous research. By employing experimental techniques like mass loss and polarization, this study uniquely assesses the inhibitor's performance in varied pH conditions, thereby contributing valuable insights to optimize the corrosion inhibitors, exemplified by $ZnCl_2$ as corrosion protection across diverse scenarios.

2. EXPERIMENTAL PROCEDURE

This study utilized two experimental techniques, namely the lost mass technique and the potentiostatic technique, to ascertain the optimal concentrations. The optimal concentrations identified were 350 ppm (pH 3.5), 575 ppm (pH 7), and 325 ppm (pH 10). The use of these techniques necessitates the preparation of samples (steel), electrolytic solutions (NaCl), and inhibitory solutions.

2.1. Sample preparation

In this study, mild steel plates (XC 18), with dimensions of (30 x 30 x 2.5) mm, were used as sample materials. As corrosion is an interfacial phenomenon between the metal and its environment, the surface condition plays a crucial role in the metal's corrosion behavior. Sample surface preparation was conducted using the following equipment: a mechanical polisher and abrasive paper.

2.2. Samples for the weight loss method

The polishing procedure was carried out using abrasive paper of various grit sizes: 180, 400, 600, and 1000 to achieve an appropriate surface condition. Subsequently, the samples were washed with a soapy solution, followed by rinsing with distilled water. After drying, they were further rinsed with acetone.

2.3. Samples for the potentiostatic method

One side of the samples (used in the potentiostatic method tests) was welded to an electrical conductor for connection to the potentiostat. Polishing was then carried out in the same manner as before. The sample was coated with an insulating layer (coil varnish), except for the side exposed to the environment.

2.4. Preparation of solutions

The preparation of the electrolytic solution (10^{-2} M NaCl) was achieved by dissolving 0.585 grams of NaCl in one liter of distilled water. The resulting electrolyte was stored in volumetric flasks.
The inhibitor used in this study is zinc chloride. Its chemical formula is $ZnCl_2$. Its molecular mass is M=136.4 g/mol.

2.5. Weight loss technique

This technique was used to study the inhibitor's effectiveness.
The purpose of measuring the weight loss is to assess the corrosion rate, defined as the weight loss per unit area and time, expressed in (g/cm^2/year). The corrosion rate is calculated using formula (1):

$$\tau = 365\frac{\Delta m}{s\cdot t} \text{ with } \Delta m = m_i - m_f \quad (1)$$

where: m_i is the initial mass of the sample before the test, m_f is the final mass of the sample after the test, S: surface area of the sample (cm^2), t represents the duration of the experiment in days.
This method, depicted in Figure (1), requires the following laboratory equipment: Samples – beakers; Precision balance - suspension wire and Nylon thread - soft-bristled toothbrush.

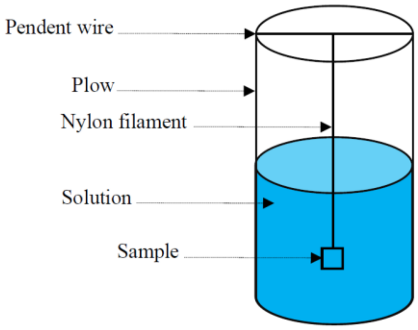


Fig. 1 Experimental Setup for the weight loss technique

Each finished sample was weighed and its mass, total surface area, as well as the solution properties (pH, concentration, etc.), and test duration were recorded in tables. pH values of 3.5, 7, and 10 were selected.

The sample was suspended in a beaker containing 400 ml of solution. The inhibitor concentrations used ranged from 0 ppm to 600 ppm. The immersion duration was set at ten days for all tests. Subsequently, the sample was removed, cleaned with water. The elimination of corrosion products from the metal surface was achieved by gently brushing with a toothbrush featuring soft bristles. Subsequently, the sample then underwent rinsing with distilled water, followed by drying and reweighing. The updated mass measurements were duly recorded in the tables.

