SYNERGISTIC INHIBITION OF ZINC CORROSION BY SOME ANIONS IN AQUEOUS MEDIA

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ABSTRACT: The corrosion inhibition of zinc in 0.1M HCl in presence and absence of some hydrazide derivatives has been investigated using mass-loss and polarization techniques. Results obtained showed that the inhibition efficiency increased with the increase of the concentration of the additives and decreased with the increase of temperature. Synergism between I⁻ , SCN⁻ and Br⁻ anions and hydrazide derivatives was proposed. The polarization curves showed that hydrazide derivatives act as mixed-type inhibitors, acting predominantly as cathodic inhibitors for zinc in 0.1M HCl .The adsorption of these hydrazide derivatives on zinc surface follows Temkin's adsorption isotherm. Some thermodynamic parameters were calculated. The kinetic parameters of corrosion of zinc in HCl solution have been studied.

Keywords: corrosion inhibition, zinc, synergism, HCl, hydrazide derivatives.

1. INTRODUCTION

Zinc is widely used in various industrial operations and the study of corrosion of zinc and its inhibition is a subject of practical significance. Many researchers in the literature [1-6] studied the corrosion inhibition of Zn in HCl using organic compounds containing nitrogen, oxygen and /or sulphur atoms. Among nitrogen containing compounds: quinoline [7], aniline[8] and ephedrine, narcotine, brucine, strycuine, etc...[9] These compounds have shown good inhibition towards zinc in acidic medium .On other hand, quinine sulphate, piperazine, caffine, barbitone and pyridine derivatives have been investigated as corrosion inhibitors for aluminum and zinc in acidic medium[10&11].

Also, thiourea was used as corrosion inhibitor for many metals [12&13], but there are many conflicting reports on the mechanism of inhibition by thiourea.The reaction of corrosion inhibitors at the metal-solution interface has been evaluated by adsorption characteristics and also by the the thermodynamics of adsorption [14&15].
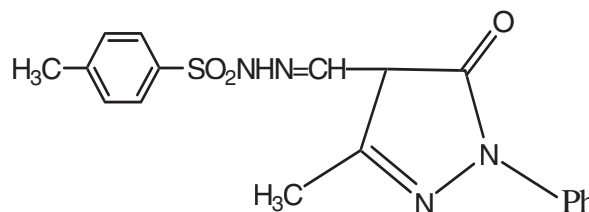
The present paper deals with the effect of some hydrazide derivatives on the corrosion of zinc in HCl solution.
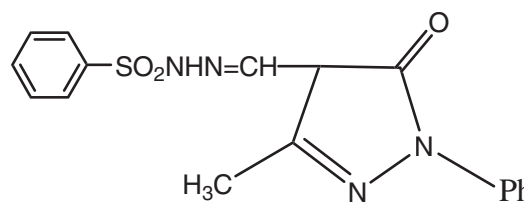
The inhibitors used are:

(a) 2- amino – N' – ((3-methyl – 5 – oxo – 1 – phenyl – 4, 5 – dihydro – 1H- pyerazol-4-yl) methylene) acetohydrazide.
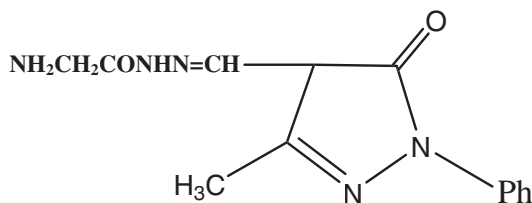
(b) 4- methyl – N' – ((3-methyl – 5 – oxo – 1 – phenyl – 4, 5 – dihydro – 1H- pyerazol-4-yl) methylene) benzenesulfonohydrazide.

(c) N' – ((3-methyl – 5 – oxo – 1 – phenyl – 4, 5 – dihydro – 1H- pyerazol-4-yl) methylene) benzenesulfonohydrazide.

