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New Electroactive compounds as corrosion inhibitors for zinc in acidic medium

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ABSTRACT

Corrosion inhibition effect of 2- [4-(methylthio) phenyl] acetohydrazide (HYD) and 5-[4-(methylthio)benzyl]-4H-1,2,4-triazole-3-thiol (TRD) on zinc in 0.1 M HCl was studied by using mass loss, polarization and electrochemical impedance spectroscopy (EIS). Effect of concentration and temperature was evaluated by mass loss method. Results indicated that the compounds are efficient, mixed type but predominantly anodic in nature. Similar trend was observed in both chemical and electrochemical results. TRD shows good inhibition efficiency than HYD. Obtained results were justified from the study of surface morphology.

Key words: Inhibition efficiency, Mass loss, Polarization, Surface morphology.

INTRODUCTION

Zinc is a metal with numerous industrial applications and is mainly used for the corrosion protection of steel [1]. Zinc is an industrially important metal and is corroded by many agents, of which aqueous acids are the most dangerous [2]. Looking at its increasing use, the study of corrosion inhibition is of paramount importance. The dissolution behavior of zinc in acidic and nearly neutral media is known to be inhibited by nitrogen and sulfur-containing organic compounds. Such compounds contain electron-donating groups that decrease the corrosion rate by increasing the hydrogen over voltage on the corroding metal [3]. Studies of the effect of organic additives on the corrosion rate of zinc have been the subject of many investigators [4−9]. It has been found that most of the organic inhibitors act by adsorption on the metal surface [10]. 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 [11].

In literature no one was investigated on zinc by using, methylthio phenyl moiety containing compounds. These are having potential characters of an inhibitor like the presence of hetero atoms nitrogen, sulphur, oxygen and an aromatic ring together. The present study was undertaken to ascertain and compare the ability of these compounds to safeguard zinc from the corrosive action of HCl. The variation of the inhibition efficiency with temperature and concentration of the inhibitor was evaluated by mass loss method. Tafel and EIS data were also used to analyze the inhibition action. The results were correlated with scanning electron microscopic (SEM) studies.

MATERIALS AND METHODS

Materials

The pure zinc plate (Cu=0.185%, Al=0.006%, Fe=0.004%, Mn=0.3%, Sn=0.003%, Pb=0.002%, Cd=0.002% and the rest zinc) were used. Zinc sheets having rectangular shape with an exposed area of 2 cm x 4 cm x 1 cm were used for mass loss method and coupons with an exposed area of 1 cm^2 (rest is covered with araldite resin) with 2.5 cm long stem were used for polarization and EIS methods. All coupons were polished by using emery papers (Grade No.: 220, 400, 600, 800 and1200), washed thoroughly with distilled water, degreased with acetone and dried at room temperature. The corrosive medium is 0.1 M HCl solutions were prepared using AR grade HCl and double distilled water.

The names, structures, physical and analytical data of inhibitor compounds are given in the Table 1. These compounds are water insoluble but highly soluble in Dimethyl formamide (DMF). To enhance the solubility of the compounds in the corroding medium, they were predissolved in small quantity (1 ml) of DMF. However same quantity of DMF is added to blank to nullify its effect.

Mass loss measurements

Mass loss measurements were performed by immersing zinc coupon in glass beaker containing 100 mL of 0.1 M HCl without and with different concentrations of inhibitor. After stipulated /elapsed time, the coupon was taken out and washed well with distilled water, dried, weighed accurately using digital balance (Precision: ± 0.1 mg).

In order to assess the effect of temperature on the corrosion of zinc, the experiment was carried out at 30º, 40º and 50 ºC respectively. A digital thermostat (± 0.5 ºC accuracy) was used for conducting experiment at different temperature. The experiment was carried out in aerated and static condition. The measurement was repeated for three times and an average value was reported. The same procedure was adopted for both the inhibitors. The inhibition efficiency IE (%) was calculated from the following relationship

$$\text{Inhibition efficiency (IE)}, \quad = \quad \frac{W_u - W_i}{W_u} \times 100$$

where, W_u and W_i are the average weight-losses of test sample after immersion in corrosive solutions with and without inhibitor, respectively.

