

Two Environmental Friendly Compounds As Zinc Corrosion Inhibitors in HCl Media

Niyazi A. S. Al-Areqi, Gamal Al-Maleeh

Abstract—The inhibitive effects of chlortrimazole (CTM) and potassium iodate (PI), two environmental friendly compounds, on the corrosion of zinc metal in HCl have been investigated using chemical (weight loss) and electrochemical (open-circuit potential) techniques. It was found that the inhibition efficiencies of CTM and PI remarkably increase as the inhibitor concentration increases, and drop with increasing temperature. CTM and PI adsorbed on the surface of zinc according to the Langmuir adsorption isotherm model at all the concentrations and temperatures studied. The mechanism of physical adsorption of CTM and PI on the surface of zinc was also proposed based on the thermodynamic parameters obtained.

Index Terms— corrosion, Inhibition, Zinc, HCl, CTM, PI

1 INTRODUCTION

ZINC is considered as one of the most important metals in the world, since it is used in different industrial applications, such as electrode material in batteries sacrificial anodes metallic coating. Therefore zinc metal has to be protected against corrosion from aggressive environments. but when exposed to humid atmosphere, they undergo rapid corrosion with the formation of a corrosion product known as white rust. [1-3]. Studies of the effect of organic additives on the corrosion rate of zinc have been the subject of many investigators [4-8]. It has been found that most of the organic inhibitors act by adsorption on the metal surface. This phenomenon is influenced by certain physicochemical properties of inhibitor molecule such as functional groups, steric factors, aromaticity, electron density at the donor atoms and the electronic structure of the molecule [9]. Chlortrimazole [1-[(2-chlorophenyl)-diphenylmethyl] imidazole is a non-toxic, cheap and environmental friendly antifungal drug that is used in the treatment of fungal disease. It contains reactive centers like N atoms containing lone pairs of electrons and aromatic rings with delocalized π electron systems which can aid the adsorption onto metal surfaces. Furthermore, it has a high molecular weight (344.845 g mol⁻¹) and likely to effectively cover more surface area (due to adsorption) of the zinc metal thus preventing corrosion from taking place [10]. Potassium iodate (214 g mol⁻¹) is anti-microbial and has oxidizing properties.

In the present work, we aim to investigate the inhibitive effect of two environmental friendly compounds, viz. chlortrimazole (CTM) and potassium iodate (PI), on the corrosion of zinc in HCl aqueous media using chemical and electrochemical measurements.

2 MATERIALS & METHODS

The chemical composition of Zinc used in the present study is 99.5% Zinc and had traces of (Cu 0.17%, Ti 0.075%, Al < 0.05%, Pb - Cd < 0.003%, Fe 0.002%, Sn 0.001% and Mg 0.0005%). It was purchased from Fisher Chem. Guide Company. Analytical grade HCl was purchased from BDH Prolabo chemicals VWR (Germany). Chlortrimazole and Potassium iodate were of analytical grade and purchased from Sigma Aldrich.

Medium	Name of inhibitor	Abbreviation	Molecular formula
100 mmol HCl	Chlortrimazole	CTM	C ₂₂ H ₁₇ ClN ₂
	Potassium iodate	PI	KIO ₃

All solutions were prepared from ordinary distilled water, thermo-stated to within ± 0.1 °C of the indicated temperature. The specimens are polished according to the methods described earlier [11,12] the corroding media were prepared as aqueous solution of HCl with concentrations of 0.5, 1.0, 1.5, 2.0 M. An aqueous solution of 1M HCl was used as a blank solution. The inhibitors were added to the HCl solution in concentrations of 0.005, 0.015, and 0.025 g/100 ml. The tested specimens were used in the form of sheets of dimensions (2cm \times 2cm). The Zinc sample was chemically cleaned [13] weighed and suspended in 100 ml of test solution, and then again weighed at the end of the reaction after fully drying. The weight loss measurement and potential of zinc specimens against a saturated calomel electrode (SCE) were simultaneously recorded as a function of time. The potentiodynamic polarization measurements were carried out using a constant-current galvanostat (Fig. 1).

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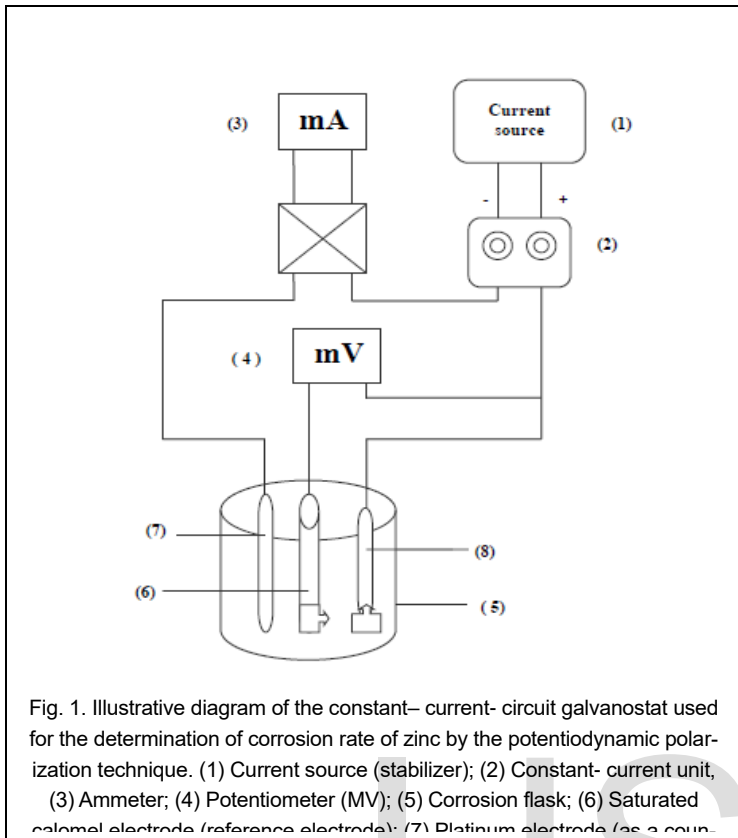