2. EXPERIMENTAL

The zinc (BDH grade) sheets used in this investigation have the following chemical composition:

Element	Pb	Fe	Cd	Cu	Zn
Weight (%)	0.001	0.002	0.001	0.003	Rest

All chemicals used were of AR grade. Specimens of zinc sheets were first polished with different grades of emery

papers, in order to obtain a smooth surface. Then degreased in acetone in an ultrasonic bath, washed by bidistelled water and dried between two fitter papers. The solutions of 0.1 M HCl was prepared with bidistilled water.

2.1 Mass loss measurements:

For mass loss measurements, rectangular zinc specimens of size 20x20x2 mm were immersed in 100 ml inhibited and uninhibited solutions and allow to stand for several intervals at 30^0C in water thermostat. The percentage inhibition efficiency (%In) of the inhibitor was calculated using the following equation:

$$\%In = \left[\frac{Mass.loss_{pure} - Mass.loss_{inh}}{Mass\,loss_{pure}}\right]x100 \quad (1)$$

2.2. Electrochemical measurements

Galvanostatic polarization studies were carried out on zinc electrode in 0.1M HCl in presence and absence of different concentrations of the inhibitors used at 30^oC. Saturated calomel electrode was used as reference electrode while a platinum wire as a counter electrode. All experiments were carried out at 30 ± 0.1^0C. 1 cm long cylindrical zinc electrode having a diameter of 1.25 mm was used as working electrode. The percentage inhibition efficiency (%In) was calculated from the following equation:

$$\%\ In\ =\ \left[\frac{i_{corr}\ -\ i_{inh}}{i_{corr}}\right]x\ 100 \quad ` \quad (2)$$

where $i_{corr.}$ and $i_{inh.}$ are the uninhibited and inhibited corrosion current densities, respectively.

3. RESULTS AND DISCUSSION

3.1. Mass – loss measurements:

Mass loss of zinc in 0.1 M HCl was determined in the absence and presence of the tested derivatives. The data in Table (1) show the effect of concentration of different additives on the percentage inhibition and indicate that by increasing the concentration of the additives, the %In. increases. This indicates that the additives behave as inhibitors over the concentration range studied. The order of decreasing inhibition efficiency of the investigated derivatives (Table1) in 0.1M HCl is:

compound (b) > compound (c) > compound (a)

Table 1. Effect of inhibitors concentrations on the percentage inhibition efficiency (% In) of zinc in 0.1 M HCl solution from mass – loss method at 30^0C.

Conc., M	(%In)		
	(a)	(b)	(c)
$1X10^{-6}$	35.2	61.4	46.2
$3X10^{-6}$	47.3	63.6	55.2
$5X10^{-6}$	50.5	65.1	57.1
$7X10^{-6}$	51.4	67.2	58.1
$9X10^{-6}$	53.5	69.2	60.5
$11X10^{-6}$	62.9	71.6	64.4

3.2. Synergistic effect:

As seen from Table (1), the percentage inhibition efficiency of the tested derivatives is low, so in order to increase these values we use KI, KSCN, and KBr in addition to the different concentrations of the investigated derivatives. Table (2) shows the % In. of the investigated derivatives in presence of $1x10^{-2}M$ of KI, KSCN, and KBr.

Table 2. Data from mass- loss of zinc dissolution in 0.1 M HCl at different concentrations of the hydrazide derivatives with addition of $1X10^{-2}$ M KI, KSCN and KBr at 30^oC.