2.6. Potentiostatic technique

This technique has been used in several studies [12,13] to investigate the effectiveness of the inhibitor. This method requires the following laboratory equipment: Samples (with electrical connection); Potentiostat (apparatus), microcomputer; Reference electrode (Saturated calomel) and Auxiliary electrode (Platinum).

The working electrode (steel), reference electrode (saturated calomel), and auxiliary electrode (platinum) are immersed in an electrolytic solution and connected to a potentiostat, which is a current source primarily responsible for maintaining a constant potential between the working electrode and the reference electrode through an amplifier. Then, the stationary current which is established after a certain time in the electrical circuit between the working electrode and an auxiliary electrode (EA) (platinum electrode) is measured [12]. This setup is linked to a microcomputer equipped with software for plotting curves: E = f (I) and E = f (log i), determining the corrosion rate in (mm/year) and the corrosion velocity in (A/cm^2).

The reference electrode is made from a special material that, in combination with the electrolyte, maintains a stable potential used as a reference point for potential measurements. Mercury/mercurous chloride electrodes (Hg/Hg_2Cl_2 in saturated KCl) are commonly used. This electrode should be positioned to avoid significant voltage drop between the working electrode and itself.

The auxiliary electrode is made from an inert material such as graphite or platinum.

The study of the material's anodic and cathodic behavior proceeds as follows:

Initially, a low potential (E < Ecorr) is applied, where the metal constitutes the cathode of the cell. Then, the potential is increased until (E > Ecorr) is reached, where the metal becomes the anode of the cell. If the working electrode is a corroding material, there is a coupling of two redox systems with the metal potential.

$M \rightarrow M^{n+} + ne^-$ with current i_a

$\mathrm{Ox} + e^- \rightarrow \mathrm{R_{ed}}$ with current i_c

According to Tafel's Law, these currents vary depending on the potential (E). Elementary curves are obtained that are not accessible through experimentation. It is the overall curve (resultant of the elementary curves) that provides $i = i_a - |i_c|$ as a function of E. The current denotes the flow of electrons between the working electrode and the auxiliary electrode.

The corrosion potential (Ecorr) corresponds to the case where $|i_a| = |i_c| = i_{corr}$. At this point, the corrosion rate is given by $|i_a| = |i_c| = i_{corr}$. It is this density that needs to be determined.

The working electrode (steel), reference electrode (calomel), and auxiliary electrode (counter electrode) were immersed in 300 ml of a solution (10.2 M NaCl in the presence or absence of an inhibitor). They were connected to a potentiostat and linked to a microcomputer equipped with software for plotting curves: E = f (I) and E = f (log i), as well as for obtaining the corrosion rate in (mm/year) and the corrosion velocity in (A/cm^2). The experimental setup for this technique is illustrated in Figure (2).

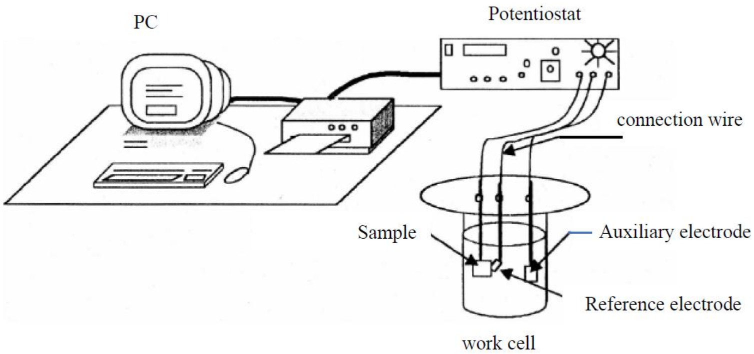


Fig. 2 Experimental Setup of the Potentiostatic Technique

3. RESULTS AND DISCUSSION

3.1. Weight loss method

The corrosion rates of steel immersed in solutions of varying pH (3.5, 7, and 10) were assessed through two methodologies: weight loss analysis and potentiostatic polarization. The experiments involved the introduction of a corrosion inhibitor (zinc chloride) to determine the most effective concentration for ensuring maximal protection.