Fig. 1. Illustrative diagram of the constant-current circuit galvanostat used for the determination of corrosion rate of zinc by the potentiodynamic polarization technique. (1) Current source (stabilizer); (2) Constant-current unit, (3) Ammeter; (4) Potentiometer (MV); (5) Corrosion flask; (6) Saturated calomel electrode (reference electrode); (7) Platinum electrode (as a coun-

3 RESULTS & DISCUSSION

3.1 Weight-loss technique

The weight loss of the zinc metal that immersed in different HCl concentrations was measured as mg/cm^2 at 25°C . The dissolution of zinc in HCl was increased as acid concentration increases. The effect of acidic concentration at 25°C on the dissolution of zinc are shown in Fig. 2 and illustrated in Table 1

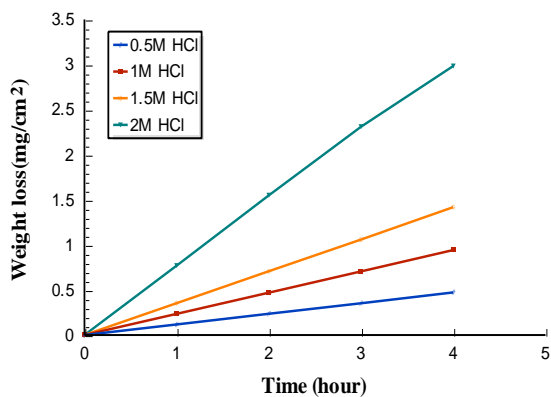


Fig. 2. Weight loss – time curves of zinc dissolution in HCl solutions with varying concentrations at 25°C .

TABLE 1
DATA OF WEIGHT LOSS AND CORROSION RATES OBTAINED FROM WEIGHT LOSS MEASUREMENTS FOR ZINC IN DIFFERENT CONCENTRATIONS OF HCL SOLUTION AT 25°C .

HCl (M)	Time (hour)	wt loss (mg/cm^2)	i_{Corr} ($\text{mg}\cdot\text{cm}^2\cdot\text{h}^{-1}$)	i_{Corr} (mpy)
0.5	1	0.118	0.0295	14.25
	2	0.236	0.0295	14.16
	3	0.353	0.0294	14.21
	4	0.473	0.0295	14.28
1	1	0.235	0.0587	28.39
	2	0.471	0.0588	28.45
	3	0.706	0.0588	28.43
	4	0.943	0.0589	28.49
1.5	1	0.354	0.0885	42.76
	2	0.708	0.0885	42.76
	3	1.06	0.0883	42.68
	4	1.419	0.0886	42.85
2	1	0.77	0.1925	93.01
	2	1.55	0.1937	93.62
	3	2.311	0.1926	93.05
	4	2.984	0.1865	90.12

absence and presence of different concentrations of CTM, and PI at 25°C are presented in Figs. 3 and 4, respectively, and their calculated data is listed in Table 2. It is clear that the corrosion rate of Zinc generally decreases with increasing inhibitor concentration in HCl solution.

The surface coverage area (Θ) and the inhibition efficiency (IE %) were calculated using the following relations [14]:

$$\Theta = (W_o - W) / W_o \quad (1)$$

$$\text{IE \%} = [(W_o - W) / W_o] \times 100 \quad (2)$$

where W_o and W indicate the weight loss in absence and presence of inhibitors, respectively. The corrosion rate (r) was calculated as [15],

$$r(\text{mpy}) = 3448W(\text{mg}) / d(\text{g}/\text{cm}^3) \times A(\text{cm}^2) \times t(\text{h}) \quad (3)$$

A ; specimen area, d ; density and t ; the exposure time.

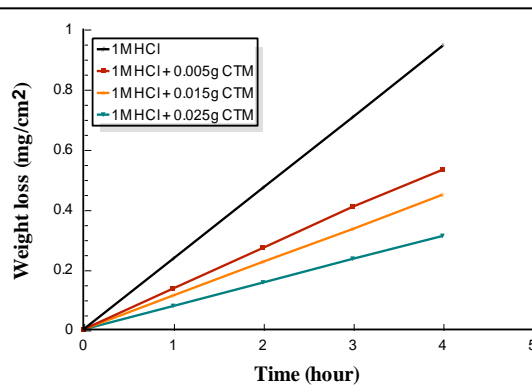


Fig. 3. Weight loss – time curves of aluminum dissolution in 1M potassium hydroxide solution at 25°C in the absence and presence of PI for various concentrations.

