

Some Hydrazide Derivatives as Inhibitors for The Corrosion of Zinc in Sodium Hydroxide Solution.

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Abstract

The influence of some hydrazide derivatives as corrosion inhibitors for zinc in 2M sodium hydroxide solution has been studied using weight loss and galvanostatic polarization techniques. In general, at constant acid concentration, inhibitor efficiency increases with increase of concentration of inhibitor and decrease with rise in temperature. Polarization studies revealed that these compounds behave as mixed inhibitors. The effect of temperature on corrosion inhibition has been studied and activation energies has been calculated. Some thermodynamic parameters are calculated and discussed. The adsorption of the inhibitors on zinc surface is found to obey Temkin's adsorption isotherm.. Addition of Ca^{+2} , Sr^{+2} , Ba^{+2} and Mg^{+2} ions to the alkaline medium containing the hydrazide derivatives increases the inhibition efficiency of the system.

Key words: corrosion, zinc, sodium hydroxide, hydrazide derivatives.

1.Introduction

Because of the wide spread use of zinc, the study of its corrosion has turned to be an outstanding subject in corrosion with the industry today. For these reasons, considerable efforts have been devoted to study the electrochemical behaviour of zinc in alkaline media. A general survey of the literature indicates that the nature and mechanism of the zinc passivation in alkaline solutions is the subject of debate. Various mechanisms involving several intermediate species have been proposed for passivation of Zn in alkaline solutions⁽¹⁻¹¹⁾. In some works, $\text{Zn}(\text{OH})_2$ has been proposed to be passivating species^(6,10). For other authors it is $\text{ZnO}^{(3,12)}$. Moreover, in certain cases, the passive film has been supposed to consist of a dual layer, composed of ZnO and $\text{Zn}(\text{OH})_2$ or of two types of $\text{ZnO}^{(3, 6, 12, 13)}$. The oxide growth on the zinc electrode under prevailing experimental conditions could be explained on the basis of the following reactions^(14,15):

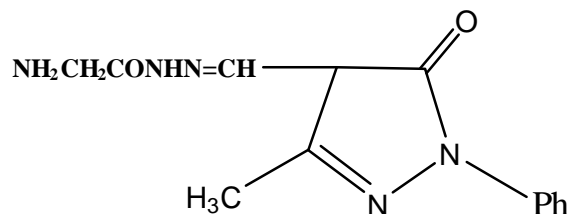


The average thickness of the passive layer formed on Zn electrode in alkaline solution changes according to the operating conditions and reaches about 50nm^(10, 16). Recently, it was found that the rate of oxide growth in the passive region increases with decreasing

concentration of alkali and increasing the imposed current density, while it decreases with increasing temperature and with stirring the solution ⁽¹⁷⁾.

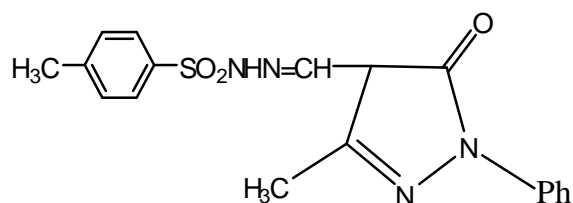
The purpose of the present contribution is to determine the influence of sodium hydroxide on the zinc corrosion in presence and in absence of the following hydrazide derivatives and the effect of Ca^{+2} , Sr^{+2} , Ba^{+2} and Mg^{+2} ions on the efficiency of these compounds was also examined. The hydrazide derivatives used in this paper are:

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

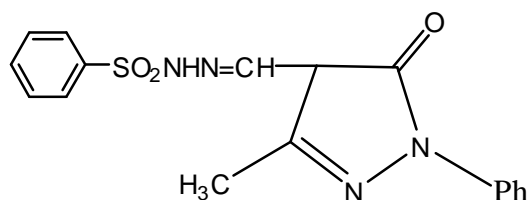


- (b) 4- methyl – N' – ((3-methyl – 5 – oxo – 1 – phenyl – 4, 5 – dihydro – 1H- pyrazol-4-yl) methylene) benzenesulfonohydrazide.

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



2.Experimental

High- purity BDH zinc sheets of the composition (in weight %): Fe, 0.002 ; Pb, 0.001. Cd, 0.001; Cu , 0.003 and the rest Zn were used. Specimens were abraded successively with different grade of emery papers, then degreased in acetone in an ultrasonic bath, washed with bi-distilled water and then dried at room temperature. The aggressive solutions were made of NaOH. Appropriate concentrations of NaOH were prepared using bidistilled water. All chemicals used were of AR grade.

2.1.Chemical measurements.

For weight loss measurements, rectangular zinc specimens of size 20x20x2mm were immersed in 100 ml of inhibited and uninhibited solutions and allow to stand for several

intervals at 30⁰C in water thermostat. The percentage inhibition efficiency (%I) of the inhibitor was calculated using the equation:

$$\%I = \frac{W_o - W}{W_o} \times 100 \quad \text{and} \quad (7)$$

$$\theta = \frac{W_o - W}{W_o} \quad (8)$$

where W and W_o are the weight losses of zinc with and without inhibitors, respectively and θ is degree of surface coverage.

2.2. Electrochemical measurements.

Galvanostatic polarization studies were carried out on zinc in 2M NaOH solution without and with different concentrations of the inhibitors used at 30⁰C. A cylindrical rod with a surface area of 0.7 cm² was used as working electrode. Saturated calmoel electrode (SCE) was used as reference electrode while a platinum wire as counter electrode. All expeniments were carried out at

30± 0.1⁰C. The inhibition efficiency (%I) is defined as:

$$\%I = \left(\frac{I_{corr} - I_{inh}}{I_{corr}} \right) \times 100 \quad \text{and} \quad (9)$$

$$\theta = \left(\frac{I_{corr} - I_{inh}}{I_{corr}} \right) \quad (10)$$

where I_{corr} and I_{inh} are the unihibited and inhibited corrosion current densities, respectively.