Conc., M	(%In)								
	KI			KSCN			KBr		
	(a)	(b)	(c)	(a)	(b)	(c)	(a)	(b)	(c)
$1x10^{-6}$	68.03	76.80	73.68	66.39	75.16	72.04	63.39	72.70	69.59
$3x10^{-6}$	68.85	78.27	74.59	67.21	76.63	72.95	64.75	74.18	70.49
$5x10^{-6}$	69.67	80.08	76.22	68.03	78.44	74.59	65.57	75.98	72.13
$7x10^{-6}$	71.31	81.47	77.04	69.67	79.83	75.40	66.39	77.37	72.95
$9x10^{-6}$	72.13	83.36	77.86	70.49	81.72	76.22	68.03	79.26	73.77
$11x10^{-6}$	72.95	85.24	78.68	71.31	83.60	77.04	68.85	81.14	74.90

It can be seen from Table (2) that the addition 10^{-2} M of KI, KSCN and KBr inhibits the corrosion of zinc to a large extent and by increasing the concentration of hydrazide derivatives ($1x10^{-6}$- $11x10^{-6}$ M) the percentage inhibition increases. This can be interpreted according to Schmitt and Bedbur [16], which proposed two types of joint adsorption namely competitive and cooperative. In competitive adsorption, the anions and cations are adsorbed at different sites on the electrode surface, and in case of cooperative adsorption, the anions are chemisorbed on the electrode surface and the cations are adsorbed on a layer of the anion, apart from the adsorption on the surface directly.

From the data of Table (2) it is seen that KI would be considered as one of the effective anions for synergistic action with respect to the investigated salts. The net increment of inhibition efficiency shows a synergistic effect of KI, KSCN and KBr with hydrazide derivatives. The synergistic effect depends on the type and concentration of anions. The inhibition efficiency in presence of these anions decreases in the order: KI > KSCN > KBr [17].The experimental results suggested that the presence of these anions in the solution stabilizes the adsorption of hydrazide

derivatives on the metal surface and improved the inhibition efficiency of these derivatives.

Fig1. Demonstrates the mass- loss time curves for the dissolution of zinc in 0.1M HCl in absence and presence of different concentrations of compound (b) without and with addition of 10^{-2} M KI at 30°C.

$$S_\theta = (1 - \theta_{1+2}) / (1 - \theta'_{1+2}) \qquad (3)$$

where $\theta_{1+2} = \theta_1 + \theta_2 - \theta_1 \theta_2$

θ'_{1+2} Measured surface coverage by the anion in combination with cation. Θ_1 and θ_2 are the surface coverage for anions and cations , respectively.
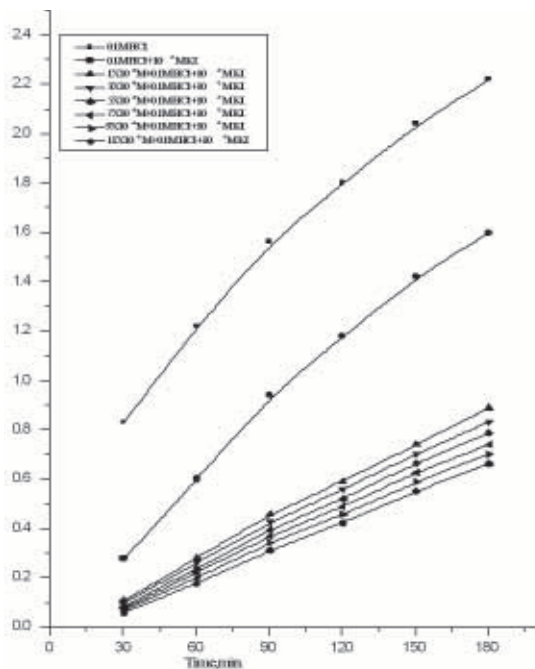

Fig. 1. Mass loss-time curves for dissolution of zinc in 0.1 M HCl in absence and presence of different concentrations of compound (b) without and with addition of 10^{-2} M KI at 30°C

Table 3. lists the variation of the synergistic parameter(s θ) in the presence of different concentrations of hydrazide derivatives. It is seen that all values of s θ are less than unity and, therefore, the adsorption of each compound antagonizes the other's adsorption.Thus, hydrazide derivatives significantly improved the coverage and thus the quality and inhibition efficiency of hydrazide derivatives on the corroding zinc.