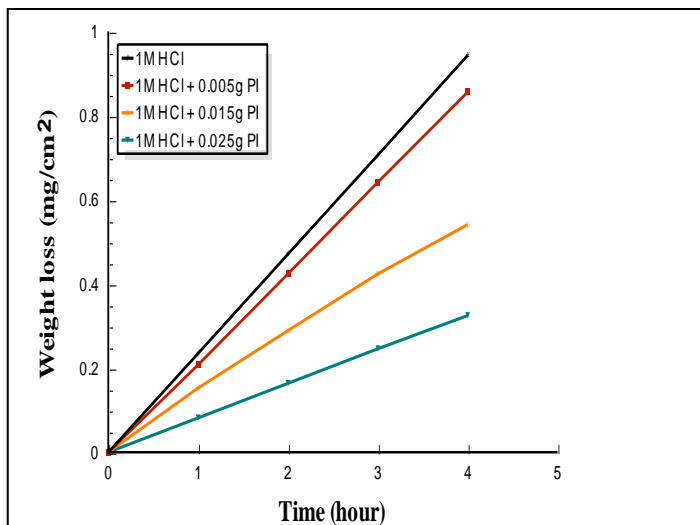


Fig 4. Weight loss – time curves of zinc dissolution in 1M HCl solution at 25 °C in the absence and presence of PI for various concentrations.

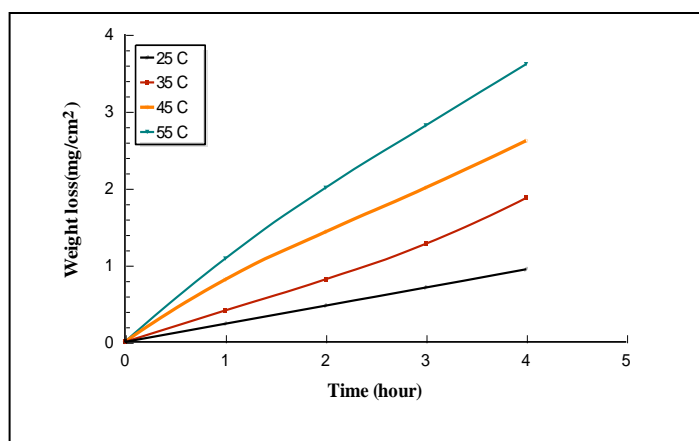


Fig. 5. Weight loss – time curves of zinc dissolution in 1M HCl at different temperatures.

The temperature dependences of the corrosion parameters of zinc in 1M HCl in absence and presence of inhibitor with The temperature dependences of the corrosion parameters concentration of 0.015 g/100 ml for both were illustrated in Figs. 5, 6, and 7 and along with relevant data as listed in Table 3. It can be observed that the corrosion rate is suddenly increased on rising the temperature of corrosion media.

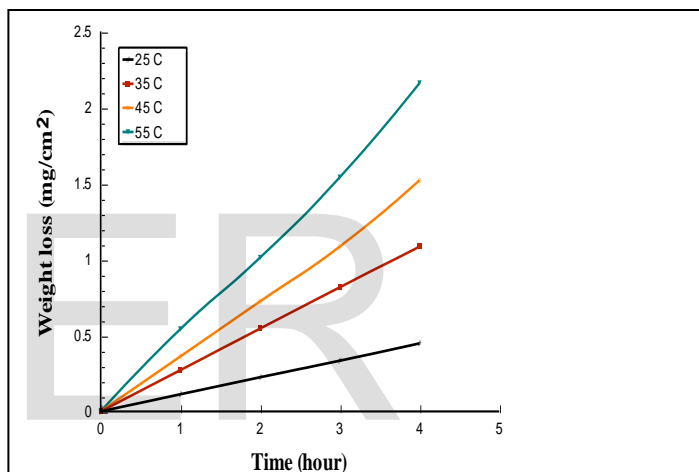


Fig 6. Weight loss – time curves of zinc dissolution in 1M HCl with CTM (0.015g/100ml) at different temperatures.

TABLE 2

DATA OF WEIGHT LOSS, CORROSION RATE, SURFACE COVERAGE AND INHIBITION EFFICIENCY OBTAINED FROM WEIGHT LOSS MEASUREMENTS FOR ZINC IN 1M HCL WITHOUT AND WITH VARIOUS CONCENTRATIONS OF TWO INHIBITORS AT 25 °C.