The corrosion rates expressed in (g/cm^2/year) as a function of inhibitor concentrations in (ppm) are provided in tables 1, 2, and 3:

Table 1. Corrosion rates of steel in a 10-2 M NaCl solution, duration 10 days, pH 3.5

Initial mass (g)	**Final mass (g)**	**Δm (g)**	**Exposed surface area (cm^2)**	**$ZnCl_2$ (ppm)**	**Corr. rate (g/cm^2/year)**
17.75	17.67	0.09	9.38	0.00	0.33
17.33	17.25	0.08	9.26	200.0	0.31
17.97	17.9	0.08	9.33	300.0	0.29
17.61	17.54	0.08	9.38	325.0	0.29
17.71	17.63	0.07	9.26	350.0	0.29
17.33	17.26	0.07	9.26	400.0	0.29
17.55	17.46	0.09	9.26	500.0	0.35

Table 2. Corrosion Rates of Steel in a Solution of NaCl with a Concentration of 10-2 mol/l, Duration: 10 Days, pH: 7

Initial mass (g)	**Final mass (g)**	**Δm (g)**	**Exposed surface area (cm^2)**	**$ZnCl_2$ (ppm)**	**Corr. rate (g/cm^2/year)**
17.53	17.51	0.02	9.38	0.0	0.08
18.2	18.19	0.02	9.33	50.0	0.06
17.24	17.23	0.01	9.41	200.0	0.06
17.69	17.67	0.01	9.41	550.0	0.05
17.96	17.96	0.01	9.35	575.0	0.04
17.43	17.42	0.01	9.33	600.0	0.05
17.53	17.51	0.02	9.38	0.00	0.08

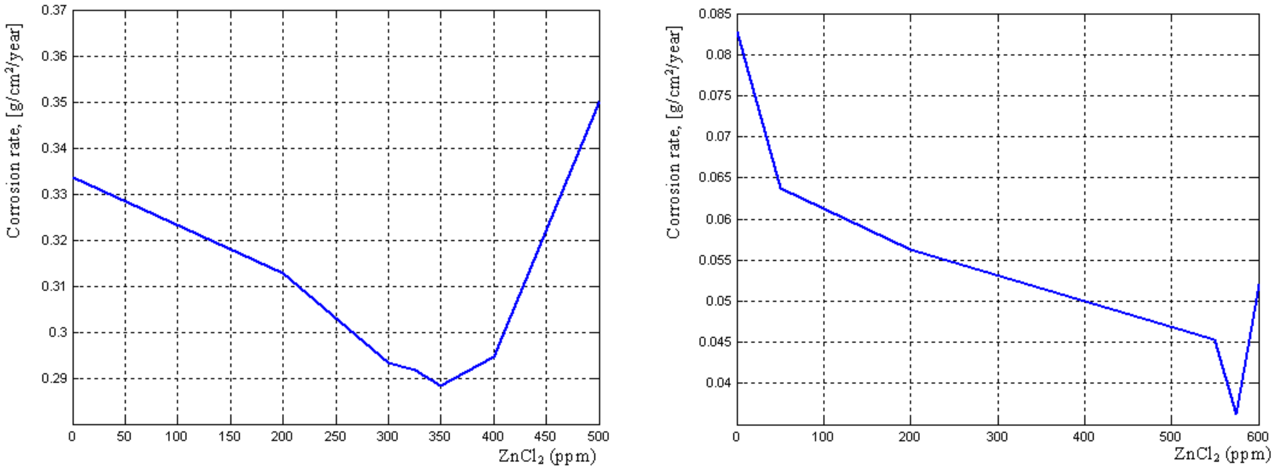
Table 3. Corrosion rates of steel in a 10-2 M NaCl solution, duration 10 days, pH 10