Electrochemical measurements

The Electrochemical measurements were carried out in CHI 660C (US make) electrochemical analyzer. The cell consists of three electrodes namely, the working electrode (zinc), counter electrode (Platinum) and reference electrode (SCE). The immersion time of 1 hour was given to allow the stabilization of the potential prior to measurements. From the Tafel profiles, corrosion potential (E_{corr}), corrosion current density (I_{corr}), cathodic and anodic Tafel slopes (b_c, b_a), were calculated.

The impedance measurements were carried out by using AC signal. The impedance data were fitted to most appropriate equivalent circuit by using ZSimp Win 3.21 software. The impedance parameters were obtained from Nyquist plots.

Surface studies

The surface morphology of the zinc samples after immersion in 0.1M HCl in absence and presence inhibitors, was analyzed using scanning electron microscopy (model: JEOL, JSM 6400)

RESULTS AND DISCUSSION

Mass loss studies

Mass loss data for zinc corrosion in 0.1M HCl in absence and presence of inhibitors, at various concentration and temperature are given in Table 2.

The variation of % IE with the concentration of inhibitors at 30º C is shown in Table.2. It can be observed that all compounds exhibit significant inhibition efficiency. Further, % IE increased with concentration of inhibitor up to certain optimal concentration (0.2 μM for both) beyond which the increase is not significant. The increasing of efficiency with the increase of concentration primarily indicate that the inhibition action is due to adsorption. Also fraction of the surface covered with inhibitor increased with increase of concentration of the inhibitor. Among the inhibitors, TRD showed the best of 98.87 % efficiency at 0.2 μM. TRD shows good efficiency than HYD. The protection ability of these compounds is primarily due to the presence hetero atoms S, N, O and π electrons of aromatic rings.

To understand the behavior of the studied inhibitors at elevated temperatures, experiment was carried out at different temperatures. It can be observed that efficiency of inhibitor at all the concentrations decreases with temperature. The adsorbed inhibitor may be disrobed at higher temperature.

Potentiodynamic polarization studies

Polarization profiles for zinc alone and with several concentrations of HYD and TRD at 30º C are presented in Fig. 1 and 2. Various electrochemical corrosion parameters like corrosion potential (E_{corr}), corrosion current density (I_{corr}), cathodic and anodic Tafel slopes (β_c, β_a), were drawn from the extrapolation of the Tafel lines and calculated %IE are summarized in Table 3. The % IE was calculated from the relation

$$IE(\%) = \frac{I^{o}_{corr} - I_{corr}}{I^{o}_{corr}} \times 100$$

Where I^{o}_{corr} and I_{corr} are the corrosion current densities in absence and presence of inhibitor respectively. Figures indicates that polarization curves in presence of the compounds are considerably deviated from the blank. Further the deviation is profound with the increase of concentration of the inhibitor. Also the arms of the curves are suppressed down to lower current density region. Again the suppression is more with the concentration. Further the position of the curve as a whole is shifted towards less negative (noble) potential region. Such changes are necessary to command the protective ability. The value of I_{corr} decreased and the % IE increased in presence of inhibitor. The % IE calculated from polarization measurements go hand in hand with the results of mass loss measurements.

It is evident from figure and table that the corrosion potential (E_{corr}) value of two compounds was shifted towards noble potential in presence of inhibitors. It acts as mixed type of inhibitor and predominately anodic inhibitor. Further the two arms of the curves, namely anodic and cathodic polarization curves are suppressed down towards the lower current density region. The value β_a decreased in presence of inhibitor and continue to decrease with the increase of concentration. This suggests that the inhibitors retard the anodic reaction. Thus inhibitor are found to be mixed type and predominating in anodic direction

All these facts infer that the studied compounds are very effective corrosion inhibitors for zinc in HCl solution and their capacity of inhibition increased with increase of concentration. Further, the concentration of inhibitors employed for the study was very small and indicated great deal of activeness of these compounds towards the zinc surface. The higher activity and effectiveness is due to the presence of number of N, S, O atoms and aromatic rings. The inhibition efficiency data showed that TRD has greater interaction with zinc compared to other compound HYD.

