

Synergistic Effect of some Halide Ions on the Inhibition of Zinc Corrosion in Hydrochloric Acid by Tetrahydro carbazole Derivatives Compounds.

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The synergistic effects of some ions such as KI, KCl and KBr on the corrosion inhibition of zinc in 0.4 M HCl by tetrahydrocarbazole derivatives compounds has been investigated using weight loss measurements. Potentiodynamic anodic polarization technique was used to measure the pitting corrosion potential and Quantum Chemical studies (Computational Study) were investigated. Results obtained show that these compounds are good inhibitors and their inhibition efficiencies (IE %) increase with the increase of inhibitor concentration. The presence of I⁻, Br⁻ and Cl⁻ anions increase the inhibition efficiency of tetrahydrocarbazole compounds due to the synergistic effect. Halide ions are normally strongly adsorbed on the zinc surface and facilitate the adsorption of organic compounds by forming intermediate bridges between the positively charge metal surface and the positive end of the tetrahydrocarbazole molecule. Thus, the inhibitor is not adsorbed directly on the metal itself but rather by columbic attraction to the adsorbed halide ions on the metal surface. It is also found that these compounds inhibit the pitting corrosion of zinc in chloride containing solution by shifting the pitting corrosion potential into more positive (noble) direction. Quantum parameters chemical parameters were constructed in order to characterize the inhibition of these compounds efficiency.

Keywords: Zinc, Tetrahydrocarbazole derivatives, synergistic effect, pitting corrosion

1. INTRODUCTION

Zinc is an industrially important metal and is corroded by many agents, of which aqueous acids are the most dangerous [1]. 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 overvoltage on the

corroding metal [2]. Hydrochloric acid is one of the most widely applied aqueous mineral acids in industry. The removal of oxide from metallic parts before applying coatings, oil well acidizing, industrial acid cleaning, acid descaling and acid pickling are some of the important fields of HCl applications. The highly corrosive nature of this acid on most metals and alloys requires some degree of restraint to achieve economic maintenance and operation of the equipment, minimize the loss of chemical products and minimize safety. The use of inhibitors is one of metals and alloys, especially in acidic media. The increase in inhibition efficiency of organic compounds in the presence of some anions has been observed by investigators[3-5] and was ascribed to synergistic effect. Halide ions are normally strongly adsorbed on the surface of a corroding metal and facilitate the adsorption of organic compounds by forming intermediate bridges between the positively charge metal surface and the positive end of the organic molecule. Thus, the inhibitor is not adsorbed directly on the metal itself but rather by columbic attraction to the adsorbed halide ions on the metal surface. Studies of the effect of organic additives on the corrosion rate of zinc had been the subject of many investigators [6-12];. Most organic inhibitors are substances with at least one functional group that considered being a reaction center for the adsorption of the compound on the corroding surface, therefore forming barrier to its direct contact with corrosive environment.

In previous work [13], tetrahydrocarbazole derivatives compounds are used as corrosion inhibitors for Zinc in 0.4M HCl solution using weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy and electrochemical Frequency Modulation Technique (EFM).

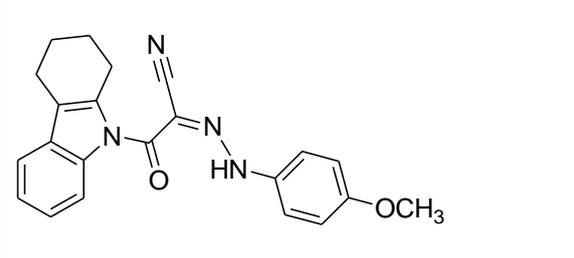
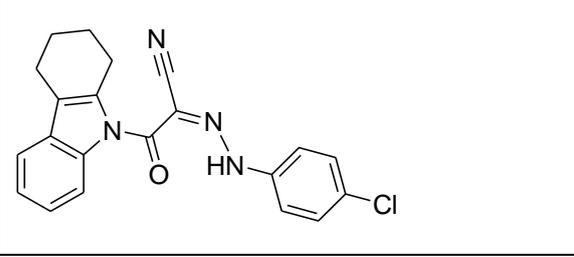
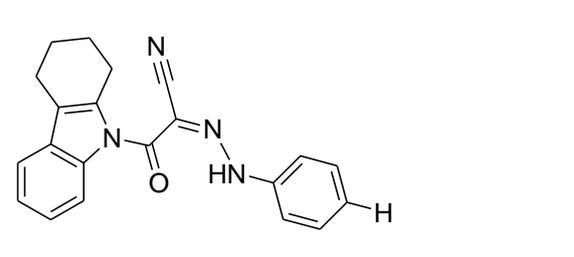
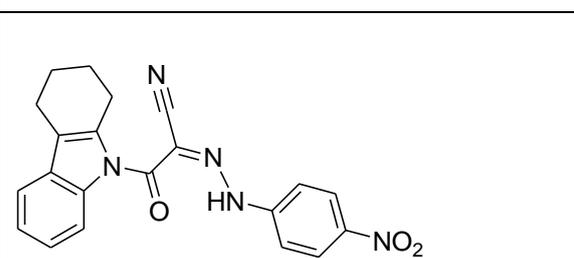
The aim of this study is to complete the previous work and investigate the synergistic effect by addition of KI, KCl and KBr on the corrosion inhibition of zinc in 0.4 M HCl by tetrahydrocarbazole derivatives compounds using weight loss measurements. Also, the pitting corrosion of Zn in chloride containing solutions and its inhibition by these compounds and quantum chemical studies were investigated.

2. EXPERIMENTAL

2.1. Materials and reagents

Zinc strips (BDH grade) containing: 0.002% Fe, 0.001% Pb, 0.003% Cu, 0.001% Cd, and rest Zn were used in this investigation. All chemicals used were of AR grade. Specimens of zinc strips were abraded successively by emery papers of different grades, i.e. 150, 320, 400 and 600, and finally polished with a 4/0 emery paper to obtain mirror like finish. Then degreased ultrasonically with ethyl alcohol and rinsed with bi-distilled water several times and dried between two filter papers. AR grade hydrochloric acid (37 %) was used for preparing the corrosive solutions. Appropriate concentration of aggressive solutions used (0.4 M HCl) was prepared using bi-distilled water. The tetrahydrocarbazole derivatives were synthesized in the laboratory using standard procedure[14]. Stock solutions of NaCl, KI, KCl and KBr (1M) were prepared using bi-distilled water. From these stocks concentrated solutions exactly of 0.1 M NaCl and 1×10^{-2} M of KI, KCl and KBr were prepared by dilution with bi-

distilled water. It was purified and characterized by IR spectroscopy and other standard techniques before use. The following derivatives of tetrahydrocarbazole were studied; Tetrahydrocarbazole derivatives were used as corrosion inhibitors in this study are listed below [14]:

Compound	Structures	Names	M. FW. & M. Wt.
(I)		(Z)-2-(2-(4-methoxyphenyl)hydrazono)-3-(5,6,7,8-tetrahydrocarbazol-9-yl)-3-oxopropanenitrile	C ₂₂ H ₂₀ N ₄ O ₂ Mol. Wt.: 372.42
(II)		(Z)-2-(2-(4-chlorophenyl)hydrazono)-3-(5,6,7,8-tetrahydrocarbazol-9-yl)-3-oxopropanenitrile	C ₂₁ H ₁₇ ClN ₄ O Mol. Wt.: 376.84
(III)		(Z)-2-(2-phenylhydrazono)-3-(5,6,7,8-tetrahydrocarbazol-9-yl)-3-oxopropanenitrile	C ₂₁ H ₁₈ N ₄ O Mol. Wt.: 342.39
(IV)		(Z)-2-(2-(4-nitrophenyl)hydrazono)-3-(5,6,7,8-tetrahydrocarbazol-9-yl)-3-oxopropanenitrile	C ₂₁ H ₁₇ N ₅ O ₃ Mol. Wt.: 387.39

2.2 Measurements

2.2.1 Weight loss measurements

For weight loss measurements, rectangular zinc specimens of size 20 x 20 x 2 mm were immersed in 50 ml inhibited and uninhibited solutions and allow to stand for several intervals at 30 ± 1°C in water thermostat. Therefore, the weight losses given by:

$$\Delta W = W_1 - W_2 \quad (1)$$

where, W_1 and W_2 are the weights of metal before and after exposure to the corrosive solution, respectively. The percentage inhibition efficiency (IE %) and the degree of surface coverage (θ) of the investigated compounds was calculated from the following equations:

$$IE \% = [1 - (\Delta W_{inh} / \Delta W_{free})] \times 100 \tag{2}$$

$$\theta = [1 - (\Delta W_{inh} / \Delta W_{free})] \tag{3}$$

where, ΔW_{free} and ΔW_{inh} are the weight losses per unit area in the absence and presence of additives, respectively. The synergistic inhibition effect was evaluated using a parameter, S_θ , obtained from the surface coverage values (θ) of the anion, cation and both. Aramaki and Hackerman[15] calculated the synergism parameter S_θ using the following equation.

$$S_\theta = 1 - \theta_{1+2} / 1 - \theta'_{1+2} \tag{4}$$

where:

$$\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1\theta_2);$$

θ_1 = surface coverage by anion; θ_2 = surface coverage by cation;

θ'_{1+2} = measured surface coverage by both the anion and cation.

3. RESULTS AND DISCUSSION

3.1 Weight – loss measurements

Fig.(1): shows the effect of increasing concentrations of compound(I) on the weight loss of Zn vs. time curves at $30 \pm 1^\circ\text{C}$. Similar curves (not shown) were obtained for the other three compounds. It is obvious that the weight loss of Zn in presence of inhibitors varies linearly with time, and is much lower than that obtained in blank solution. The linearity obtained indicated the absence of insoluble surface film during corrosion and that the inhibitors were first adsorbed onto the metal surface [16].

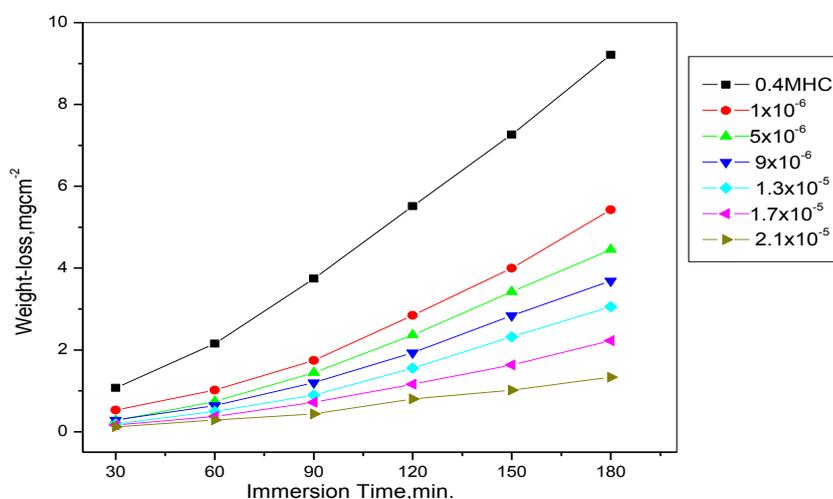


Figure 1. Weight-loss versus immersion time for Zinc in the absence and presence different concentrations of compound(I) at 30°C .

The calculated values of the percentage inhibition efficiency (I %) are listed in Table (1). Inspection of Table (1) reveals that, the inhibition efficiency increases with an increase in inhibitor concentration. This behavior could be attributed to the increase of the number of adsorbed molecules at the metal surface. At one and the same inhibitors concentration, I % decreases in the following order: (I) > (II) > (III) > (IV).

Table 1. Effect of inhibitors concentrations on the percentage inhibition efficiency (I %) of zinc in 0.4 M HCl solution from weight – loss method at $30 \pm 1 \text{ }^\circ\text{C}$.

[Inhibitor], M	% IE			
	(I)	(II)	(III)	(IV)
1×10^{-6}	53.4	38.1	30.0	28.2
5×10^{-6}	61.4	51.2	46.2	44.4
9×10^{-6}	68.0	58.8	56.1	55.7
1.3×10^{-5}	76.0	68.3	66.8	64.1
1.7×10^{-5}	80.8	79.4	78.6	74.1
2.1×10^{-5}	88.4	84.3	82.8	77.5

3.2 Synergistic effect

Figures.(2-4) represent the weight loss time curves for zinc dissolution in 0.4M HCl in the presence of 10^{-2} M of I, Br⁻, Cl⁻ and also in the presence of different concentrations of organic additives.

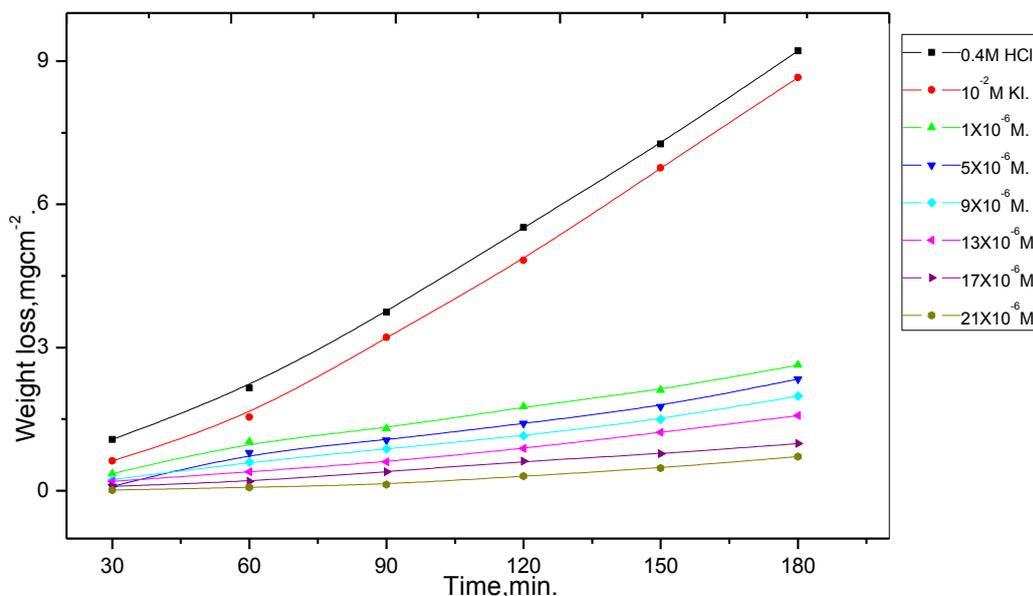


Figure 2. Weight loss-time curves for Zn in 0.4M HCl in absence and presence of different concentration of compound (I) without and with addition of 10^{-2} M KI at 30°C .