Medium	Conc.	Wt. loss (mg/cm ²)	Θ	IE%	r _{Corr} (mpy)
HCl	1M	0.943	0	0	28.49
CTM	0.005 g	0.531	0.4369	43.69	16.04
	0.015 g	0.448	0.5249	52.49	13.53
	0.025 g	0.311	0.6702	67.02	9.39
PI	0.005 g	0.856	0.0923	9.23	25.85
	0.015 g	0.541	0.4263	42.63	16.34
	0.025 g	0.325	0.6554	65.54	9.82

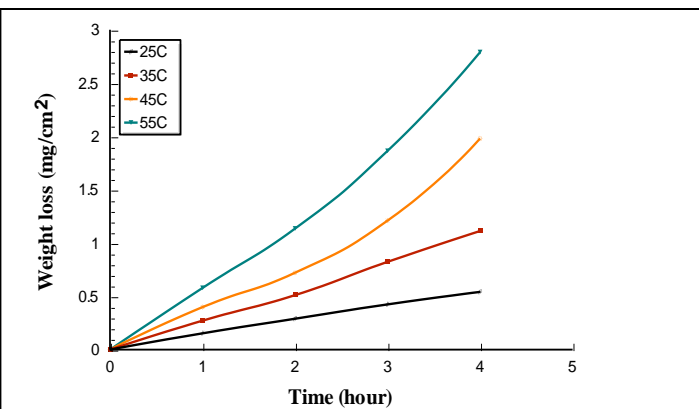


Fig 7. Weight loss – time curves of zinc dissolution in 1M HCl with PI (0.015g/100ml) at different temperatures.

TABLE 3

DATA OF WEIGHT LOSS, CORROSION RATE, SURFACE COVERAGE AND INHIBITION EFFICIENCY OBTAINED FROM WEIGHT LOSS MEASUREMENTS FOR ZINC IN 1M HCL WITHOUT AND WITH 0.015 G OF TWO INHIBITORS AT DIFFERENT TEMPERATURES.

Medium	T (°C)	Wt. loss (mg/cm ²)	θ	IE(%)	i _{Corr} (mpy)
HCl	25	0.943	-	-	28.5
	35	1.87			56.5
	45	2.614			78.9
	55	3.608			109
CTM	25	0.448	0.525	52.5	13.5
	35	1.084	0.420	42.0	32.8
	45	1.521	0.418	41.8	43.6
	55	2.161	0.401	40.1	51.5
PI	25	0.541	0.4263	42.63	16.34
	35	0.694	0.405	40.5	20.9
	45	0.781	0.242	24.2	23.6
	55	0.885	0.226	22.6	26.7

The study of the temperature effect allowed to investigate the thermodynamic activation and adsorption parameters. The activation energy (ΔE_a^*) of corrosion reaction is calculated according to the Arrhenius dependence [16],

$$k_r = A \exp(-\Delta E_a^*/RT) \quad (4)$$

where k_r is the specific rate constant and is equal to the ratio (dW/dt).

$$\log k_r = \log A - (\Delta E_a^*/2.303 RT) \quad (5)$$

$$\text{or } \Delta E_a^* = 2.303 RT \times (\log A - \log k_r) \quad (6)$$

TABLE 4

THERMODYNAMIC ACTIVATION PARAMETERS FOR THE CORROSION OF ZINC IN 1M HCL IN ABSENCE AND PRESENCE OF 0.015G OF TWO INHIBITORS AT DIFFERENT TEMPERATURES.

Medium	T (°K)	ΔE_a^* (kJ/mol.)	ΔH^* (kJ/mol.)	ΔS^* (J/mol./degree)	ΔG^* (kJ/mol.)
HCl	298	35.590	38.068	17.021	32.996
	308	35.068	37.629	16.747	32.471
	318	35.329	37.972	16.481	32.731
	328	35.535	38.262	16.224	32.941
CTM	298	41.338	43.816	17.023	38.743
	308	40.452	43.013	16.747	37.855
	318	40.899	43.543	16.481	38.302
	328	41.242	43.969	16.224	38.647
PI	298	44.327	46.804	17.003	41.734
	308	43.973	46.534	16.728	41.382
	318	43.968	46.612	16.462	41.377
	328	43.359	47.086	16.205	41.771

Accordingly, the value of k_r is simply obtained from the slope of weight loss versus time curves. Plotting of $\log k_r$ versus $1/T$ for the zinc corrosion in the presence and absence of inhibitors (Fig. 8) gives a straight line whose slope is equal to ΔE^* with an intercept of $\log A$. The Gibb's free energy of activation (ΔG^*) was computed from the transition-state equation [17,18] as follows:

$$k_r = (RT/Nh) \exp(-\Delta G^*/RT) \quad (7)$$

$$\text{or } \log k_r/T = \log(R/Nh) - (\Delta G^*/2.303RT) \quad (8)$$

where h is the Blanck's constant, R is the universal gas constant, and N is Avogadro's number. Hence, plotting of $\log k_r/T$ versus $1/T$ gives a straight line whose slope is equal to $(-\Delta G^*/2.303R)$ with an intercept of $\log(R/Nh)$. Fig. 9 shows plots of $\log k_r/T$ versus $1/T$ for the zinc corrosion, in the presence and absence of inhibitors. Values of ΔG^* were obtained from the magnitude of slope according to the following formula:

$$\Delta G^* = -2.303R \times (\text{Slope}) \quad (9)$$

The corresponding enthalpy (ΔH^*) and entropy (ΔS^*) of activation were then calculated using equation (10) and (11), respectively:

$$\Delta H^* = \Delta E^* + RT \quad (10)$$

$$\Delta S^* = (\Delta H^* - \Delta G^*)/T \quad (11)$$

The estimate values of thermodynamic activation parameters without and with inhibitors for the zinc corrosion in 1M HCl solution are summarized in Table 4.