EIS studies

The electrochemical impedance spectra of zinc in absence and presence of various concentrations of inhibitors at 30°C is presented as Nyquist plot in Fig 3 and 4. The experimental data and calculated inhibition efficiency are summarized in the table 3.

The %IE at different concentration of each inhibitor in 0.1 M HCl were calculated from the corresponding electrochemical impedance data according to equation.

$$IE = \frac{R_{ct} - R_{ct}^{I}}{R_{ct}^{I}} \times 100$$

where R_{ct} and R_{ct}^{I} are the charge transfer resistances in the presence and absence of inhibitors. It is evident from these plots that the impedance response of zinc has significantly altered after the addition of inhibitors to the corrosive solutions. The results obtained from electrochemical impedance spectroscopy (EIS) method can be interpreted in terms of the equivalent circuit of the electrical double layer shown in Fig. 5 .

The semicircle in all cases corresponds to a capacitive loop. The semicircle radii depend on the inhibitor concentration. The diameter of the capacitive loop increased with increase of inhibitor concentration, the increase is significant in case of TRD. The Nyquist plots obtained in the real system represent a general behavior where the double layer on the interface of metal/solution

does not behave as a real capacitor. On the metal side electrons control the charge distribution where as on the solution side it is controlled by ions. As ions are much larger than the electrons, the equivalent ions to the charge on the metal will occupy quite a large volume on the solution side of the double layer. From the Table 3, it was clear that charge transfer resistance values were increased and the capacitance values decreased with increasing concentration of inhibitor. Decrease in the capacitance, which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that the inhibitor molecules act by adsorption at the metal/solution interface. This indicated the formation of a surface film on the zinc. In all the methods TRD shows good efficiency

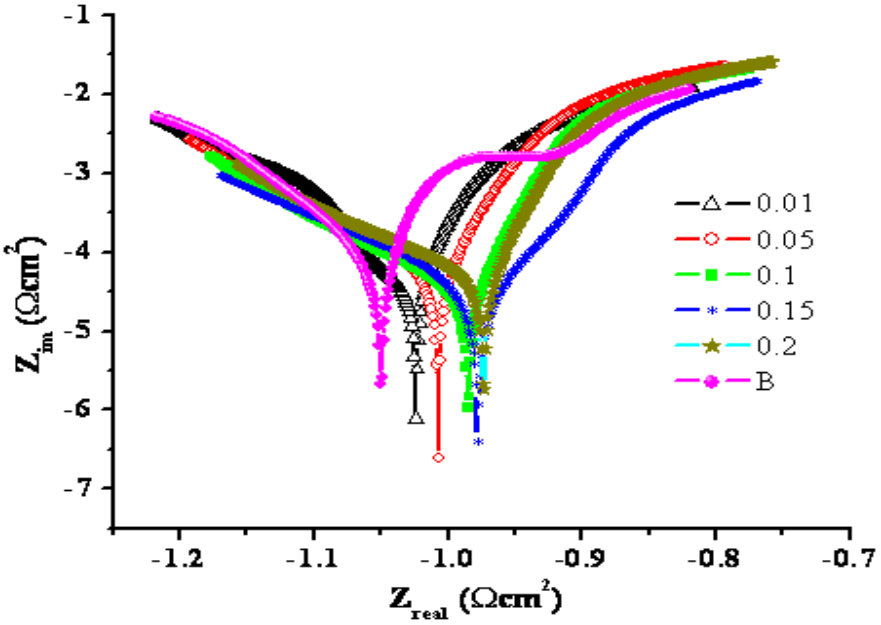


Fig. 1. Polarization profile of zinc in presence of different concentration of inhibitor(HYD) in HCl medium