Initial mass (g)	**Final mass (g)**	**Δm (g)**	**Exposed surface area (cm^2)**	**$ZnCl_2$ (ppm)**	**Corr. rate (g/cm^2/year)**
17.7	17.68	0.02	9.14	0.0	0.06
17.65	17.64	0.01	9.35	100.0	0.05
18	17.99	0.01	9.24	200.0	0.04
17.54	17.53	0.01	9.21	275.0	0.04
16.62	16.61	0.01	9.24	300.0	0.04
17.74	17.73	0.01	9.49	325.0	0.03
17.85	17.84	0.01	9.49	400.0	0.04

3.2. Graphical representations

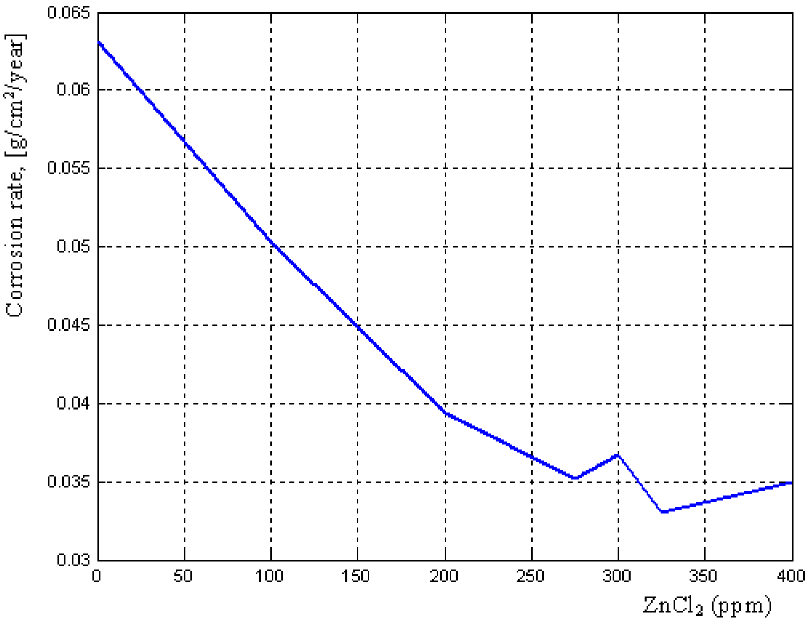
The findings outlined in tables 1, 2, and 3, depicted in figures 3 and 4, indicate a marginal decline in the corrosion rate of mild steel as the concentrations of the $ZnCl_2$ inhibitor increase.

The lowest corrosion rates observed align with specific concentrations: “350 ppm, 575 ppm, and 325 ppm” for pH levels of “3.5, 7, and 10”, respectively. This reduction is likely due to the development of a thin layer of zinc hydroxide formed through the interaction between Zn^{2+} ions introduced by the inhibitor and OH^- ions generated during the reduction of oxygen and water in proximity to the cathodes, as illustrated in Equations (2) and (4). This hydroxide layer acts as an insulating barrier with low conductivity, impeding cathodic access to the metal surface, consequently diminishing the corrosion rate. The decline in pH levels is probable due to the reaction involving Fe^{2+} ions in the presence of water, where OH^- ions are consumed for the formation of the protective zinc hydroxide layer according to Equation (3).