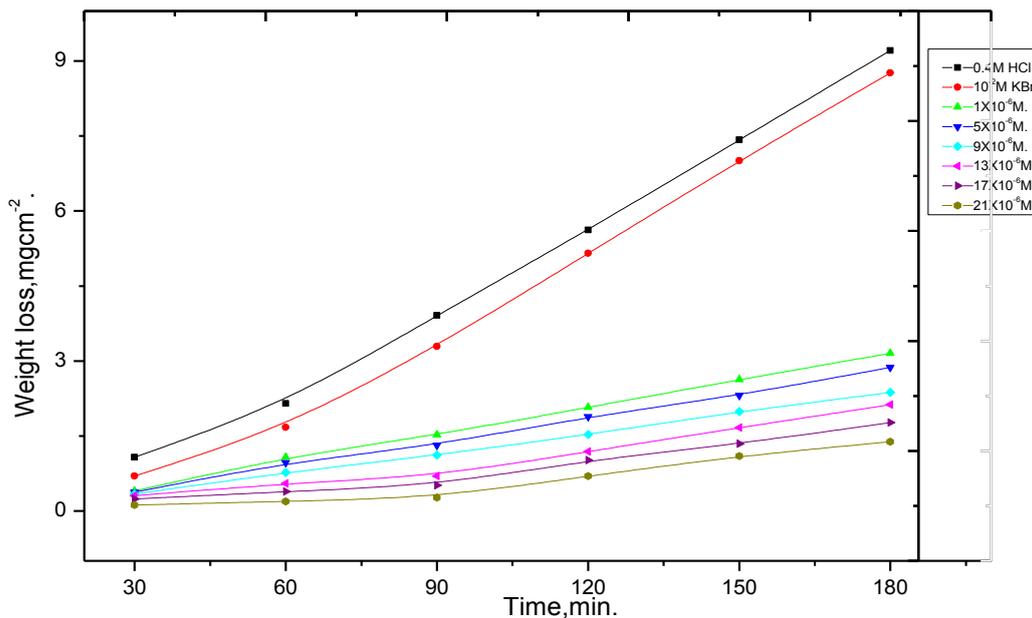


Figure 3. Weight loss-time curves for Zn in 0.4M HCl in absence and presence of different concentration of compound (I) without and with addition of 10⁻²M KBr at 30⁰c.

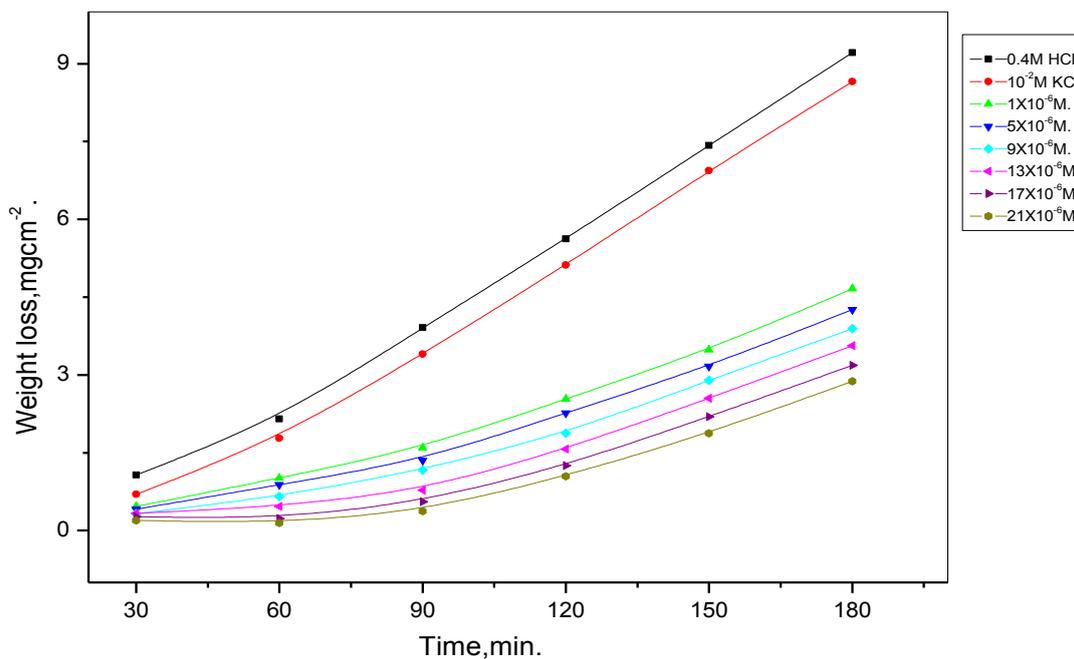


Figure 4. Weight loss-time curves for Zn in 0.4M HCl in absence and presence of different concentration of compound (I) without and with addition of 10⁻²M KCl at 30⁰C.

The calculated inhibition efficiency values (% IE) are shown in Tables (2-4). It is observed that % IE of the inhibitors increases on addition of these different anions due to synergistic effects[17]

The strong chemisorption of these anions on the metal surface is responsible for the synergistic effect of these ions in combination with cation of the inhibitor. The cation is then adsorbed by columbic attraction on the metal surface where these anions are already adsorbed by chemisorption. Stabilization of these adsorbed anions with cations leads to greater surface coverage and therefore, greater inhibition.

Table 2. Inhibition efficiency of all inhibitors at different concentrations of tetrahydrocarbazole derivatives in presence of 1×10^{-2} M KI after 90 min. immersion at 30 ± 1 °C

[Inhibitor] ,(M)	% IE			
	(I)	(II)	(III)	(IV)
1×10^{-6}	61.1	58.4	56.0	53.9
5×10^{-6}	68.5	64.9	62.2	60.5
9×10^{-6}	73.8	71.2	70.6	69.5
1.3×10^{-5}	81.9	80.5	78.1	75.7
1.7×10^{-5}	88.0	86.1	85.2	83.2
2.1×10^{-5}	96.1	93.2	91.6	90.1

Table 3. Inhibition efficiency of all inhibitors at different concentrations of tetrahydrocarbazole derivatives in presence of 1×10^{-2} M KBr after 90 min. immersion at 30 ± 1 °C.

[Inhibitor] ,(M)	% IE			
	(I)	(II)	(III)	(IV)
1×10^{-6}	58.3	57.0	53.9	52.7
5×10^{-6}	64.0	62.6	60.2	58.4
9×10^{-6}	69.4	67.7	67.6	66.3
1.3×10^{-5}	80.8	78.1	75.4	72.9
1.7×10^{-5}	86.0	84.1	82.2	80.6
2.1×10^{-5}	92.7	90.2	89.0	86.4

The calculated synergism parameters; S_{θ} are given in Tables.(5-7). It is seen that the values of S_{θ} are more than unity, thereby suggesting that the enhanced inhibition efficiency caused by the addition of anions to the inhibitors is due only to the synergistic effect.

Table 4. Inhibition efficiency of all inhibitors at different concentrations of tetrahydrocarbazole derivatives in presence of 1×10^{-2} M KCl after 90 min. immersion at 30 ± 1 °C.