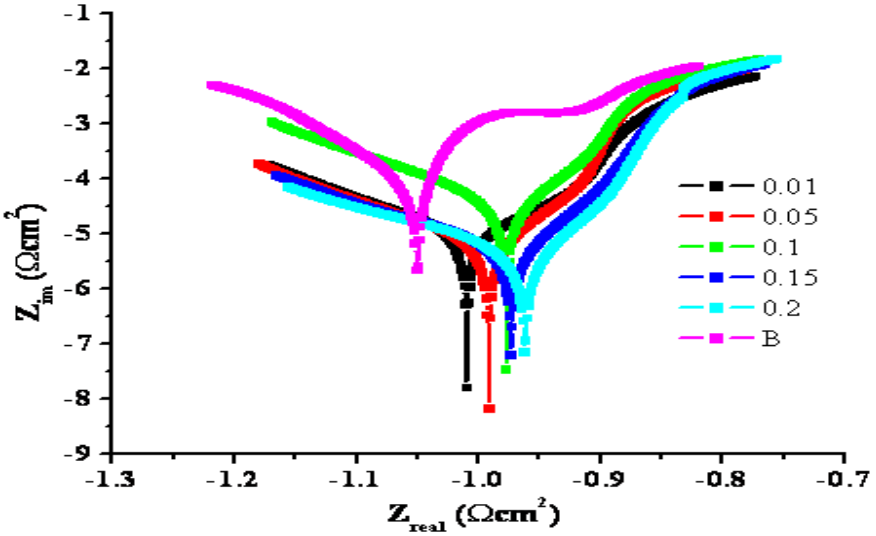


Fig. 2. Polarization profile of zinc in presence of different concentration of inhibitor (TRD) in HCl medium

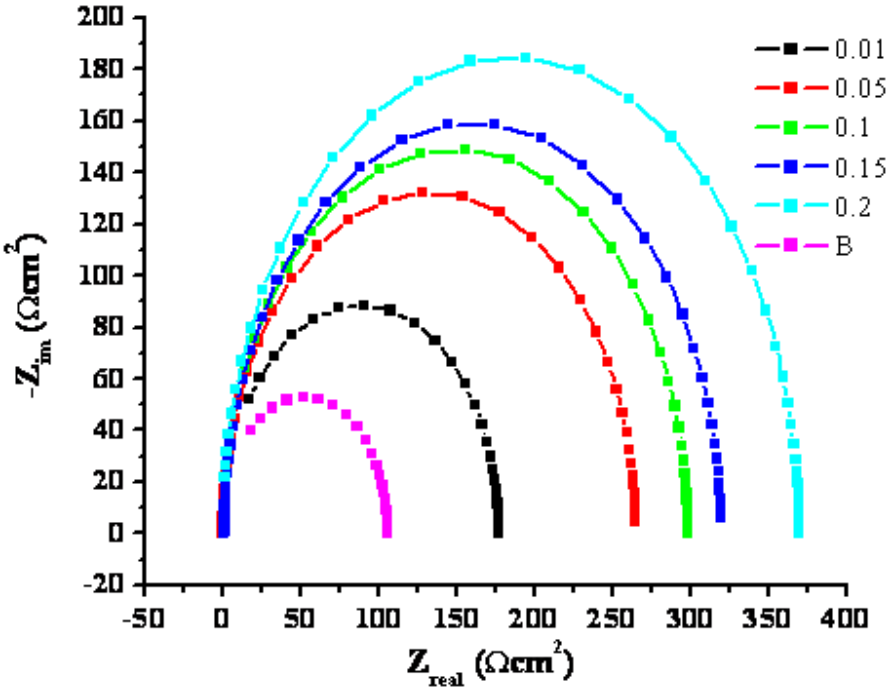


Fig . 3 Nyquist plots for zinc in HCl containing different concentrations of inhibitor (HYD) .