(a) pH= 3.5

(b) pH= 7



(c) pH= 10

Fig. 3. Comparison of Corrosion Rates of Steel in a "10-2 M NaCl" Solution in the Presence of Zinc Chloride after 10 Days of Immersion at Different pH Levels

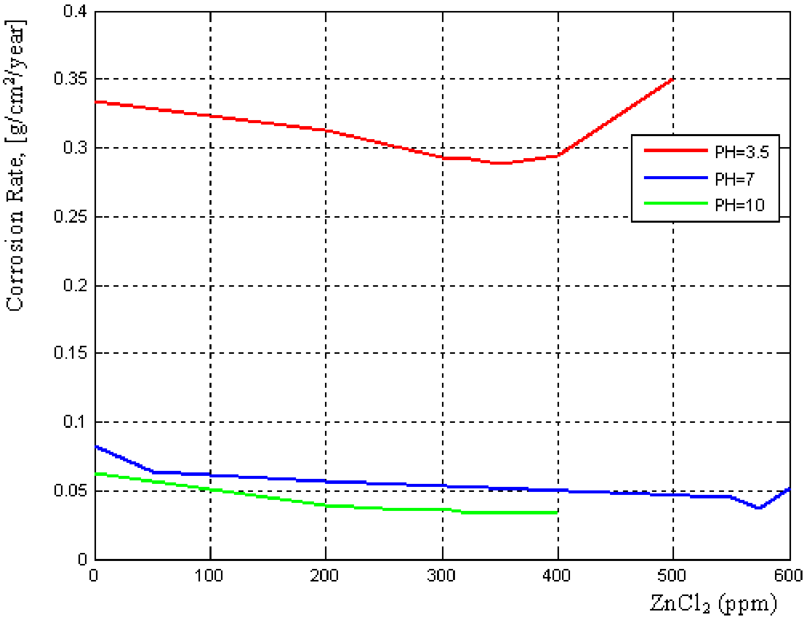


Fig. 4. Corrosion rates of steel in a “10-2 M NaCl” solution in the presence of zinc chloride after 10 days of immersion, “pH=3.5, 7 and 10”

$$Fe \rightarrow Fe^{2+} + 2e \tag{2}$$

$$Fe^{2+} + H_2O \rightarrow Fe(OH)^{+} + H^{+} \tag{3}$$

$$Zn^{2+} + 2OH^{-} \rightarrow Zn(OH)_2 \tag{4}$$

This reaction induces a slightly acidic environment, disrupting the stability of the protective layer. Moreover, the presence of the aggressive Cl- anion initiates assaults on vulnerable areas of the protective layer, encouraging irregular oxygen adsorption and the formation of localized cells on the metal. These two phenomena lead to the dissolution of the hydroxide layer and prevent its reformation, rendering the protection non-durable. This necessitates either the presence or combination of this inhibitor with others for sustained protection.

3.1.1. Potentiostatic Method

This section will present the findings derived from the potentiostatic technique and discuss the outcomes of corrosion inhibition tests conducted on mild steel in “10^{-2} M NaCl”, both in the absence and presence of the inhibitor.

The inhibitor concentrations utilized in this technique mirror those employed in the weight loss method.

Table 4. Corrosion rates of steel using the potentiostatic technique (10 days of immersion), pH 3.5

$ZnCl_2$ (ppm)	**Corrosion rate (mm/year)**	**I (mA/cm^2)**	**Ecorr (mV)**	**b_a**	**b_c**
0.00	0.35	0.03	-650.90	99.2	- 433.2
200.00	0.35	0.03	-660.00	105.7	- 441.2
300.00	0.30	0.03	-655.80	102.0	- 403.8
325.00	0.28	0.02	-650.20	91.9	- 429.8
350.00	0.27	-0.02	-647.50	104.1	- 368.2
400.00	0.34	0.03	-660.50	110.8	- 476.1
500.00	0.41	0.03	-663.70	111.7	- 479.8

Without the inhibitor, the corrosion current density measures around 0.03 mA/cm^2. Introduction of zinc chloride results in decreased current densities. Between concentrations of “200.0 to 350.0 ppm”, the inhibitor's effectiveness escalates with rising concentrations. Optimal protection is observed at 350.0 ppm. Nevertheless, in the range of “350.0 to 500.0 ppm”, the inhibitory efficiency diminishes despite increasing inhibitor concentration, these results are in agreement with those reported by Bensaada S. et al. [2].