[Inhibitor] (M)	IE%			
	(I)	(II)	(III)	(IV)
1×10^{-6}	55.8	53.6	52.4	42.0
5×10^{-6}	62.5	61.3	58.5	48.7
9×10^{-6}	67.8	65.5	61.7	57.6
1.3×10^{-5}	78.5	69.9	66.9	64.1
1.7×10^{-5}	84.7	75.8	74.8	73.5
2.1×10^{-5}	89.7	88.0	85.1	82.0

Table 5. Synergism parameter (S_0) for different concentrations of tetrahydrocarbazole derivatives with addition of 1×10^{-2} M KI at 30 ± 1 °C.

Corrosive medium	Synergism Parameter (S_0)						
	Conc.(M)	1×10^{-6}	5×10^{-6}	9×10^{-6}	1.3×10^{-5}	1.7×10^{-5}	2.1×10^{-5}
0.4 M HCl	(I)	1.19	1.22	1.22	1.32	1.60	2.95
	(II)	1.48	1.39	1.43	1.62	1.48	2.31
	(III)	1.59	1.42	1.49	1.51	1.44	2.05
	(IV)	1.55	1.40	1.45	1.47	1.54	2.27

Table 6. Synergism parameter (S_0) for different concentrations of tetrahydrocarbazole derivatives with addition of 1×10^{-2} M KBr at 30 ± 1 °C.

Corrosive medium	Synergism Parameter (S_0)						
	Conc.(M)	1×10^{-6}	5×10^{-6}	9×10^{-6}	1.3×10^{-5}	1.7×10^{-5}	2.1×10^{-5}
0.4 M HCl	(I)	1.11	1.07	1.04	1.25	1.37	1.59
	(II)	1.43	1.30	1.27	1.44	1.29	1.61
	(III)	1.51	1.35	1.35	1.34	1.20	1.56
	(IV)	1.51	1.33	1.31	1.32	1.33	1.65

Table 7. Synergism parameter (S_{θ}) for different concentrations of tetrahydrocarbazole derivatives with addition of 1×10^{-2} M KCl at $30 \pm 1^{\circ}\text{C}$.

Corrosive medium	Synergism Parameter (S_{θ})						
	Conc. (M)	1×10^{-6}	5×10^{-6}	9×10^{-6}	1.3×10^{-5}	1.7×10^{-5}	2.1×10^{-5}
0.4 M HCl	(I)	1.056	1.03	0.99	1.11	1.254	1.124
	(II)	1.335	1.26	1.19	1.051	0.849	1.308
	(III)	0.828	0.69	0.72	0.604	0.512	0.518
	(IV)	0.939	0.819	0.718	0.721	0.833	1.252

According to Schmitt and Bedbur [18], there are two types of the adsorption of cations and anions on the metal surface which are competitive and cooperative (Fig.5)[19]. In competitive adsorption the cations and anions are adsorbed at different sites on the electrodes surface, while in cooperative adsorption, the anions are chemisorbed on the metal surface and the cations are adsorbed by columbic attraction on a layer of anions. In our case, since Zn surface acquires negative charge in acidic solutions[20] and the investigated compounds are protonated in acidic media (acquire positive charge), we can conclude that, the inhibitors firstly adsorbed on Zn surface and the anions (I^{-} , Br^{-} , Cl^{-}) are adsorbed by coulombic attraction on a layer of cations. This process is similar to so-called phenomenon of anion induced adsorption. The data in Tables (5-7) indicated that this cooperative effect increased in the order: $\text{Cl}^{-} < \text{Br}^{-} < \text{I}^{-}$, suggesting a possible role by the radii of the halide ions which also increase in the order: Cl^{-} (0.09nm) < Br^{-} (0.114nm) < I^{-} (0.135nm)

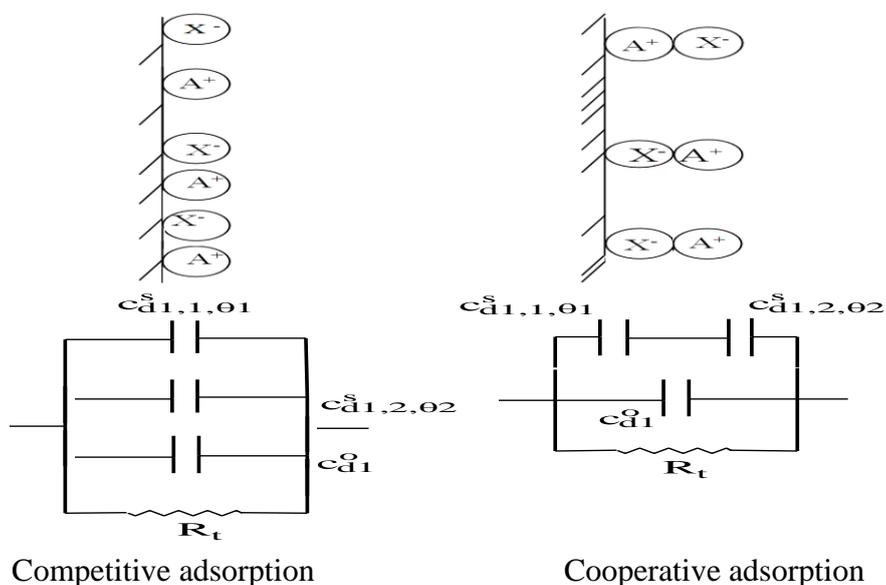


Figure 5. Schematic diagrams and equivalent circuits of competitive and cooperative adsorption of anions and cations.

3.3. Pitting corrosion of zinc

3.3.1 Effect of NaCl concentration

Pitting corrosion is an electrochemical process in which the pit act as a fixed anode and the remainder of the passive surface acts as cathode. The formation of a pit depends on number of factors including type and concentration of attacking (depassivating) anions, type of material present and relative concentration of other anions as well as temperature[21-23]. For pitting corrosion by halogen ion to effect the solution that should contain an oxidizing agent. The interesting feature of pitting corrosion of Zn electrode by halide ions in aqueous solution is that, it does not start directly after the presence of the metal in the corrosive medium but that, a certain time, so called induction period elapses before dissolution starts. The time decreases as the concentration of the depassivation anion increases [24,25]. Pitting corrosion does not occur unless the potential of the working electrode surpasses a certain definite value, normally known as the (break through) or critical potential [26]. The value of this potential depends on the type materials halide concentration and the presence of other anions [27]. The value of the pitting potential or induction period can be taken as a measure of the resistance of protective film towards corrosion. The critical pitting potential always define as the potential below which the metal surface remains passive and above which pits nucleate and develop. The potential for most metal and alloys shift to negative direction as the concentration of the aggressive halogen ion increases[28]. Pitting corrosion of zinc as other metals and alloys occurs when passivity breakdown takes place at local points on the surface exposed to the corrosive environments at which anodic dissolution proceed, whilst the major part of the surface remain passive. Two basic conditions must be fulfilled for the initiation and propagation of pitting corrosion. The major part is that the metal surface should be covered with an electronically conducting, passivating, inhibiting film on which the cathodic partial reaction takes place. This film can be formed naturally, or be produced through alloying with an appropriate metal or by oxidizing agents with redox potentials equal to, or higher than, the corresponding Flade potential and / or by anodic protection. Secondly, the medium should contain an aggressive agent. Chloride ion is the most dangerous pitting agent and for this reason pitting corrosion is sometimes referred to as "Chloride-corrosion". Figure (6) represents the potentiodynamic anodic polarization curves of zinc electrode in different concentrations of NaCl solution at a scanning rate 1mV/sec. The slow scan rate permits that the pitting initiation occurs at less potential[29]. It is clear that from this figure that, the higher Cl^- ion concentration results in a sudden and marked increase of current density at same definite potential denoting the destruction of the passive film and initiation of visible pits. The higher concentration of Cl^- ion, the higher is the shift of pitting potential to active direction. Examination of the electrode surface after polarization experiments showed visible pits whose number per unit area increases with the increase Cl^- ion content of the solution. Also, the increase in Cl^- ion concentration shifts the critical pitting potential into negative (active) direction. This effect could be attributed to adsorption of aggressive anion on the bare metal surface.