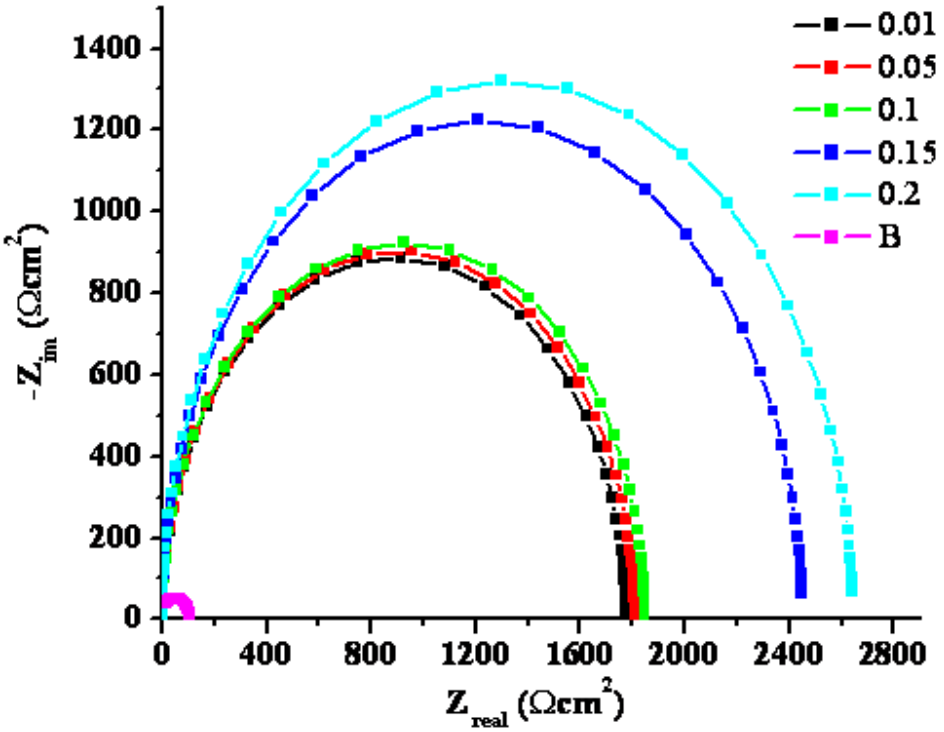


Fig . 4 Nyquist plots for zinc in HCl containing different concentrations of inhibitor (TRD)