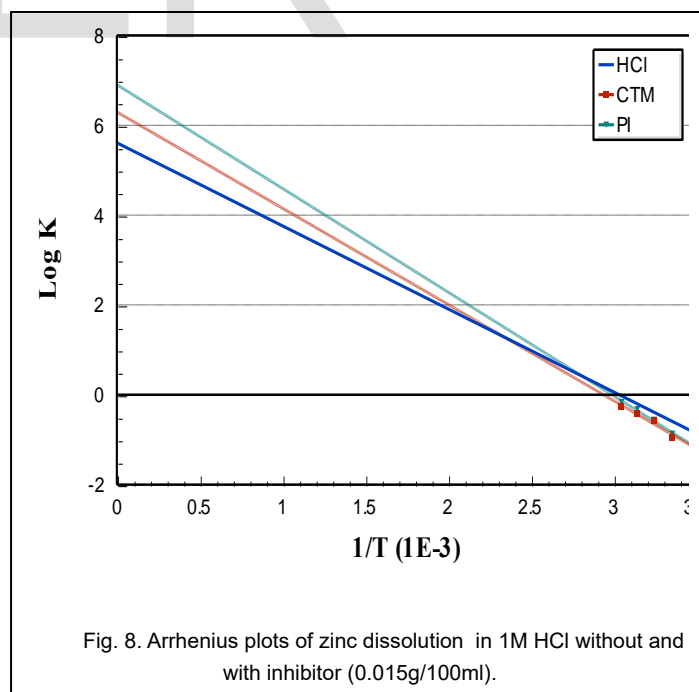


Fig. 8. Arrhenius plots of zinc dissolution in 1M HCl without and with inhibitor (0.015g/100ml).

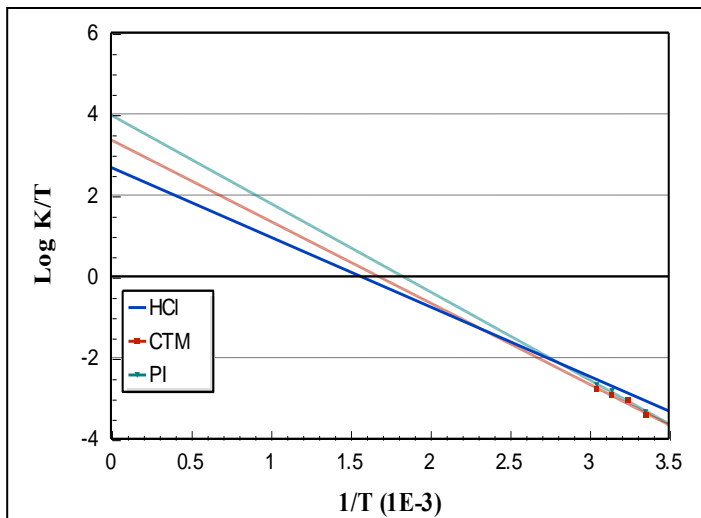


Fig. 9. Evaluation of $\log(R/Nh)$ and free energy for zinc dissolution in 1M HCl without and with (0.015g/100ml) inhibitor.

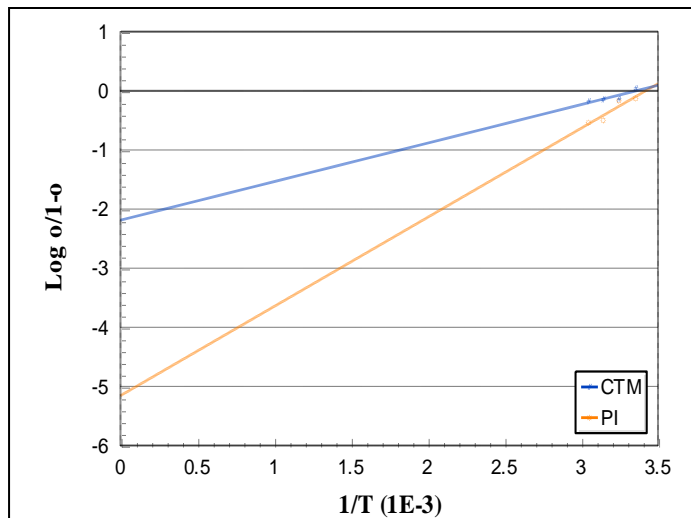


Fig. 10. Evaluation $\log C\beta$ and adsorption free energy ΔG_{ads} for zinc dissolution in 1M HCl with (0.015g/100ml) inhibitor.

The Langmuir adsorption isotherm was fitted well to the experimental data and was applied to investigate the adsorption process of the investigated inhibitors on zinc surface [19]. The Gibbs free energy of adsorption (ΔG_{ads}^0) was evaluated by applying the empirical formula illustrated below:

$$\log(\theta / 1 - \theta) = \log C\beta - (\Delta G_{ads}^0 / 2.303RT) \quad (12)$$

where β is the adsorption equilibrium constant and C is the concentration of inhibitor. The parameter, $\log C\beta$ was obtained from extrapolation of the $\log(\theta / 1 - \theta)$ versus $1/T$ plots to $\log(\theta / 1 - \theta) = 0$, as clearly depicted in Fig. 10 showing the temperature dependence of adsorption of inhibitors on the surface of zinc.