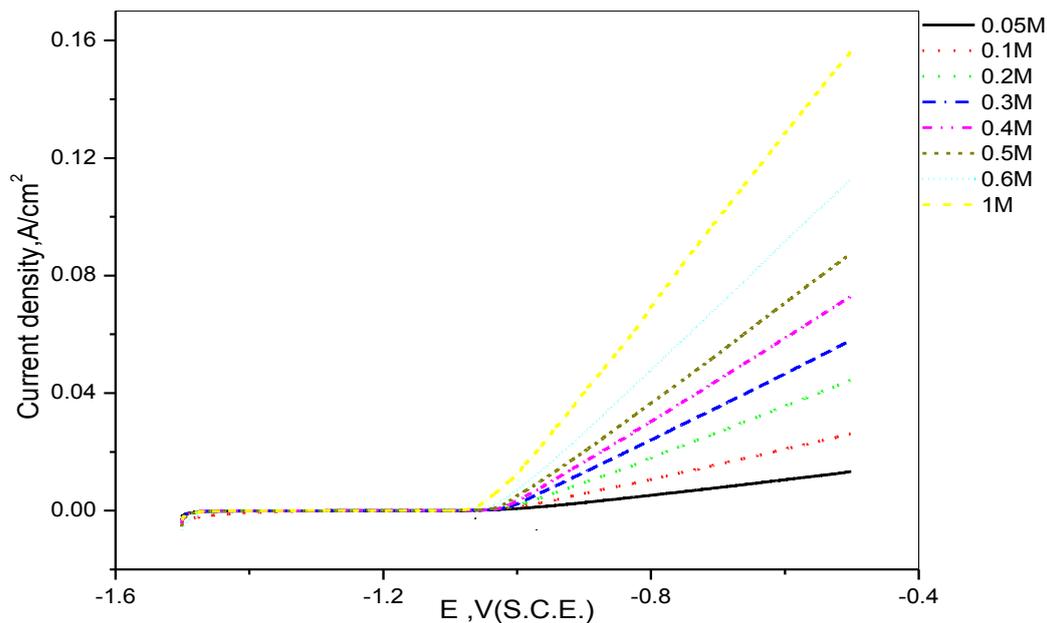


Figure 6. Potentiodynamic anodic polarization curves of zinc electrode in different concentrations of NaCl solution at scan rate 1mVs^{-1} and 30°C .

The dependence of the pitting corrosion potential of zinc electrode on chloride ions concentrations can be clearly seen in Fig.(7). This figure represents the plot of pitting potential E_{pitt} . Vs. the logarithm of chloride ion concentration. Straight line relationship was obtained satisfying the following equation:

$$E_{\text{pit.}} = a_1 - b_1 \log C_{\text{Cl}^-} \tag{5}$$

where a_1 and b_1 are constants which depend on both the nature of the electrode and type of aggressive anions. As the concentration of chloride ions increases the pitting potential is shifted to more negative direction indicating the destruction of passive film and initiation of pitting corrosion. It seems likely that in the presence of halide ions (Cl^-) in the solution, the high specific adsorbabilities of these anions[30] imply a competitive adsorption at the metal surface level between these anions and OH^- ion which is essential for zinc dissolution and formation of ZnO film. On the basis of this assumption, it is possible that the adsorbed X^- ions can participate directly and reacts with zinc atoms leading to the formation of the soluble ZnX_4^{-2} complexes [31] according to the overall reaction:



Therefore, it can be concluded that, the charges consumed through the anodic peak correspond to the electro formation of both ZnO and ZnX_4^{-2} .

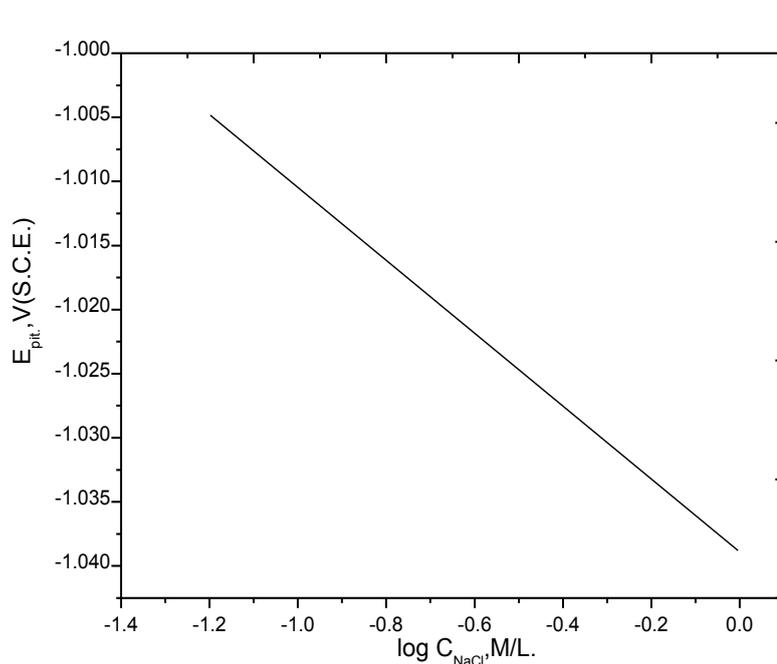


Figure 7. The linear dependence of E_{pit} vs. $\log C_{NaCl}$ for Zn at scan rate 1mvs^{-1} and 30°C .

3.3.2 Effect of scanning rate

Fig.(8) shows the effect of increasing scanning rate on the potentiodynamic anodic polarization of zinc electrode in 0.1 M NaCl at $30\pm 1^{\circ}\text{C}$. It is clear that by increasing the scanning rate (v) the values of pitting potential (E_{pit}) shifts to more positive direction. Such behavior can be explained [32] in terms of incubation time (the time required for X^{-} to penetrate the passive ZnO film). When scan rate is high, an initiation of passivity breakdown can be noticed only at more positive potential corresponding to a sufficiently short pit incubation time.