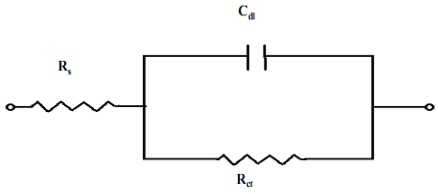


Fig. 5. Equivalent circuit used to interpret the results of EIS

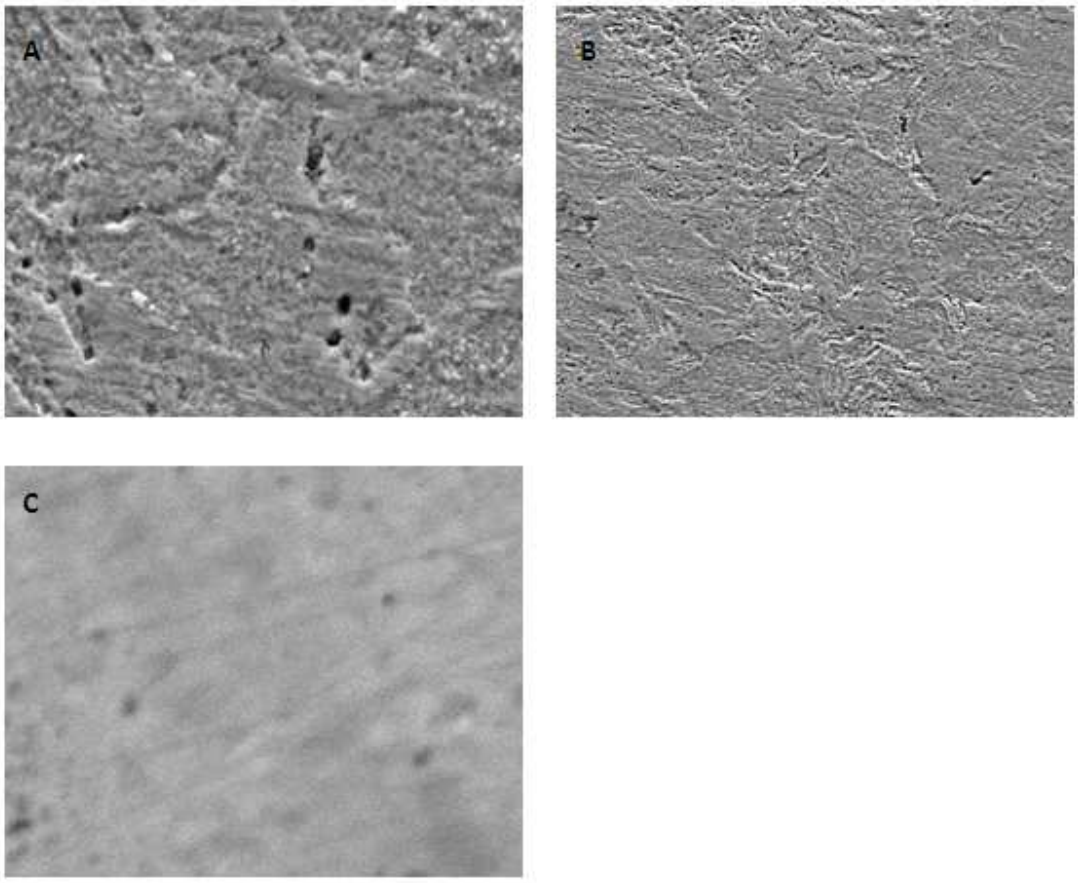


Fig. 6. SEM images of zinc surface. (A) Absence of inhibitor, (B) presance of HYD, (C) presence of TRD.

Scanning electron microscopic study

The scanning electron micrograph (SEM) were recorded to establish the interaction of organic molecules with the metal surface. The SEM images which shows the features of zinc surface after immersed in 0.1 M HCl at 30 ºC for 4 h in absence and presence optimum concentration of HYD and TRD are depicted in Fig.6. The metal surface immersed in 0.1 M HCl was rough, full of metal imperfections like pits, cavities, voids and cracks. These imperfections are essentially due to the washing away of the soluble corrosion products from the metal surface and due to hydrogen embrittlement. SEM images (Fig b and c) of the specimens immersed in the inhibitor solutions are in better conditions having retained smooth surface and polish. There appears the

presence of few imperfections of least depth. This indicated that the inhibitor molecules hinder the dissolution of zinc by forming organic film on the zinc surface and there by reduced the rate of corrosion. The SEM image of the zinc specimen immersed in the TRD was least affected which reinforce the earlier results.