Hydrazide derivatives are nitrogen and oxygen-containing organic compounds, which contain unshared electron pairs. In strong acidic solutions these hydrazide derivatives may be protonated, leading to positive charge in

Table 3. Synergism parameter (s θ) for different concentrations of hydrazide derivatives with addition of 1×10^{-2} M KI, KSCN and KBr at 30°C.

Conc., M	sθ								
	KI			**KSCN**			**KBr**		
	(a)	**(b)**	**(c)**	**(a)**	**(b)**	**(c)**	**(a)**	**(b)**	**(c)**
1×10^{-6}	0.832	0.839	0.905	0.818	0.810	0.880	0.799	0.772	0.848
3×10^{-6}	0.841	0.862	0.920	0.825	0.828	0.893	0.811	0.786	0.858
5×10^{-6}	0.850	0.896	0.949	0.833	0.856	0.918	0.805	0.805	0.877
7×10^{-6}	0.871	0.926	0.946	0.851	0.879	0.912	0.805	0.822	0.870
9×10^{-6}	0.882	0.976	0.963	0.860	0.918	0.927	0.833	0.848	0.881
11×10^{-6}	0.894	0.999	0.961	0.871	0.965	0.922	0.841	0.789	0.884

molecule. It is also known that Zn surface has positive charge due to (E_{corr}-Eq=0),thus it is difficult for the positively charged hydrazide derivatives to approach the positively charged Zn surface ,due to the electrostatic repulsion ,this is why these derivatives can not act as excellent inhibitors for Zn corrosion in 0.1M HCl solution without containing anions .In case of presence I^-, SCN^- and Br^- ions, these anions adsorbed on Zn surface and makes the surface negatively charged by means of electrostatic attraction, after that ,protonated hydrazide derivatives are easily reached the surface of Zn metal.

3.3. Adsorption isotherm:

Assuming the corrosion inhibition was caused by the adsorption of hydrazide derivatives, and the values of surface coverage for different concentrations of inhibitors in 0.1M HCl were evaluated from mass loss measurement using the following equation:

$$\theta = [\text{Mass loss}_{(pure)} - \text{Mass loss}_{(inh.)} / \text{Mass loss}_{(pure)}] \qquad (4)$$

From the values of (θ), it can be seen that the values of (θ) increased with increasing the concentration of hydrazide derivatives. Using these values of surface coverage, one can utilize different adsorption isotherms to deal with experimental data. The Temkin adsorption isotherm was applied to investigate the adsorption mechanism, by plotting (θ) vs log C, a straight lines were obtained (Fig.2). On the other hand, it is found that Kinetic- thermodynamic model of El-Awady et al [18] which has the formula:

$$\text{Log} (\theta/1 - \theta) = \log K' - y \log C \qquad (5)$$

Is valid and verify the present adsorption data (Fig.3). The equilibrium constant of adsorption $K = K'^{(1/y)}$, where 1/y is the number of the surface active sites occupied by one hydrazide molecule and C is the bulk concentration of the inhibitor. From Table (3) it is noted that ΔG_{ads} values have a negative sign indicating that the adsorption process proceeds spontaneously and increase as the percentage inhibition increases. Table (4) shows the calculated thermodynamic parameters.

Table. 3. Inhibitor binding constant (K), Free energy of binding ΔG$_{ads}$, number of active sites (1/y) and later interaction parameter (a) for hydrazide derivatives at 30°C.