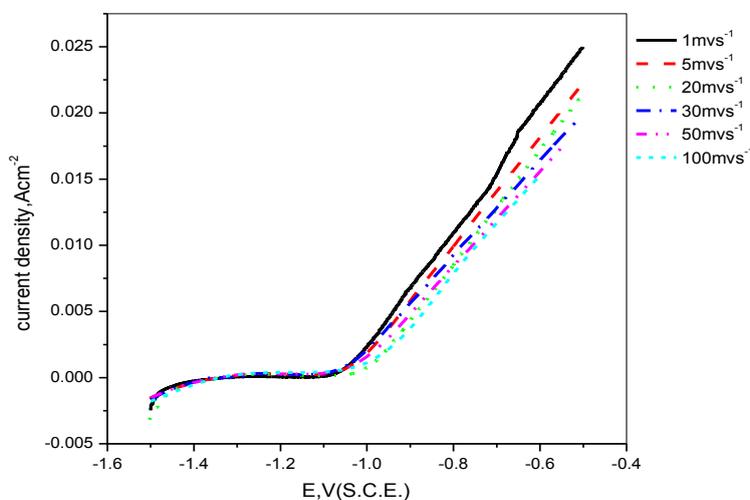


Figure 8. Potentiodynamic anodic curves for Zn in 0.1 M NaCl at different scan rate at 30°C .

Fig.(9) represents the relationship between E_{pit} and $v^{1/2}$. Straight line relationship was obtained accordance with the following equation :

$$E_{pit} = a_2 + b_2 v^{1/2} \tag{7}$$

Where, a_2 and b_2 are constants depending on the nature of metal used. This suggests that the active dissolution process of Zn electrode in diffusion control.

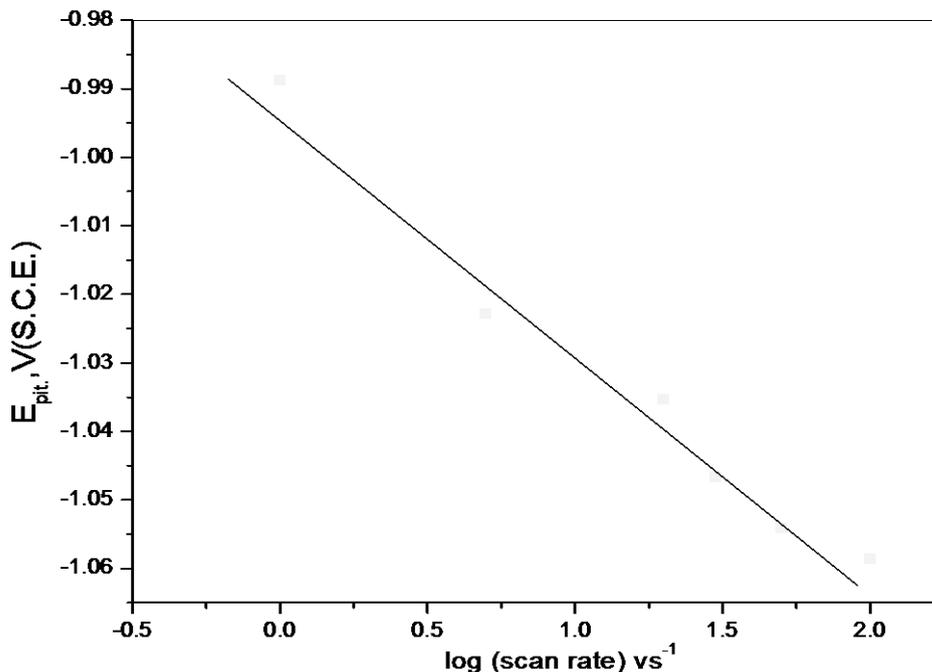


Figure 9. The linear dependence of E_{pit} vs. $\log(\text{scan rate})$ for Zn in 0.1M NaCl at 30°C.

3.3.3. Effect of addition of tetrahydrocarbazole derivatives on the potentiodynamic anodic polarization curves of zinc electrode in 0.1M NaCl.

The primary step in the action of corrosion inhibitor in neutral solution usually is the adsorption of inhibitors on the metal surface [33]. The adsorption process depends upon electronic characteristic of the inhibitor, the nature of surface, temperature, steric effect, multilayer adsorption and the degree of surface activity. Figure (10) represent the effect of different concentrations of inhibitor (I) (5×10^{-6} , 9×10^{-6} , 1.3×10^{-5} , 1.7×10^{-5} and 2.1×10^{-5} M), on the potentiodynamic anodic polarization curves of zinc electrode in 0.1 M NaCl at a scanning rate 1mV/sec, and at $30 \pm 1^\circ\text{C}$. It was found that the pitting potential of zinc electrode is shifted to more positive (noble) direction with increasing the concentration of additives. This indicates that increased resistance to pitting attack.

Fig.(11) shows the relationship between pitting potential; E_{pit} and logarithm of molar concentration of the added compounds. Straight line relationship was obtained and the following conclusions can be drawn:

i) The increase of inhibitor concentration causes the shift of pitting potential into more positive values in accordance with the following equation:

$$E_{pit} = a_3 + b_3 \log C_{inh}. \tag{8}$$

where, a_3 and b_3 are constants which depend on both the composition of additives and the nature of the electrode.

ii) Inhibition afforded by these compound using the same different concentrations of the additives decreases in the following order: (I) > (II) > (III) > (IV)

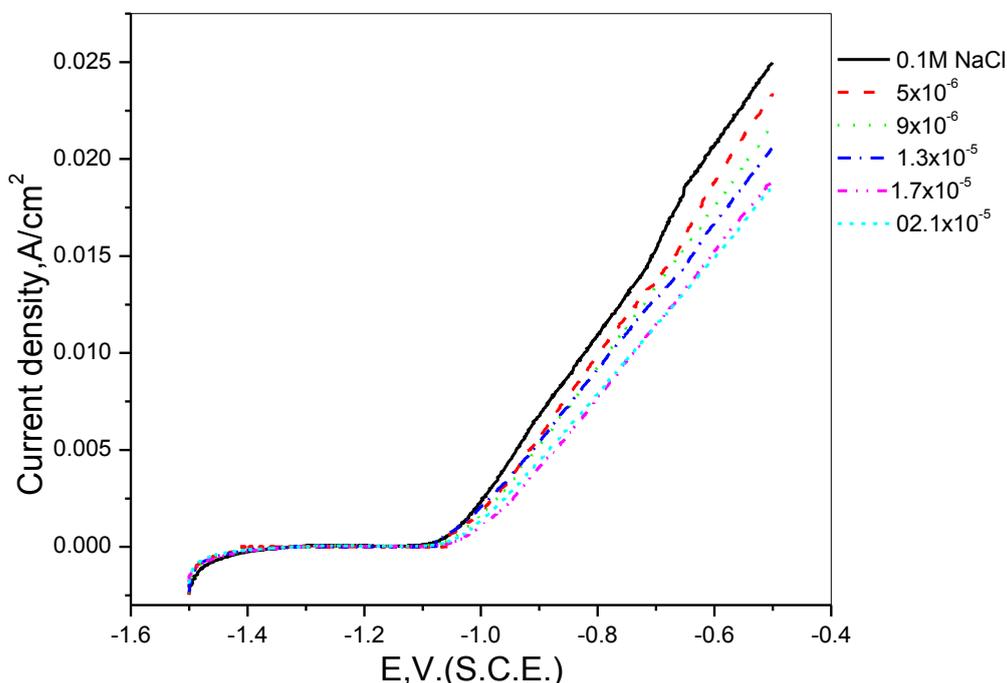


Figure 10. Potentiodynamic anodic curves for zinc in 0.1M NaCl in the absence and presence of different concentrations of compound (I) at 30°C and scan rate 1mVs⁻¹.