3. Results and discussion

3.1. weight loss measuements:

Zinc samples were dissolved under unstirred conditions in 2M NaOH without and with various concentrations (1X10⁻⁶ – 11X10⁻⁶ M) of different additives used at 30⁰C.

Fig 1. shows the effect of the period of immersion on the corrosion of zinc in presence and absence of different concentrations of compound (b) in alkali media. The curves are characterized by an initial slow rise in weight- loss followed by a sharp rise. The curves obtained in the presence of additives fall below that of alkali. The weight loss of zinc depends upon the type and the concentration of the additives.

The inhibition efficiency (%I) of various inhibitors, decreases in the order (Table 1):

$$\text{Compound (b)} > \text{compound (c)} > \text{compound (a)}$$

3.2. Synergistic effect: Effect of the addition of 0.02% Ca⁺², Sr⁺², Ba⁺², Mg⁺² ions to different concentrations of additives on the corrosion inhibition of Zn in 2M NaOH using weight less technique was studied.

the percentage inhibition efficiency brought about by 0.02% of these cations. From the results obtained it was found that Ba²⁺ > Sr²⁺ > Ca²⁺ > Mg²⁺. This has a qualitative correspondence the inereasing atomic weight of these cations and it may be explained on the basis of their basicity which increase by increasing atomic weights.

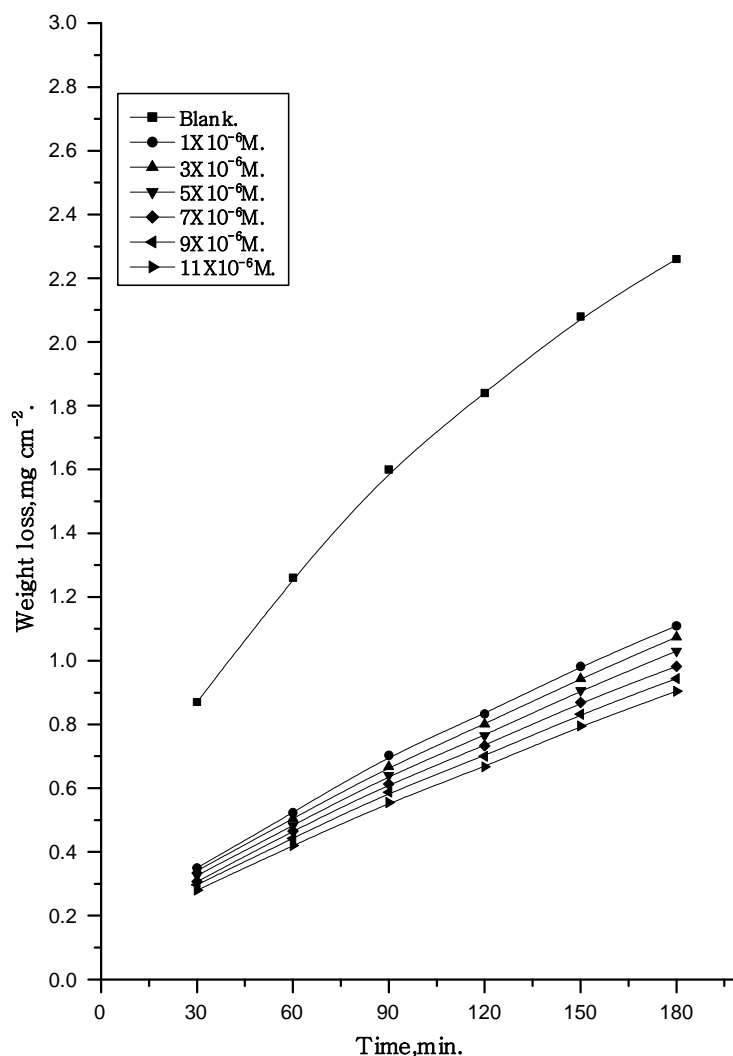


Fig.(1):Weight loss-time curves for dissolution of zinc in 2M NaOH in absence and presence of different concentrations of compound (b) at 30°C.

Table (1): Data from weight loss of zinc dissolution in 2 M NaOH at different concentrations of the hydrazide derivatives at 30°C.

Conc., M	% Inhibition (%I)		
	(a)	(b)	(c)
1x10 ⁻⁶	44.44	58.49	49.92
3x10 ⁻⁶	45.23	59.92	50.79
5x10 ⁻⁶	46.03	61.66	52.38
7x10 ⁻⁶	47.61	63.01	53.17
9x10 ⁻⁶	48.41	64.84	53.96
11x10 ⁻⁶	49.20	66.66	54.76

Table (2): Data from weight loss of zinc dissolution in 2M NaOH at different concentrations of the hydrazide derivatives with addition of 0.02% BaCl₂ at 30°C.

Conc., M	% Inhibition (%I)		
	(a)	(b)	(c)
1x10 ⁻⁶	65.87	75.15	71.34
3x10 ⁻⁶	66.66	76.58	72.22
5x10 ⁻⁶	67.46	78.33	73.80
7x10 ⁻⁶	69.04	78.96	74.60
9x10 ⁻⁶	69.84	81.50	75.39
11x10 ⁻⁶	70.63	84.12	76.19

Table (3): Data from weight loss of zinc dissolution in 2M NaOH at different concentrations of the hydrazide derivatives with addition of 0.02% SrCl₂ at 30°C.

Conc., M	% Inhibition (%I)		
	(a)	(b)	(c)
1x10 ⁻⁶	64.28	73.57	69.76
3x10 ⁻⁶	65.07	75.00	70.63
5x10 ⁻⁶	65.87	76.74	72.22
7x10 ⁻⁶	67.46	78.09	73.01
9x10 ⁻⁶	68.25	79.92	73.80
11x10 ⁻⁶	69.04	81.74	74.60

Table (4): Data from weight loss of zinc dissolution in 2M NaOH at different concentrations of the hydrazide derivatives with addition of 0.02% CaCl₂ at 30°C.