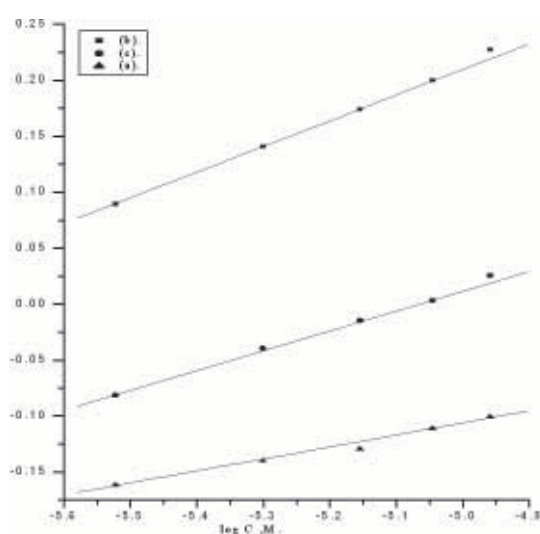| Corrosive medium	inhibitors	Kinetic model			Temkin		
		1/y	K	-ΔG$_{ads.}$, kJ mol^{-1}	a	K	-ΔG$_{ads.}$, kJ mol^{-1}
0.1 M HCl	(a)	9.31	10022.90	33.27	21.45	101020.82	33.33
	(b)	4.35	798065.44	44.20	9.69	771792.45	44.24
	(C)	5.62	11564.22	39.94	12.94	115008.18	39.46

Fig. 2. Curve fitting of corrosion data for zinc in 0.1 M Hcl in presence of different concentrations of hydrazide derivatives to the Tem kin adsorption isotherm at 30°C

Table (4): Thermodynamic parameters for the adsorption of 11X10^{-6} M hydrazide derivatives in 0.1 M HC1 on zinc surface .

Corrosive medium	inhibitors	Thermodynamic parameters		
		-ΔG$_{ads.}$, kJ mol^{-1}	-ΔS$_{ads.}$, J mol^{-1}K^{-1}	-Q, kJ mol^{-1}
0.1 M HCl	(a)	33.33	29.86	21.92
	(b)	44.25	18.46	19.15
	(C)	39.46	21.89	19.85

The negative values of Q suggested that the adsorption of inhibitor molecules onto Zn surface is an exothermic process; the magnitude of the heat of adsorption reaches the magnitude of heat of chemical reaction, which is the result of the transfer of electrons from the N or O atoms in the inhibitor molecules to the d-orbital of Zn atom. The negative values of ΔS$_{ads}$ may be explained in the following way: before the adsorption of inhibitors onto Zn surface, inhibitor

molecules freely move in the bulk solution, but with the progress in the adsorption ,inhibitor molecules were orderly adsorbed onto Zn surface, as a result, a- decrease in entropy.
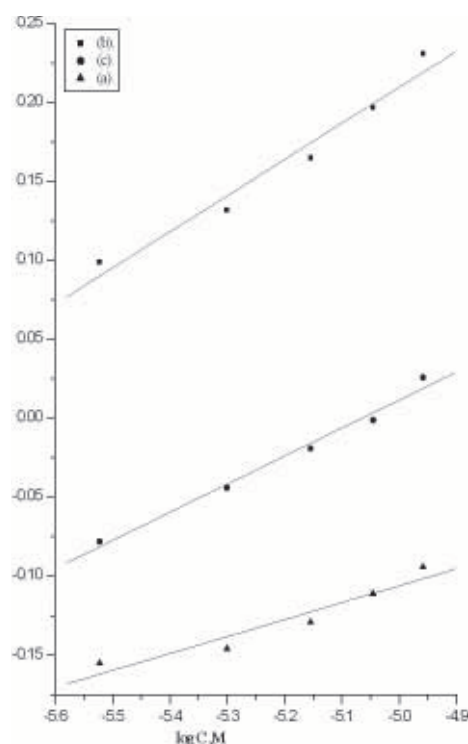

Fig. 3. Curve fitting of corrosion data for zinc in 0.1M HCl in presence of different concentrations of hydrazide derivatives to the kinetic at 30°C

3.4. Effect of Temperature:

The effect of temperature (30 – 55°C) on the performance of the inhibitors at a concentration of 11x 10^{-6} M for zinc in 0.1M HCl was studied using mass-loss measurements. Plots of log k (corrosion rate) against 1/ T (absolute temperature) [Fig 4] for Zinc in 0.1M HCl at a constant concentration (11x10^{-6} M) of all additives, gave straight lines. The values of the slopes obtained at different temperatures permit the calculation of Arrhenius activation energy (E$_a^*$). The activation energy values obtained from these lines were found to be 5.39 kJ mol^{-1} for 0.1M HCl and 6.75 – 5.87 kJ mol^{-1} for acid containing inhibitors(19) [Table 5].