The shift of pitting potential of zinc electrode into the noble (positive) direction upon addition of increased concentrations of derivatives could be explained in view of the oxide film theory of passivity proposed by Hoar, et., al.,[34]. According to this theory inhibitors are adsorbed on the active sites of the oxide through which Cl⁻ ions would otherwise penetrate the oxide film, causing pitting. In this way the inhibitor contaminates the oxide and making it more conductors, thereby favoring oxide growth and pitting inhibition. In another explanation one can also, attribute the inhibiting action of these anions to their low polarizability. These anions are expected to concentrate in the diffuse part of the double layer and inhibit pitting corrosion through the reduction of the zeta potential at the oxide film solution interface. This reduces in turn the potential field and retards the electrochemisorption of the Cl⁻ ions from the solution on the oxide film.

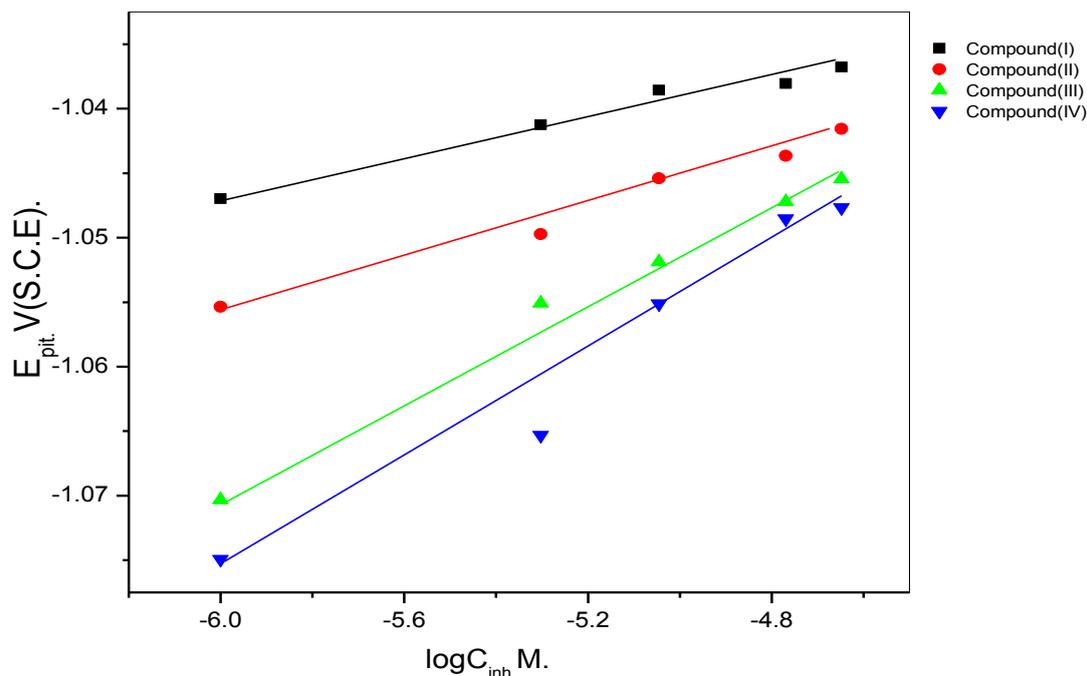


Figure 11. The linear dependence of $E_{pit.}$ vs. $\log C_{inh.}$ for Zn in 0.1M NaCl at scan rate 1mvs^{-1} and 30°C

Two major effects seem to be possible for the inhibition of pitting corrosion. First is the competitive adsorption between aggressive and inhibitive compounds. The adsorption of the latter ions predominates and the electrode will be protected. In this case, the pitting corrosion potential is shifted into the anodic direction. This mechanism seems to be the most effective way to avoid pitting corrosion. A second way is related to the incorporation of the inhibitive molecules into the passive layer on the metal surface forming an improved stability against the aggressive ions. Once, when pitting corrosion has been started, the inhibitor can be adsorbed within the pits preventing active metal dissolution. As shown from the figures, the order of decreasing $E_{pit.}$ of Zn in the presence of the investigated compounds is in agreement with the order of decreasing % IE of these compounds, obtained from weight loss and potentiodynamic polarization measurements. This sequence is in accordance with that obtained from weight-loss measurements.

3.4. Quantum Chemical Studies (Computational Study)

Quantum chemical calculations have been widely used to study the reaction mechanisms and to interpret the experimental results as well as to solve chemical ambiguities. This is a useful approach to investigate the reaction mechanisms of the inhibitor molecule and the metal surface. The structural and electronic parameters of the inhibitor molecules can be obtained by means of theoretical calculations using the computational methodologies of quantum chemistry[35]. Pearson introduced the quantities of electronic hardness (η) and softness (σ) in his hard-soft-acid-base principle[36] (HSAB) in the early stage of the reactivity theory. The species

are classified as soft (hard) if their valence electrons are easy (hard) to polarize or to remove and the relationship between hardness or softness and the chemical reactivity was given through the HSAB principle, A soft base will interact favorably with a soft acid, sharing electrons, to form bonds of covalent character. Hard acids prefer hard bases and form bonds dominated by electrostatic forces or ionic character as shown in Fig. (12). The concepts of electro negativity (χ) [37] and global hardness (η) [38,39] are given by:

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{v(r)} \tag{9}$$

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{v(r)} = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_{v(r)} \tag{10}$$

where μ is the chemical potential, E is the total energy, N is the number of electrons, and $v(\vec{r})$ is the external potential of the system.

The global hardness (η), softness (σ), and chemical potential (μ) were calculated in terms of I_P and E_A from the following equations:

$$\eta = \frac{I_P - E_A}{2} \tag{11}$$

$$\sigma = \frac{1}{\eta} = \frac{2}{I_P - E_A} \tag{12}$$

$$\mu = -\frac{I_P + E_A}{2} \tag{13}$$

Where I_P is the ionization potential and E_A is the electron affinity.

Geometric and electronic structures of the inhibitors were calculated by optimization of their bond lengths and bond angles. The optimized molecular structures of the inhibitors are given in Fig. (12).

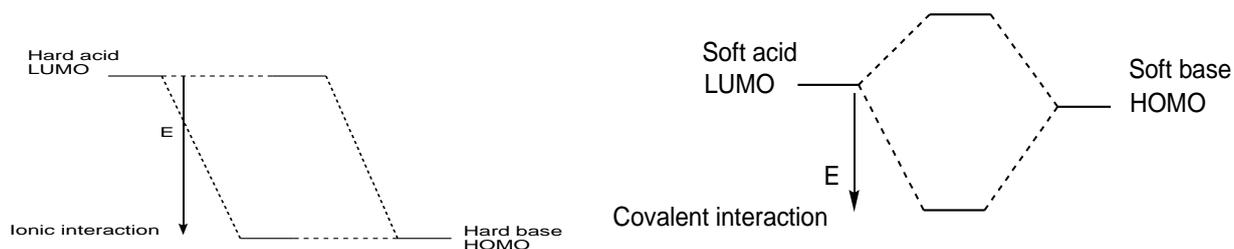


Figure 12. HSAB Principle- Molecular Orbital Theory.

Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies, (LUMO – HOMO) energy gap ΔE and dipole moment, μ are given in Table (8). It clear that the value of electro negativity charges of O_{10} and O_{11} , which connect to the donating electrons, were irrelevant to the inhibition efficiency. These results suggested that the adsorption might not be attributed to the chemical bond between the electronegative atoms and the metal surface. The dipole of the inhibitors changed irregularly, which provide that the adsorptions might not be arisen from intermolecular electrostatic force.