Conc., M	% Inhibition (%I)		
	(a)	(b)	(c)
1x10 ⁻⁶	61.90	71.19	67.38
3x10 ⁻⁶	62.69	72.61	68.25
5x10 ⁻⁶	63.49	74.36	69.84
7x10 ⁻⁶	65.07	75.71	70.63
9x10 ⁻⁶	65.87	77.53	71.42
11x10 ⁻⁶	66.66	79.36	72.22

Table.(5): Data from weight loss of zinc dissolution in 2M NaOH at different concentrations of the hydrazide derivatives with addition of 0.02% MgCl₂ at 30°C.

Conc., M	% Inhibition (%I)		
	(a)	(b)	(c)
1x10 ⁻⁶	59.52	68.80	65.00
3x10 ⁻⁶	60.31	70.23	65.87
5x10 ⁻⁶	61.11	71.98	67.46
7x10 ⁻⁶	62.69	73.33	68.25
9x10 ⁻⁶	63.49	75.15	69.04
11x10 ⁻⁶	64.28	76.98	69.84

It is also observed from Tables (2-5) that the inhibition efficiency of the inhibitors increases in the presence of Ca²⁺, Sr²⁺, Ba²⁺ and Mg²⁺. This may be due to the fact that these cations are chemisorbed on the zinc surface and aids in bringing negatively charged species inclusive of the zincate ion closer to the metal surface, thus enhancing inhibition efficiency as has actually been observed.

The synergistic parameter ,s_θ, was calculated using equation (11). The plots of the synergism parameter (s_θ) (in case of BaCl₂) against various concentrations of inhibitors is given in Fig (2), and corresponding values are show in Table (6)

$$S_{\theta} = (1 - \theta_{1+2}) / (1 - \theta_{1+2}^{-}) \quad (11)$$

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.

Table. (6): Synergism parameter (S_θ) for different concentrations of the hydrazide derivatives and in presence of 0.02 % BaCl₂.

Corrosive medium	Synergism parameter (S _θ)						
	Conc., M	1x10 ⁻⁶	3x10 ⁻⁶	5x10 ⁻⁶	7x10 ⁻⁶	9x10 ⁻⁶	11x10 ⁻⁶
2M NaOH	(a)	0.813	0.821	0.829	0.846	0.855	0.864
	(b)	0.835	0.855	0.884	0.879	0.950	1.007
	(c)	0.873	0.885	0.908	0.921	0.935	0.950

Since most of these values of s_θ are about unity (similar results were obtained in case of SrCl₂, CaCl₂ and MgCl₂ and are not shown), the higher inhibition efficiency of cation and additives can be calculated as brought out by synergistic effect.

3.3.Adsorption isotherm.

Fig (3) demonstrates the variation of the degree of surface coverage with the logarithmic of concentration of the additives from weight loss technique.

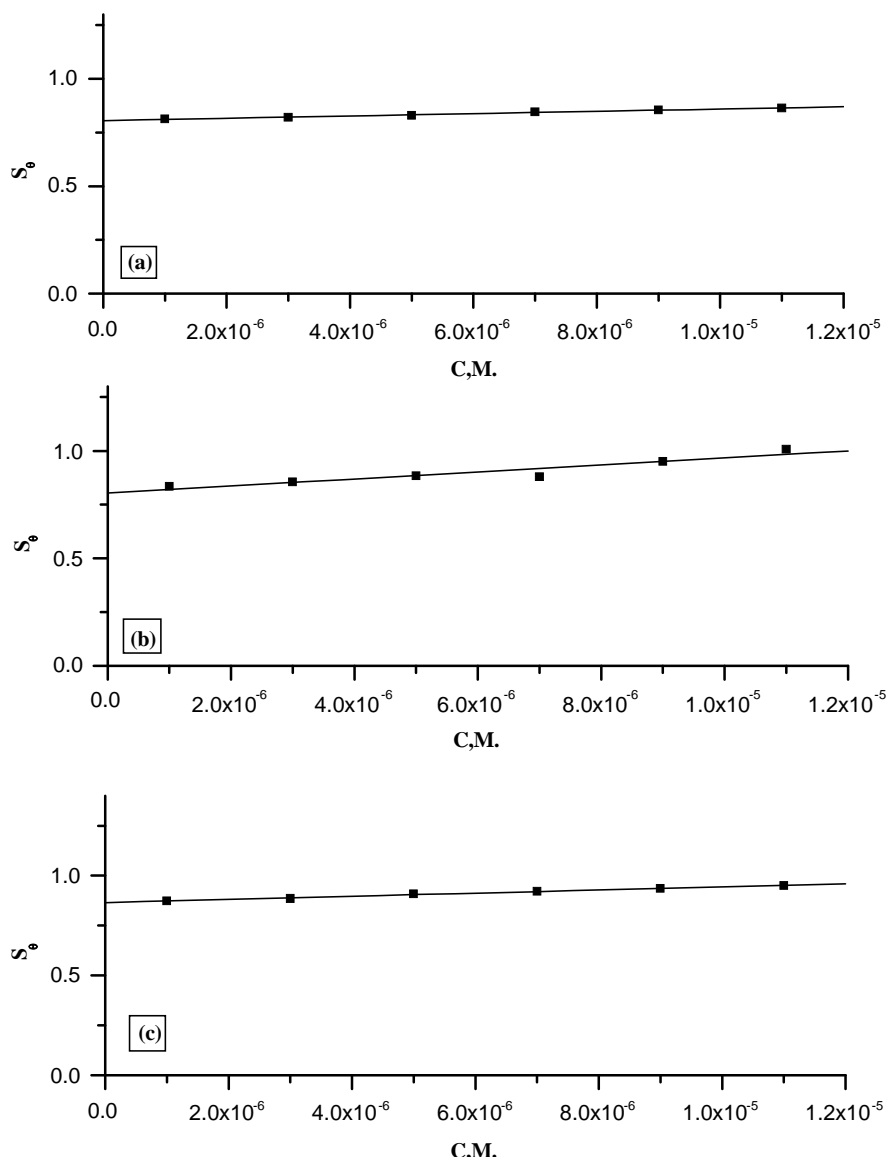


Fig.(2):Plots of synergism parameter (S_s) versus the concentration of hydrazide derivatives for the dissolution of zinc in 2M NaOH with addition of 0.02% $BaCl_2$ at 30°C.