Table. (5): Activation parameters of the dissolution of zinc in 0.1M HC1 in the absence and presence of 11x10^{-6} M hydrazide derivatives.

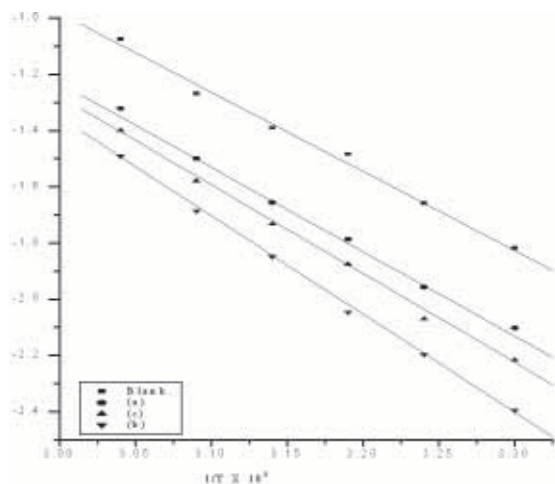| Corrosive medium	inhibitors	Activation parameters		
		E$_a^*$, kJ mol^{-1}	ΔH*, kmol^{-1}	-ΔS*, Jmol^{-1}k^{-1}
0.1 M HCl	Free acid	5.39	5.00	79.11
	(a)	5.87	5.42	69.21
	(b)	6.76	5.99	53.95
	(C)	6.02	5.58	66.45

Fig. 4. Log corrosion rate vs.l / T for the dissolution of zinc in presence of 11×10^{-6} M of hydrazide derivatives

Activation parameters for corrosion of zinc were calculated from Arrhenius – type plot. $k = A \exp(-E_a^* / RT)$ (6)

and transition state- type equation :

$k = RT / Nh \exp(\Delta S^* / R) \exp(-\Delta H^* / RT)$ (7)

The relation between log k / T vs. 1 / T gives straight line, from its slope, ΔH^* can be computed and from its intercept ΔS^* can be also computed Fig (5).

Table (5) exhibits the values of apparent activation energy E_a^*, enthalpies ΔH^* and entropies ΔS^* for zinc dissolution in 0.1M HCl solution in absence and presence of 11×10^{-6} M different additives. The presence of hydrazide derivatives increases the activation energies of zinc indicating strong adsorption of the inhibitor molecules on the metal surface and the presence of these additives induces energy barrier for the corrosion reaction and this barrier increases with increasing the additive concentrations.
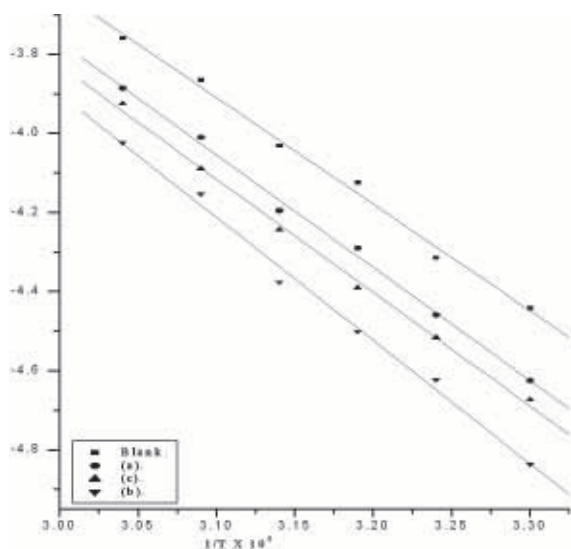