Table 5. Corrosion rates of steel using the potentiostatic technique (10 days of immersion), pH 7

$ZnCl_2$ (ppm)	**Corrosion rate (mm/year)**	**I (mA/cm^2)**	**Ecorr (mV)**	**b_a**	**b_c**
0.00	0.08	7.01	-570.90	101.2	- 579.4
50.00	0.07	5.74	-578.80	80.4	- 306.6
200.00	0.07	5.68	-536.80	184.6	- 39.8
550.00	0.05	3.89	-544.00	170.5	- 1276.5
575.00	0.01	1.14	-406.30	81.4	- 58.9
600.00	0.05	4.52	-567.50	116.3	- 49.4

Without the inhibitor, the corrosion current density measures around 7.01 µA/cm^2. Upon introducing zinc chloride, there's a decrease in current densities. Between concentrations of “500.0 to 575.0 ppm”, the inhibitor's effectiveness rises with increasing concentration, reaching optimal protection at 575.0 ppm. However, within the range of “575.0 to 600.0 ppm”, the inhibitory efficiency diminishes despite higher inhibitor concentrations.

Table 6. Corrosion rates of steel using the potentiostatic technique (10 days of immersion), pH 10

$ZnCl_2$ (ppm)	**Corrosion rate (mm/ year)**	**I (mA/cm^2)**	**Ecorr (mV)**	**b_a (mV)**	**b_c (mV)**
0.00	0.08	6.58	-542.50	187.0	- 48.4
100.00	0.07	5.99	-609.60	326.8	- 35.6
200.00	0.06	4.92	-565.20	356.5	- 51.3
275.00	0.04	3.16	-484.50	130.2	- 2028.7
300.00	0.04	3.65	-561.10	157.4	- 981.4
325.00	0.03	2.89	-535.50	92.5	- 144.7
400.00	0.04	3.06	-589.80	300.0	- 34.6

Without the inhibitor, the corrosion current density measures approximately 6.58 µA/cm^2. Upon introducing the zinc chloride inhibitor, there is a reduction in current densities. Between concentrations of “100.0 to 325.0 ppm”, the inhibitor's effectiveness amplifies with rising concentrations, reaching optimal protection at 325.0 ppm. However, within the range of “325.0 to 400.0 ppm”, the inhibitory efficiency diminishes despite the increase in inhibitor concentration.

3.1.2. Graphical representations

Upon examination of the cathodic branches of the polarization curves (figure 5), there seems to be no notable difference between the curves obtained with and without the inhibitor.

In the anodic region, the introduction of $ZnCl_2$ induces a distinct change in the curve shape compared to the curve acquired without the inhibitor. The anodic slopes depicted by the Tafel lines undergo alterations in the presence of this inhibitor, leading to a reduction in the partial anodic current density. Notably, the inclusion of the inhibitor causes a shift in the potential towards more positive values. This promotes the formation of passive or inhibitory films on the metal surface, thereby reducing the reactivity of XC18 with its corrosive environment [13]. Moreover, it has been found that Zn^{2+} inhibits the corrosion of carbon steel via adsorption at cathodic sites [14]

It has been demonstrated that the addition of $ZnCl_2$ to the environment results in effective protection of mild steel at optimal concentrations of 350 ppm (pH 3.5), 575 ppm (pH 575), and 325 ppm (pH 325).