The adsorption isotherm follows that of Temkin adsorption isotherm ⁽¹⁸⁾. For such an isotherm θ_{inh} is a linear function of $\log C$ according to the equation:

$$\ln KC = a \theta \quad (12)$$

Where K is the equilibrium constant of the adsorption reaction, C is the inhibitor concentration in the bulk of the solution, a is the interaction parameter and θ is the surface coverage. (i.e), the fraction of the surface covered by the inhibitor molecules.

On the other hand, it is found that the Kinetic- Thermodynamic model of El -Awady et al ⁽¹⁹⁾.

$$\log \{ \theta / (\theta - 1) \} = \log K + y \log C \quad (13)$$

is valid to operate the present adsorption data. The equilibrium constant of adsorption

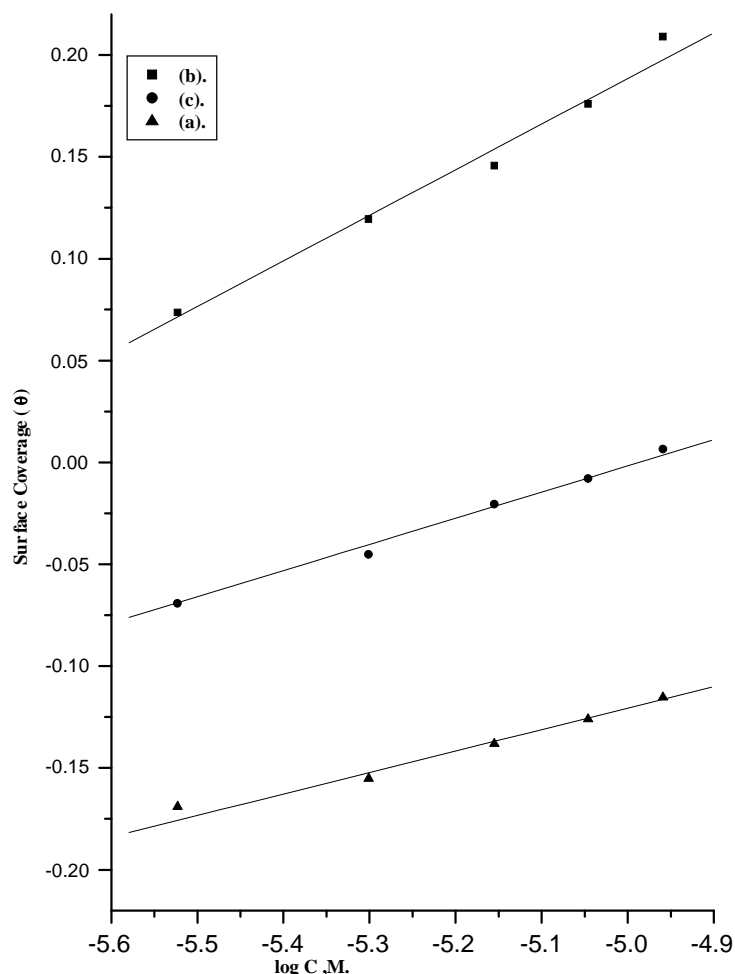


Fig.(3): Curve fitting of corrosion data for zinc in 2M NaOH in presence of different concentrations of hydrazide derivatives to the Temkin isotherm at 30°C.

$K = K' (1/y)$ where $1/y$ is the number of the surface active sites occupied by one hydrazide and C is the bulk concentration of the inhibitor. The plotting $\log \theta / (1 - \theta)$ against $\log C$ at 30°C is given in Fig (4), where straight line relationships were obtained suggesting the validity of this model for all cases studied. The calculated values of $1/y$, K and ΔG_{ads} are given in Table (7).

Inspection of the data of this Table shows that the large values of ΔG_{ads} and its negative sign, indicate that the adsorption of hydrazide compounds on the zinc surface is proceeding spontaneously and is accompanied by a highly- efficient adsorption.

It is worth noting that the value of $1/y$ is more than unity. This means that the given inhibitor molecules will occupy more than one active sites. In general, the values of ΔG_{ads} obtained from El- Awady et al model are comparable with those obtained from Temkin isotherm.

The entropies of adsorption ΔS_{ads}^0 were calculated from the relation between

ΔG_{ads}^0 and T :