Fig. 5. Log corrosion rate / T vs.l / T for the dissolution of zinc in presence of 11×10^{-6} M of hydrazide derivatives

3.5. Electrochemical measurement

Fig (6) shows the galvanostatic polarization curves (E vs,log i) of zinc dissolution in 0.1M HCl, in presence of different concentrations of compound (b). An increase in the concentration of inhibitor shifts the polarization curves towards more negative potentials. For cathodic Tafel lines, and towards more positive potentials for anodic Tafel lines. Polarization data suggested that the additives behave as mixed – type inhibitors. The corrosion potential (E_{corr}), cathodic Tafel slope (β_c), anodic Tafel lines (β_a), degree of surface coverage (θ) and percentage inhibition efficiency (%In) were derived from the curves of Fig(6), are recorded in Table (6).The results in this Table show that the corrosion potential is found to shift to a more positive direction, which probably means that in this case the zinc surface behaves as a noble metal, this is caused by the formation of the strong adsorption layer which protects Zn surface from corrosion.
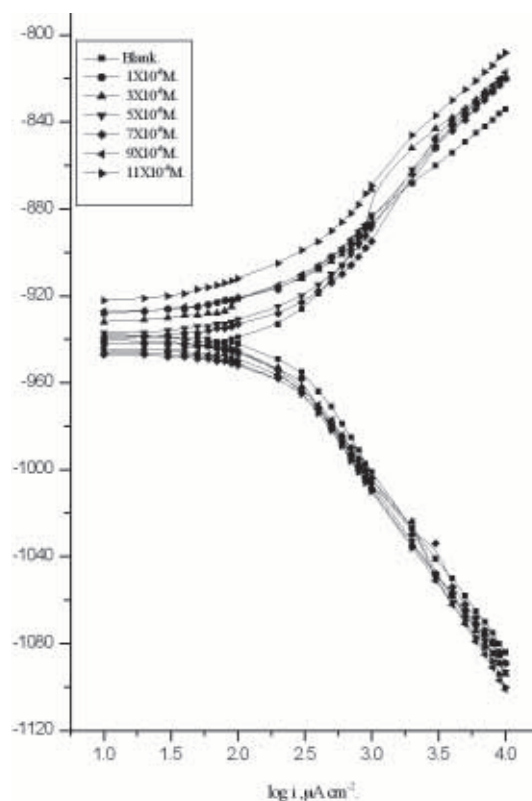

Fig. 6. Galvanostatic polarization curves of dissolution of zinc in 0.1M HCl in presence
And absence different concentrations of compound (b) at

Table. (6): The effect of concentrations of compound (b) on the free corrosion potential ($E_{corr.}$), corrosion current density ($i_{corr.}$), Tafel slopes (β_a & β_c), inhibition efficiency (%In) and degree of surface coverage (θ) of zinc in 0.1M HCl at 30°C.

Conc., M.	$-E_{corr.}$, mV.	$i_{corr.}$, $\mu A\ cm^{-2}$.	β_a, mV dec^{-1}.	β_c, mV dec^{-1}.	θ	%In
0	942.5	274.1	87.3	98.2	-------	------
1×10^{-6}	931.7	105.6	50.5	80.4	0.614	61.4
3×10^{-6}	952.6	99.5	55.0	82.3	0.636	63.6
5×10^{-6}	935.9	95.5	56.7	74.4	0.651	65.1
7×10^{-6}	936.0	89.7	55.2	64.2	0.672	67.2
9×10^{-6}	927.7	84.3	51.5	79.7	0.692	69.2
11×10^{-6}	925.0	77.6	55.3	79.1	0.716	71.6

The order of inhibition efficiency derived from this method is:

compound (b) > compound (c) > compound (a).