The values of enthalpy (ΔH_{ads}) and entropy (ΔS_{ads}) of adsorption were calculated from equations (13) and (14), respectively [19]:

$$\log k = \log k_0 - (\Delta H_{ads} / 2.303RT) \quad (13)$$

$$\log k = (\Delta S_{ads} / 2.303R) - (\Delta H_{ads} / 2.303RT) \quad (14)$$

where k_0 is a coefficient connected with the entropy of adsorption and k is the adsorption coefficient. The thermodynamic adsorption parameters (ΔG_{ads}^0 , ΔS_{ads} and ΔH_{ads}) for dissolution of zinc in HCl in the absence and presence of inhibitors were illustrated in Table 5.

TABLE 5
THERMODYNAMIC ADSORPTION PARAMETERS FOR THE CORROSION OF ZINC IN 1M HCL IN PRESENCE OF 0.015 G OF TWO INHIBITORS AT DIFFERENT TEMPERATURES.

Inhibitor	T (°K)	ΔH_{ads} (KJ/mol.)	ΔS_{ads} (J/mol./degree)	ΔG_{ads} (KJ/mol.)
CTM	298	23.163	120.43	-12.726
	308	25.023	120.43	-12.070
	318	25.857	120.43	-12.440
	328	26.862	120.43	-12.640
PI	298	27.613	132.12	-11.756
	308	28.761	132.12	-11.929
	318	31.697	132.12	-10.315
	328	32.937	132.12	-10.396

However, more information may be deduced from values of ΔG_{ads} . Generally, it has been found that if the value of ΔG_{ads} is up to -20 kJ mol^{-1} , the adsorption can be regarded as physisorption, and consequently the inhibition acts due to the electrostatic interaction between the charged molecules and the charged metal, while chemisorption is predominantly seen for those adsorptions whose ΔG_{ads} values are around or higher than -40 kJ mol^{-1} . The chemisorption occurs as a result of the charge sharing or transferring from inhibitor molecules to the metal surface to form a covalent bond, which is the fact behind the inhibition action of this type of adsorption [20,21]. In the light of this concept, the adsorption of these inhibitors on the zinc metal the lower values of

ΔG_{ads} range from -10.315 to -12.726 kJ mol^{-1} of CTM and PI inhibitors are due to physisorption. The negative values of ΔG_{ads} indicate that the inhibitor is spontaneous adsorbed on the zinc surface for all inhibitors.

3.2 Open- circuit potential measurements

The open- circuit potential of the zinc metals immersed in HCl solution at different concentrations were measured as a function of time up to reaching teady- state values. In the absence of inhibitor, the steady- state potentials are approached to be more negative values by increasing the HCl concentration as clearly shown in Fig. 11.

Figs 12, and 13 present the steady- state potentials measured for the zinc corrosion in 1 M HCl solution in the presence of CTM, and PI at varying concentrations respectively. The measured values of the immersion potential (E_{im}) and steady- state potential ($E_{s.s.}$) in the absence and presence of different concentrations of inhibitors are listed in Table 6. It can be observed that the extent of the potential rise is inversely dependent on the concentration of inhibitors. This may be due to the complex formation between inhibitor and corrosion product that is dissolved in the medium and the formation of a protective layer at the interfacial metal- corrosive medium.

Figs 14 to 16 show the temperature dependence of steady- state potentials measured for the Zinc corrosion in aqueous HCl solution in the absence and presence of inhibitors. Generally, the higher the temperature within the range of 25 - 55 °C, the higher is the potential measured for aluminum electrode. This suggests a very high rate of the complementary anodic reaction under these conditions.

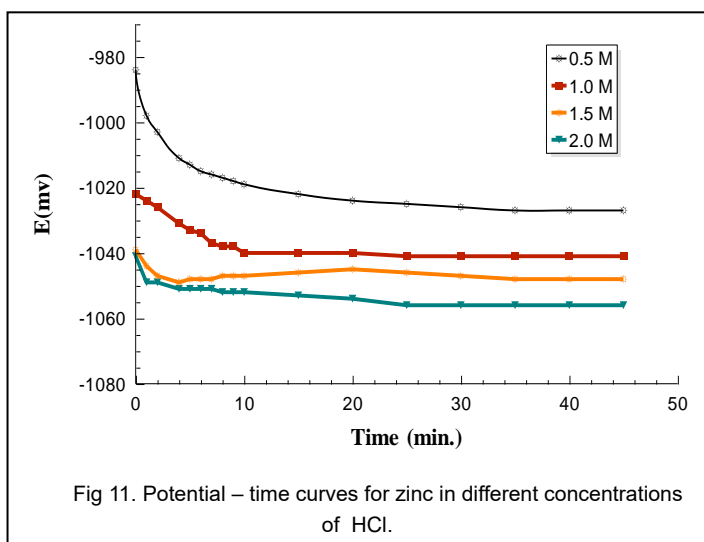


Fig 11. Potential – time curves for zinc in different concentrations of HCl.