$$\Delta S_{ads}^0 = \{ \delta \Delta G_{ads}^0 / \delta T \} \quad (14)$$

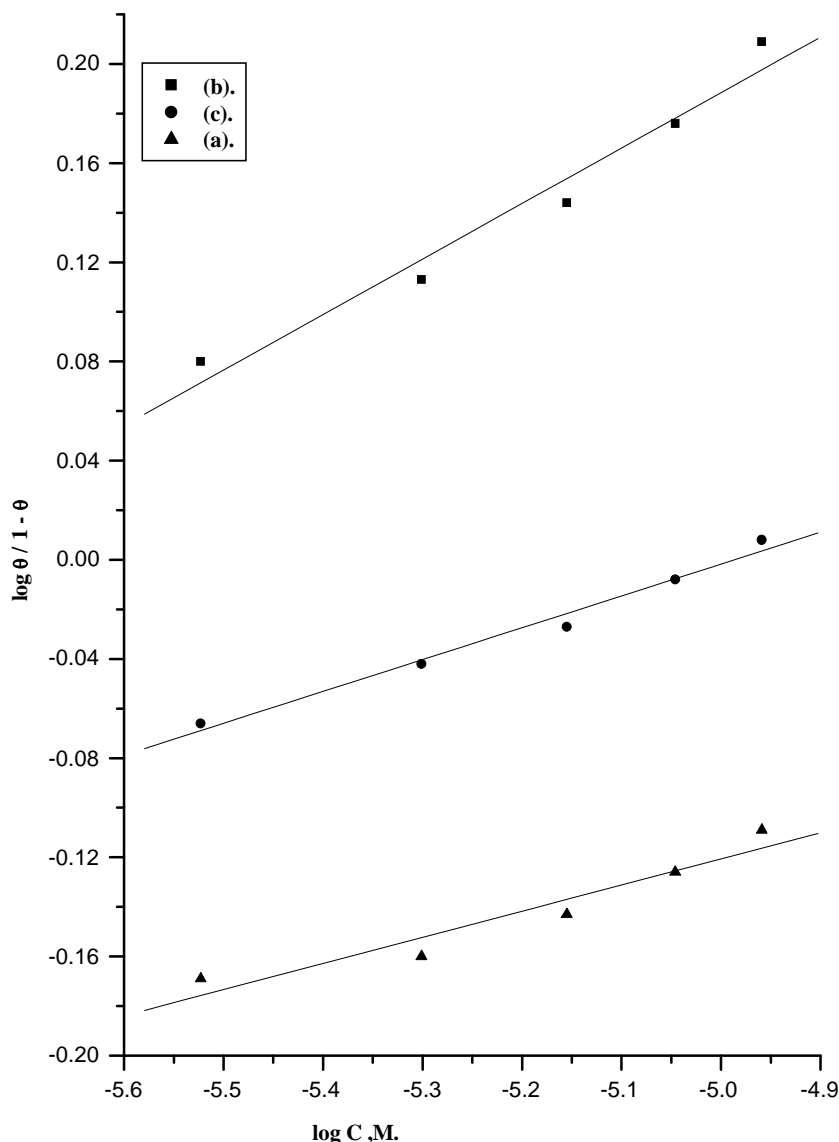


Fig.(4): Curve fitting of corrosion data for zinc in 2M NaOH in presence of different concentrations of hydrazide derivatives to the kinetic model at 30°C.

Table.(7): Inhibitor binding constant(K), Free energy of 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	$\Delta G_{ads}, \text{KJmol}^{-1}$	a	K	$\Delta G_{ads}, \text{KJmol}^{-1}$
2 M Na OH	(a)	9.48	6883.72	32.03	21.85	6238.30	32.11
	(b)	4.46	678316.42	43.78	10.28	641889.62	43.69
	(C)	5.78	96149.17	38.97	13.92	95961.18	39.00

For calculating the values of heat of adsorption (Q) of the various inhibitors, plots were drawn of $\log (\theta / 1 - \theta)$ vs $1/T$. The Q values obtained from the slopes of these plots. Fig (5) .

The values of ΔS^0_{ads} and Q are tabulated in Table (8). From these results it may be generalized that the more efficient inhibitor has more negative ΔG_{ads} value and less values of ΔS_{ads} and Q .

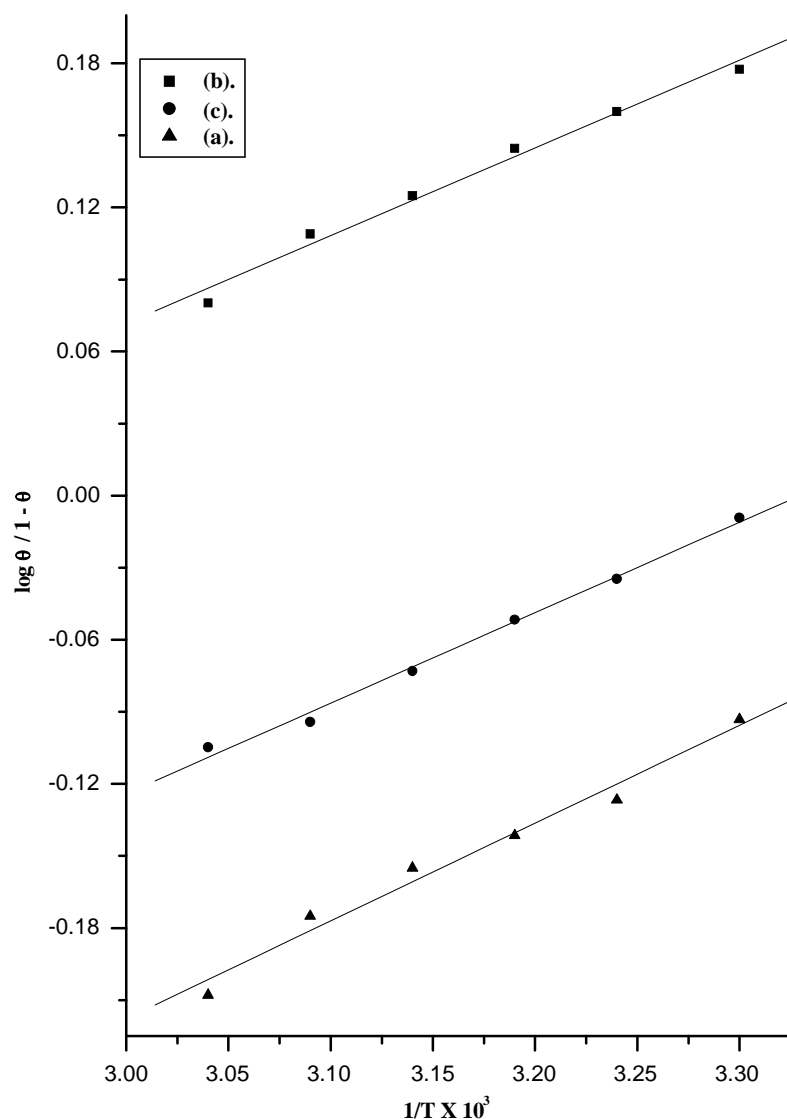


Fig.(5): $\log \theta / 1 - \theta$ vs. $1/T$ for the dissolution of zinc in 2M NaOH in presence of 11×10^{-6} M of hydrazide derivatives.