3.5. Mechanism of inhibition

Skeletal representation of the mode of adsorption of the compounds is shown in Fig (7), and clearly indicates the active adsorption centers.
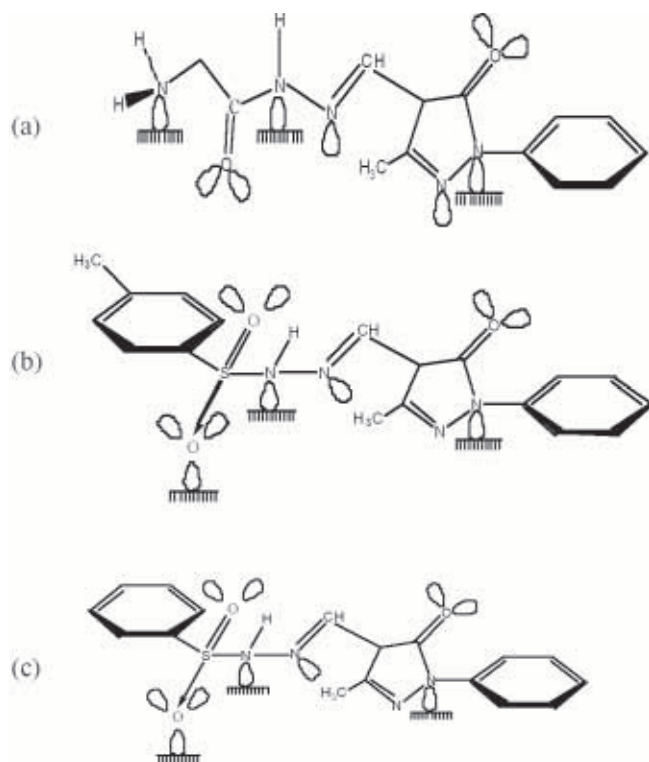

Fig. 7. Skeletal representation of the mode of adsorption of the tested derivatives

The order of decreasing inhibition efficiency of hydrazide derivatives in 0.1M HCl is: compound (b) > compound (c) > compound (a)

The inhibition efficiency of these compounds depends on many factors [19], which include the number of adsorption active centers in the molecule and their charge densities, molecular size, mode of adsorption, heat of hydrogenation and formation of metallic complexes.

The obtained results of the additives (Table 1) indicate that: Compound (b) exhibits excellent inhibition power due to:(i) its larger molecular size that may facilitate better surface coverage, (ii) its adsorption through three active centers as shown from Fig (8),and (iii) the presence of p-CH$_3$ (σ =-0.17) which is highly electron releasing group which enhance the delocalized π-electrons on the active centers of the compound. Compound (c) comes after compound (b) in inhibition efficiency inspite of it has three active centers, because it has lesser molecular size than compound (b) and has no substituent in p-position (H-atom with σ =0.0) which contributes no charge density to the molecule .Compound (a) has the lowest inhibition efficiency, inspite of it has three active centers, this is because it has the lowest molecular size and has no aromatic ring [as in compound c] which covers more surface area than the aliphatic ones which are present in compound (a).

4. CONCLUSIONS

In the basis of the above discussion, the following conclusions may be easily drawn:

1- All the additives studied are found to perform well as a corrosion inhibitors in HCl solution and the inhibiting efficiency values of the examined compounds follow the order: compound (b) > compound (c) > compound (a) at all the studied concentrations range.

2- The hydrazide derivatives behave as mixed-type inhibitors for Zn corrosion in 0.1M HCl.

3- The inhibition efficiency increases with decrease in temperature and increases with the increase in the concentrations of the studied compounds.

4- The adsorption of these derivatives onto the Zn surface follows Temkin adsorption isotherm.

5- The presence of KI, KSCN and KBr improves the inhibition efficiency, indicating that there is a synergistic effect between hydrazide derivatives and these anions.

6- The electrochemical measurements are in good agreement with the mass-loss measurements. This improves the validity of the results obtained.

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