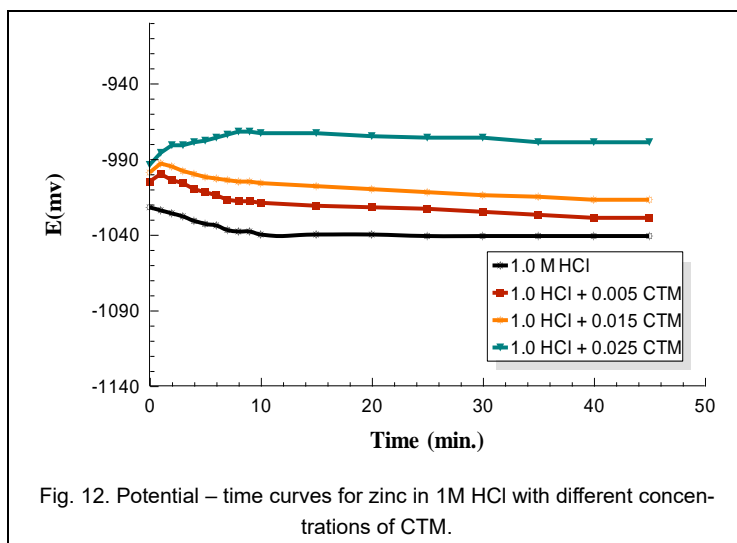


Fig. 12. Potential – time curves for zinc in 1M HCl with different concentrations of CTM.

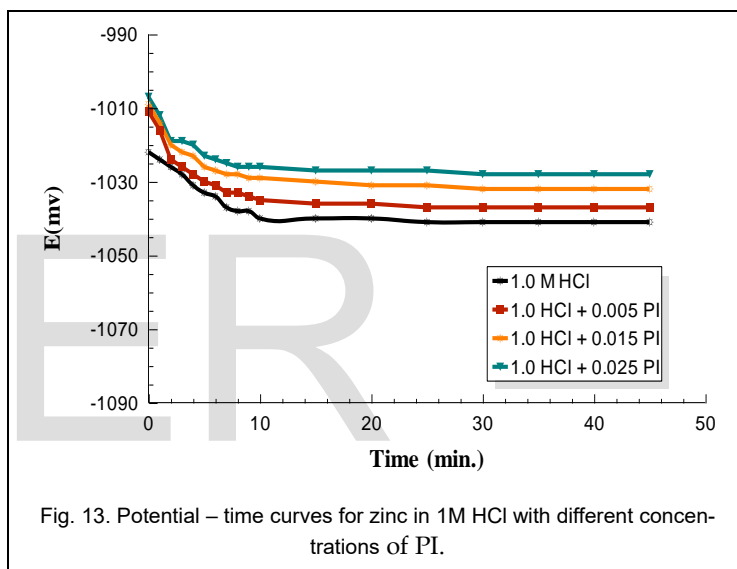


Fig. 13. Potential – time curves for zinc in 1M HCl with different concentrations of PI.

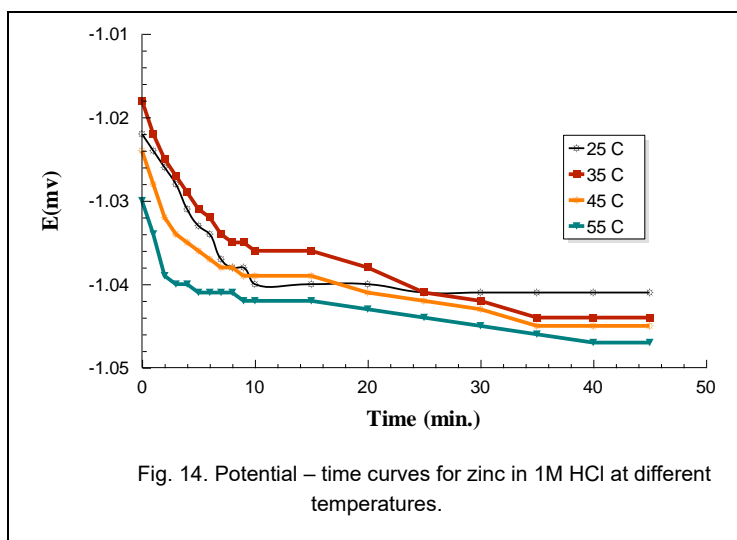


Fig. 14. Potential – time curves for zinc in 1M HCl at different temperatures.

TABLE 6

VALUES OF E_{im} AND E_s FOR ZINC CORROSION IN 1M HCL IN ABSENCE AND PRESENCE OF INHIBITOR AT VARYING CONCENTRATIONS.