Table.(8): Thermodynamic parameters for the adsorption of hydrazide derivatives in 2M NaOH on zinc surface.

Corrosive medium	inhibitors	Thermodynamic parameters		
		$-\Delta G^0_{\text{ads}},$ KJ mol ⁻¹	$-\Delta S^0_{\text{ads}},$ J mol ⁻¹ K ⁻¹	$-Q,$ KJ mol ⁻¹
2 M NaOH	(a)	32.11	25.98	21.28
	(b)	43.79	18.02	19.10
	(C)	39.00	21.52	19.69

3.4. Effect of Temperature:

The effect of temperature (30- 55⁰C) on the performance of the inhibitor at concentration of 11×10^{-6} M for zinc in 2M NaOH was studied using weight loss measurements. Plots of log k (corrosion rate) against $1/T$ (absolute temperature), (Fig 6), for zinc in 2M NaOH at constant concentration for all additives (11×10^{-6} M), give straight lines

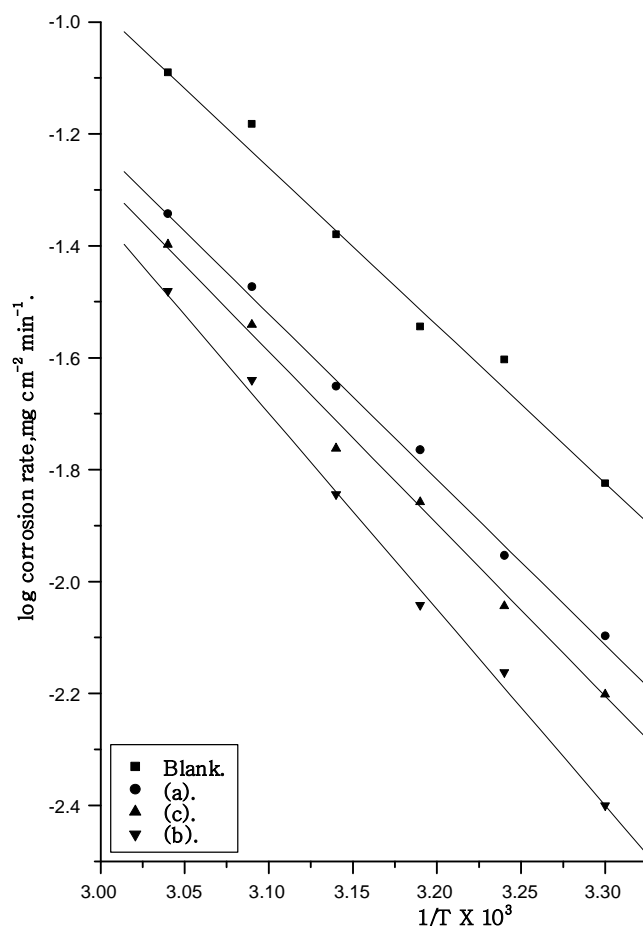


Fig.(6):log corrosion rate vs.1/T for the dissolution of zinc in presence of 11×10^{-6} M of hydrazide derivatives.

Table.(9): Activation parameters of the dissolution of zinc in 2M NaOH in absence and presence of 11×10^{-6} M hydrazide derivatives.

Corrosive medium	inhibitors	Activation parameters		
		E_a^* , kJ mol ⁻¹	ΔH^* , KJ mol ⁻¹	$-\Delta S^*$ J mol ⁻¹ k ⁻¹
2 M NaOH	Free alkali	5.38	4.93	78.45
	(a)	5.71	5.41	68.66
	(b)	6.71	5.98	53.62
	(C)	5.90	5.53	66.01