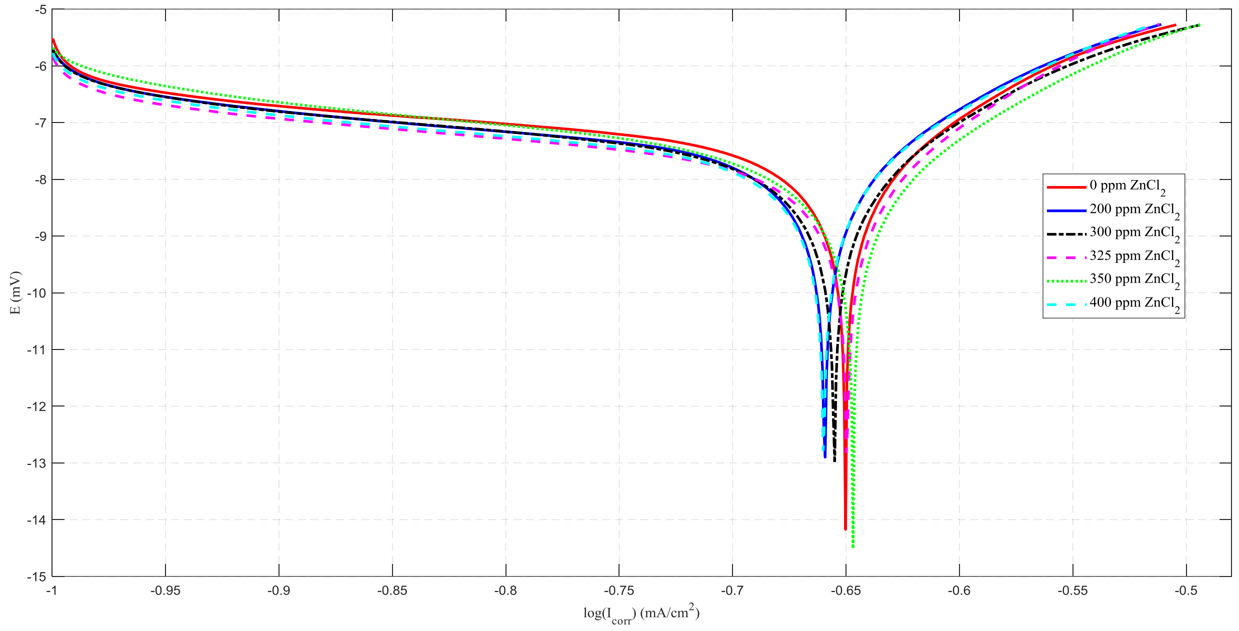


Fig. 5. Polarization curve of XC38 in a “10-2 M NaCl” solution after 10 days of immersion at different $ZnCl_2$ concentration levels “pH=3.5”

4. CONCLUSIONS

The research explored the corrosion tendencies of mild steel across diverse pH environments, assessing the effectiveness of $ZnCl_2$ as a corrosion inhibitor. The primary goal was to ascertain the most effective $ZnCl_2$ concentrations for safeguarding mild steel immersed in a sodium chloride solution across pH levels of 3.5, 7, and 10. Results indicated a reduction in the corrosion rate with increasing $ZnCl_2$ concentrations, with the most effective concentrations being 350 ppm (pH 3.5), 575 ppm (pH 7), and 325 ppm (pH 10).

The findings support previous research on corrosion inhibitors, emphasizing the pivotal role of $ZnCl_2$ in protecting metals from deterioration in diverse environments. The study fills gap in previous research by specifically evaluating $ZnCl_2$ efficacy across different pH levels, providing essential insights into optimizing its usage for corrosion protection.

Experimental techniques such as the weight loss method and potentiostatic technique were employed to measure corrosion rates. Graphical representations, polarization curves, and numerical data illustrated the inhibitory effects of $ZnCl_2$. While the cathodic branches showed minimal differences between curves with and without the inhibitor, alterations in the anodic domain confirmed the inhibitor's impact on reducing partial anodic current density and shifting potentials to more positive values.

This study contributes essential data on $ZnCl_2$ efficiency in environments with distinct pH levels, crucial for industries reliant on metallic materials. The findings provide a framework for selecting appropriate $ZnCl_2$ concentrations to combat corrosion effectively, thereby extend the longevity of metallic structures and components in various applications.

Conflicts of Interest: There is no conflict of interest.

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