Medium	Concentration	Zinc	
		E _{im} (mV)	E _s (mV)
HCl	1M	-1022	-1041
CTM	0.005	-1005	-1029
	0.015	-999	-1017
	0.025	-994	-979
PI	0.005	-1011	-1037
	0.015	-1009	-1032
	0.025	-1007	-1028

The measured open - circuit potential at constant temperature with respect to SCE, can be considered as a relative emf of single zinc electrode. The temperature coefficient of the emf is defined as $(\partial E/\partial T)_p$, while the changes in the thermodynamic parameters can be calculated as [22,23]:

$$\Delta S^* = nF(\partial E/\partial T) \tag{16}$$

$$\Delta G^* = -nF\Delta E_{cell} \tag{17}$$

$$\Delta E_{cell} = E_b - E_{inh} \tag{18}$$

$$\Delta H^* = \Delta G + T\Delta S \tag{19}$$

$$\Delta E^* = \Delta H - RT \tag{20}$$

where, n = 2 for zinc, F is Faraday constant, and E_b and E_{inh} are the measured potential in the absence and presence of inhibitors, respectively. The changes in the thermodynamic parameters at different temperature in the steady state are illustrated in Table 7.

TABLE 7

THE THERMODYNAMIC ACTIVATION PARAMETERS FOR STEADY- STATE CORROSION OF ZINC IN 1M HCL IN ABSENCE AND PRESENCE OF INHIBITOR AT DIFFERENT TEMPERATURES.

Medim	T (°K)	-ΔE* (kJ/mol)	ΔG* (kJ/mol)	-ΔH* (kJ/mol)	-ΔS* (J/mol./degre)
HCl	298	13405	0	10928	36670
	308	13276	579	10715	
	318	13533	772	10889	
	328	13597	1158	10870	
CTM	298	24318	2316	21840	81060
	308	25983	1544	23423	
	318	27263	1158	24619	
	328	28350	965	25623	
PI	298	30463	772	27985	96500
	308	31318	965	28757	
	318	33138	193	30494	
	328	35344	-965	32617	

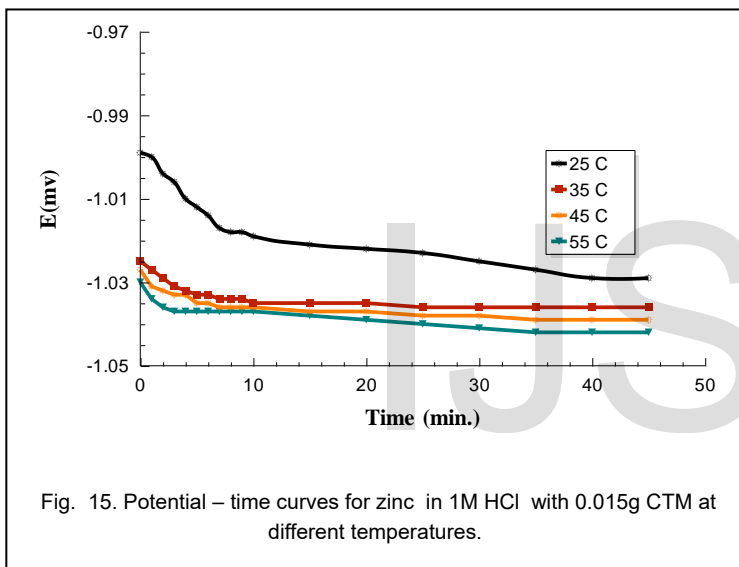


Fig. 15. Potential – time curves for zinc in 1M HCl with 0.015g CTM at different temperatures.

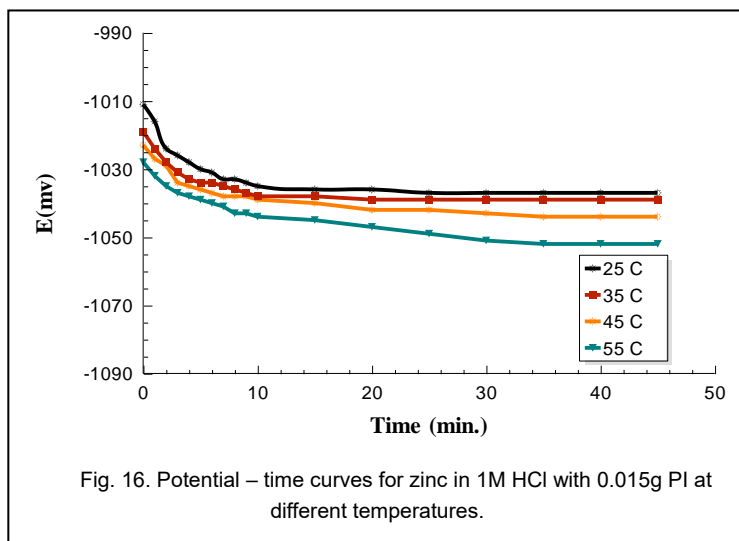


Fig. 16. Potential – time curves for zinc in 1M HCl with 0.015g PI at different temperatures.

4 CONCLUSION

- The dissolution of Zinc in HCl solution was increased as the HCl concentration increased and the corrosion rate of Zinc was also increased on rising temperature of corroding media.
- CMT and PI show a good inhibitive effects on the corrosion of Zinc in HCl media and their inhibition efficiency follows the order: CTM > PI.
- Inhibition efficiency of both CMT and PI for the dissolution of Zinc in HCl solution decreased with increasing temperature.
- ΔH* and ΔH_{ads} values indicate that the majority adsorption type is physical adsorption for both two environmental friendly inhibitors.

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