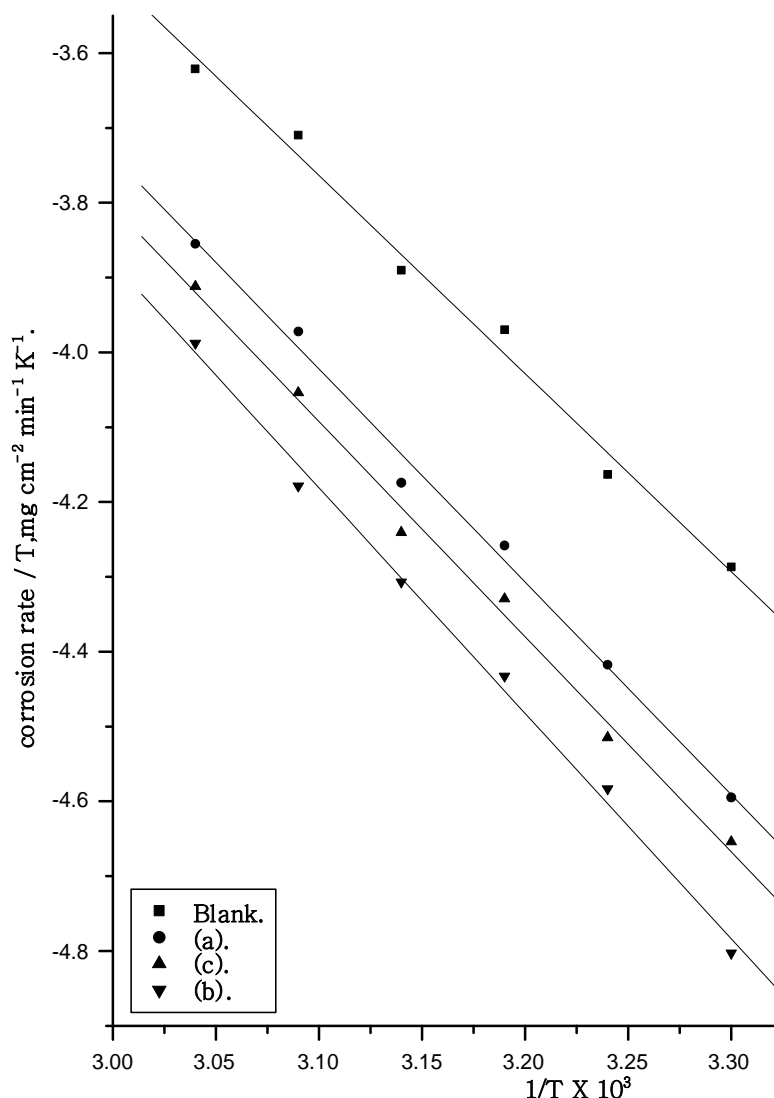


Fig.(7):log corrosion rate / T vs.1/T for the dissolution of zinc in presence of 11×10^{-6} M of hydrazide derivatives.

The values of the slopes obtained at different temperatures permit the calculation of Arrhenius activation energy (E_a^*). The activation energy values obtained from this Fig. were found to be 5.38 KJ mol^{-1} and $6.71 - 5.71 \text{ KJmol}^{-1}$ for free and alkali containing inhibitors Table (9).

Activation parameters for corrosion of zinc in 2M NaOH were calculated from Arrhenius – type plot:

$$k = A \exp (- E_a^* / RT) \quad (15)$$

And transition state – type equation:

$$k = RT / Nh \exp (\Delta S^* / R) \exp (- \Delta H^* / RT) \quad (16)$$

The almost similar values of E_a^* suggest that the inhibitors are similar in the mechanism action and the order of the efficiency many be related to the preexponential factor A in equation (15). This is further related to concentration, steric effects, metal surfac characters.

The relationship between $\log k/T$ vs. $1/T$ gives stlaight line (Fig.7), from its slope, ΔH^* can be calculated and from its intercept ΔS^* can be also calculated .

the presence of derivatives increases the activation energies of zinc indicating strong adsorption of the inhibitor molecules on the metal surface. The presence of these additives induce energy barrier for the corrosion reaction and this barrier increases with increasing the additive concentration. The higher values of ΔS^* is explained on the basis that the process of adsorption exhibits a rise in the enthalpy of the corrosion process.

The calculated activation entropies, ΔS^* , for zinc in 2M NaOH solution are large and negative. The presence of these additives lowers the values of ΔS^* . The changes in ΔS^* are directly proportional to the concentration of the additives. This phenomenon was discussed before as inhibitor-free acid solutions, the transition state of the rate determining step represents a more orderly arrangement relative to the initial state, and hence a negative values for ΔS^* are produced. In the presence of inhibitor, the system passes from less orderly to a more random arrangement and hence . an increase in the values of ΔS^* is observed.

3.5. Galvanostatic measurement

Fig (8) shows the galvanostatic polarization curves (E vs. log I) of zinc dissolution in 2M NaOH, in presence of different concentrations of compound (b). An increase in the concentration, of inhibitor shifted 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 used act as mixed-type inhibitors ($\beta_a = \beta_c$). The corrosion kinetic parameters such as corrosion current density ($i_{corr.}$), corrosion potential ($E_{corr.}$), cathodic Tafel slope (β_c), anodic Tafel lines (β_a), degree of surface coverage (θ) and percentage inhibition(%I) were derived from the curves Fig. 8 are recorded in Table (10) .

Table. (10): 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 (%I) and degree of surface coverage (θ) of zinc in 2M NaOH at 30°C.

Concentration, M	$-E_{corr.}$, mV.	$i_{corr.}$, $\mu A\ cm^{-2}$.	β_a , $mV\ dec^{-1}$.	β_c , $mV\ dec^{-1}$.	θ	%I
0	1048.3	269.1	78.7	95.2	-----	-----
1×10^{-6}	1047.6	130.2	59.3	83.5	0.525	52.5
3×10^{-6}	1051.0	124.9	64.7	86.7	0.545	54.5
5×10^{-6}	1043.7	122.4	61.0	84.6	0.554	55.4
7×10^{-6}	1034.1	119.6	55.3	91.1	0.563	56.3
9×10^{-6}	1025.5	112.7	51.3	100.5	0.588	58.8
11×10^{-6}	1032.8	103.8	59.3	87.0	0.621	62.1

3.6. Chemical structure and corrosion inhibition of zinc

Skeletal representation of the mode of adsorption of the hydrazide derivatives is shown in Fig (9) , and clearly indicates the active adsorption centers.

The order of decreasing inhibition efficiency of the investigated hydrazide derivatives in 2M NaOH is :

$$\text{compound (b)} > \text{compound (c)} > \text{compound (a)}$$

The inhibition efficiency of the compounds depends on many factors ⁽¹⁹⁾, which include the number of adsorption active centers in the molecule and their charge density, molecular size, mode of a desorption, heat of hydrogenation and formation of metallic complexes.