Table 1. The name, structure, physical and analytical data of compounds

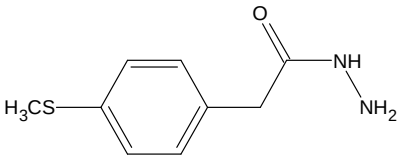
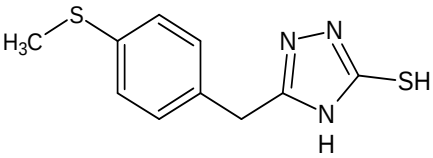
Structure, IUPAC and abbreviated name	Physical and analytical data
 2-[4-(methylthio) phenyl] acetohydrazide **(Hydrazide derivative-HYD)**	m.p 136-138 ^{0}C (colorless). IR (KBr, cm^{-1}): 3344 (NH, NH_2), 3203 (NH_2), 2963 (C-H), 1622 (CO-NH); LCMS (m/z): 196 (M^+), Anal. Calcd. (%) for $C_9H_{12}N_2OS$: C 55.09, H 6.16, N 14.27. S 16.34, Found: C 55.06, H 6.15, N 14.20, S 16.26.
 3-(4-methylthiobenzyl)-1,2,4-triazole-5-thione **(Triazole derivative-TRD)**	m.p 195–197 °C (colorless solid). IR (KBr, cm^{-1}): 3154 (NH), 2593 (C-S); ^{1}H-NMR(DMSO-*d*6, δ ppm): 2.49 (s, 3H, SCH_3), 3.53 (s, 2H,CH_2), 7.18 (d, Ar-H, *J* = 8.36 Hz), 7.26 (d, Ar-H, *J* = 8.36 Hz), 13.30 (brs, 2H, NH/SH); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 16.12, 32.13, 127.51, 128.25, 131.99, 139.21, 152.16, 167.10; LCMS (m/z): 237 (M^+); Anal. Calcd. (%) for $C_{14}H_{19}N_3S$: C-50.60, H-4.67, N-17.70, S-27.02, Found: C-50.56, H-4.71, N-17.79, S-27.05.

Table 2 corrosion parameters for zinc at different temperature obtained from mass loss measurements

Corrosion inhibitor	Inhibitor Concentration	% η_w at different temperature (4 hr)		
	µM	30º C	40º C	50º C
HYD	Blank	-	-	-
	0.01	55.27	50.68	47.31
	0.05	64.58	57.42	54.25
	0.1	75.44	68.17	60.68
	0.15	82.72	73.56	69.17
	0.2	90.45	80.39	71.48
TRD	Blank	-	-	-
	0.01	94.75	86.48	80.67
	0.05	96.43	89.74	82.48
	0.1	97.65	92.13	85.16
	0.15	98.48	94.26	88.23
	0.2	98.87	95.35	90.37

Table 3 Electrochemical corrosion parameters for zinc obtained from polarization and impedence method

	Polarization						EIS		
Inhibitor	Inhibitor con^{n} (µM)	E_{corr}vs SCE (mV)	I_{corr} µA cm^{-2} x 10^{-4}	βc mV/decade	βa mV/decade	% η_p	R_{ct} Ωcm^2	% η_p	Cdl X10^{-6} (F)
HYD	Blank	-1.050	1.823	0.082	1.345		106		4.034
	0.01	-1.024	0.912	0.102	0.103	49.97	177.3	40.21	3.348
	0.05	-1.007	0.825	0.114	0.076	54.74	265	60.00	11.01
	0.1	-0.985	0.521	0.118	0.078	71.42	298.5	64.49	2.867
	0.15	-0.978	0.252	0.139	0.045	86.18	318.6	66.73	9.838
	0.2	-0.973	0.097	0.138	0.088	94.6	369.9	71.34	8.811
TRD	Blank	-1.050	1.823	0.082	1.345		106		4.034
	0.01	-1.009	0.0873	0.129	0.0513	95.21	1775	94.03	1.873
	0.05	-0.991	0.0368	0.138	0.0295	97.98	1809	94.14	1.793
	0.1	-0.977	0.0220	0.134	0.040	98.79	1847	94.26	3.293
	0.15	-0.973	0.0346	0.166	0.0362	98.10	2450	95.67	1.721
	0.2	-0.962	0.0214	0.176	0.0304	98.82	2643	95.99	1.598

CONCLUSION

Both TRD and HYD reduced the corrosion rate of zinc considerably in HCl medium. The IE% resulted from electrochemical and weight loss measurements were in good agreement. The rate of corrosion decreased with inhibitor concentration and increased with temperature. These results show that both TRD and HYD are good corrosion inhibitor for zinc in HCl medium.

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