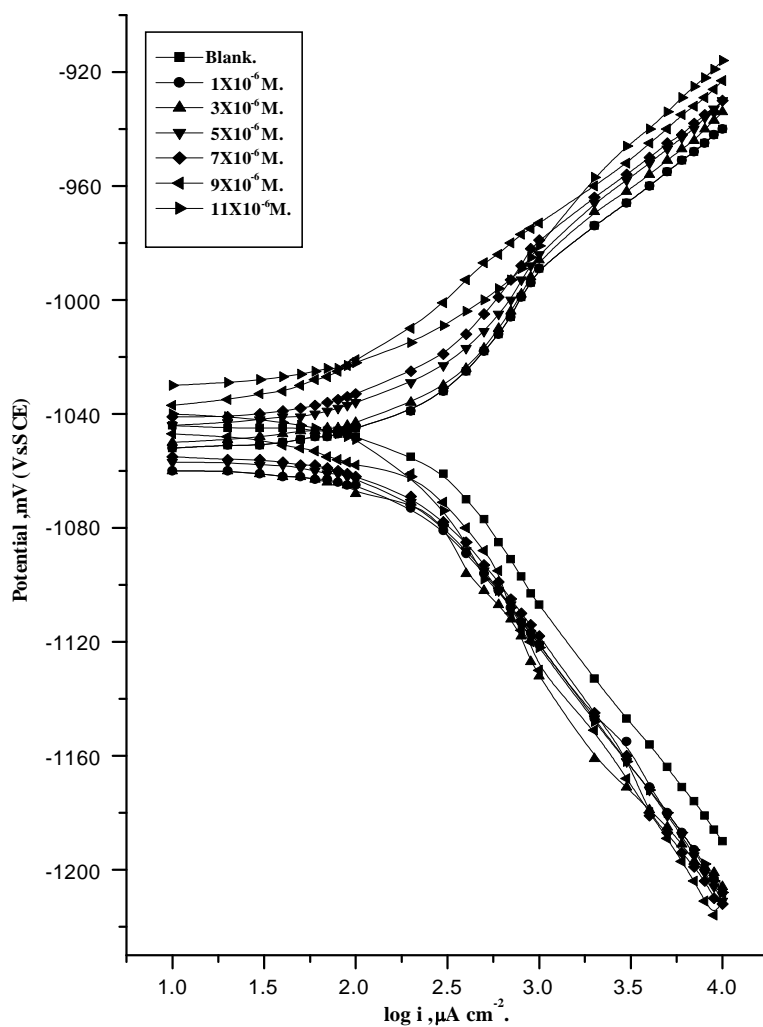
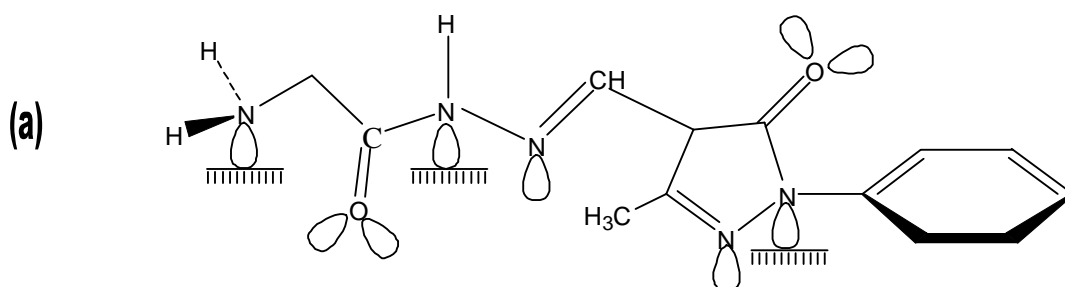
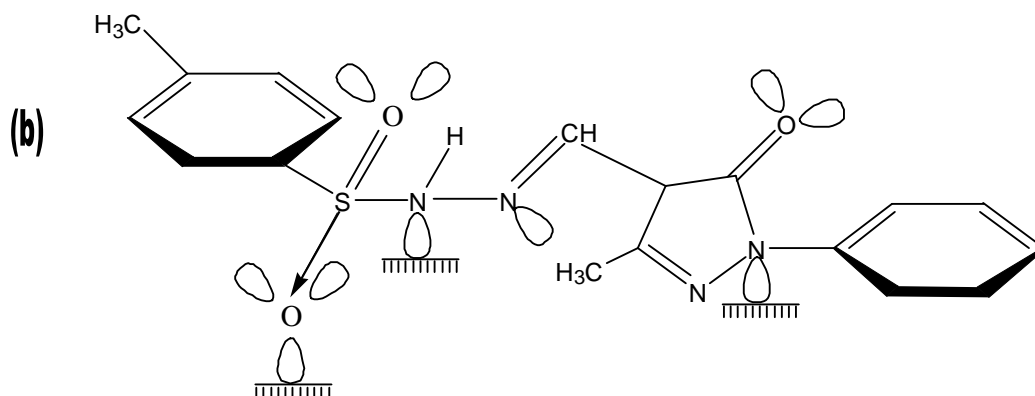


Fig.(8):Galvanostatic polarization curves for the dissolution of zinc in 2M NaOH in presence and absence of different concentrations of compound(b) at 30°C.





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 (9),and (iii) the presence of p-CH₃ ($\sigma = -0.17$) 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 and has no substituent in p-position (H-atom with $\sigma = 0.0$) which contributes no charge density to the molecule .

Compound (a) has the lowest inhibition efficiency,in spite of it has three active centers.this is because it has the lowest molecular size and the aromatic ring in compound (c) covers more surface area than the aliphatic ones in compound (a).

4.Conclusion

- 1- All the additives are found to perform well as a corrosion inhibitors in sodium hydroxide solution and the inhibiting efficiency values of the examined compounds follow the order: compound (b) > compound (c) > compound (a) at all the studied concentrations.
- 2-The compounds studied are found to act as mixed-type inhibitors,
- 3- the protection efficiency increases with a decrease in temperature or an increase in the concentration of the studied compounds .
- 4- The adsorption of" these compounds was found to follow Temkin's adsorption isotherm.
- 5- The addition of Ba²⁺, Ca²⁺, Sr²⁺, Mg²⁺, was found to increase the percentage inhibition due to synergistic effect.

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