Table 8. Quantum chemical parameters for the investigated tetrahydrocarbazole derivatives by MNDO

MNDO liquid phase	$E_{\text{Homo}}(\text{eV})$	$E_{\text{Lumo}}(\text{eV})$	$\Delta E(\text{eV})$	μ (D)
Compound(I)	8.780	1.306	7.474	3.531
Compound(II)	8.786	1.239	7.547	3.597
Compound(III)	8.789	1.196	7.593	5.162
Compound(IV)	8.805	1.379	7.426	5.281

Highest occupied molecular orbital energy (E_{HOMO}) and lowest unoccupied molecular orbital energy (E_{LUMO}) are very popular quantum chemical parameters and were shown in Fig. (14) and these orbitals also called frontier orbitals. It had reported that the E_{HOMO} often associated with the electron donating ability of the molecule. High value of E_{HOMO} indicate a tendency of the molecule to donate electrons to act with acceptor molecules with low- energy, empty molecular orbital. According to Wang et al[40],the high values of the E_{HOMO} facilitate adsorption and hence inhibition efficiency by influencing the transport process through the adsorbed layer. The E_{HOMO} values decrease in the order (I) > (II) > (III) > (IV). Large values of energy gap (ΔE) implies increased electron stability and low reactivity, while low values reader good inhibiting efficiency , because energy to remove an electron from the last occupied orbital will below (Delley,1990) . The inhibitor energy gap increases in the order (I) > (II) > (III) > (IV), indicating that least stable molecule is the strongest inhibitor. Similarly, the E_{LUMO} represents the ability of the molecule to accept electrons. The lower value of E_{LUMO} suggests the molecule accepts electrons more probable [41, 42].From Fig. (13), we can see that the electron density of the frontier orbital is well proportioned. Table (8) is showed that the ΔE decreased with increasing the inhibition efficiency, it indicates that the more unstable of the inhibitors, the stronger interaction between the inhibitors and the meta l surface. Thus, the interactions are between the inhibitors and the metal surface might be ascribed to the hyper conjugation interactions – π stacking.

Figure (13) shows the Mullikan charges on oxygen and nitrogen atoms present in inhibitors molecules. Where Mullikan population analysis [44] is mostly used for the calculation of the charge distribution in a molecule. These numerical quantities are easy to obtain and they provide at least a qualitative understanding of the structure and reactivity of molecules. Furthermore, atomic charges are used for the description of the molecular polarity of molecules. Figure (14), we present the optimized structures and the HOMO and LUMO diagrams of investigated compounds obtained by MNDO. The spatial distribution of the HOMO and the LUMO are important for understanding the adsorption[43].

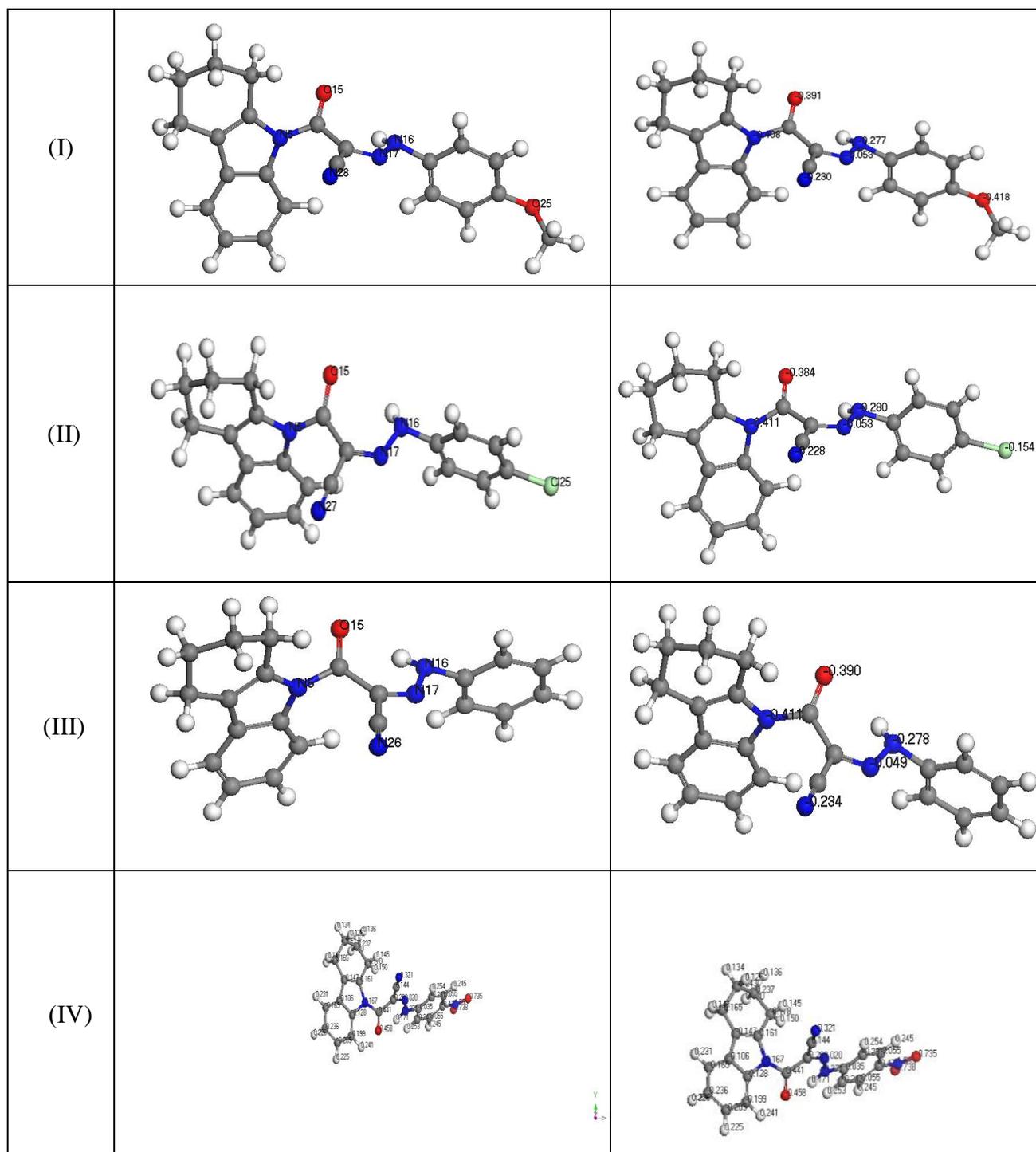


Figure 13. Mullikan atomic charges of investigated inhibitors (I – IV) preferences of the inhibitors.

Considering that the inhibitors would be electron donors with respect to the Zn surface, the HOMO distribution would be of particular importance. The HOMO distribution maps of investigated inhibitors are very similar and show location near tetrahydrocarbazole site, suggesting that these sites could be involved in adsorption. The LUMOs of all four inhibitors have very similar spatial distribution. The dipole moment (μ) is another indicator of the electronic distribution in a molecule and is one of the properties used to discuss and to rationalize the structure. Although, there is a lack of

agreement in the literature on the correlation between the dipole moment and inhibition efficiency[45,46] the comparison between the calculated dipole moment of compound (I) and compound (IV) reveals that the lowest { compound(I) molecule} has better inhibition efficiency.

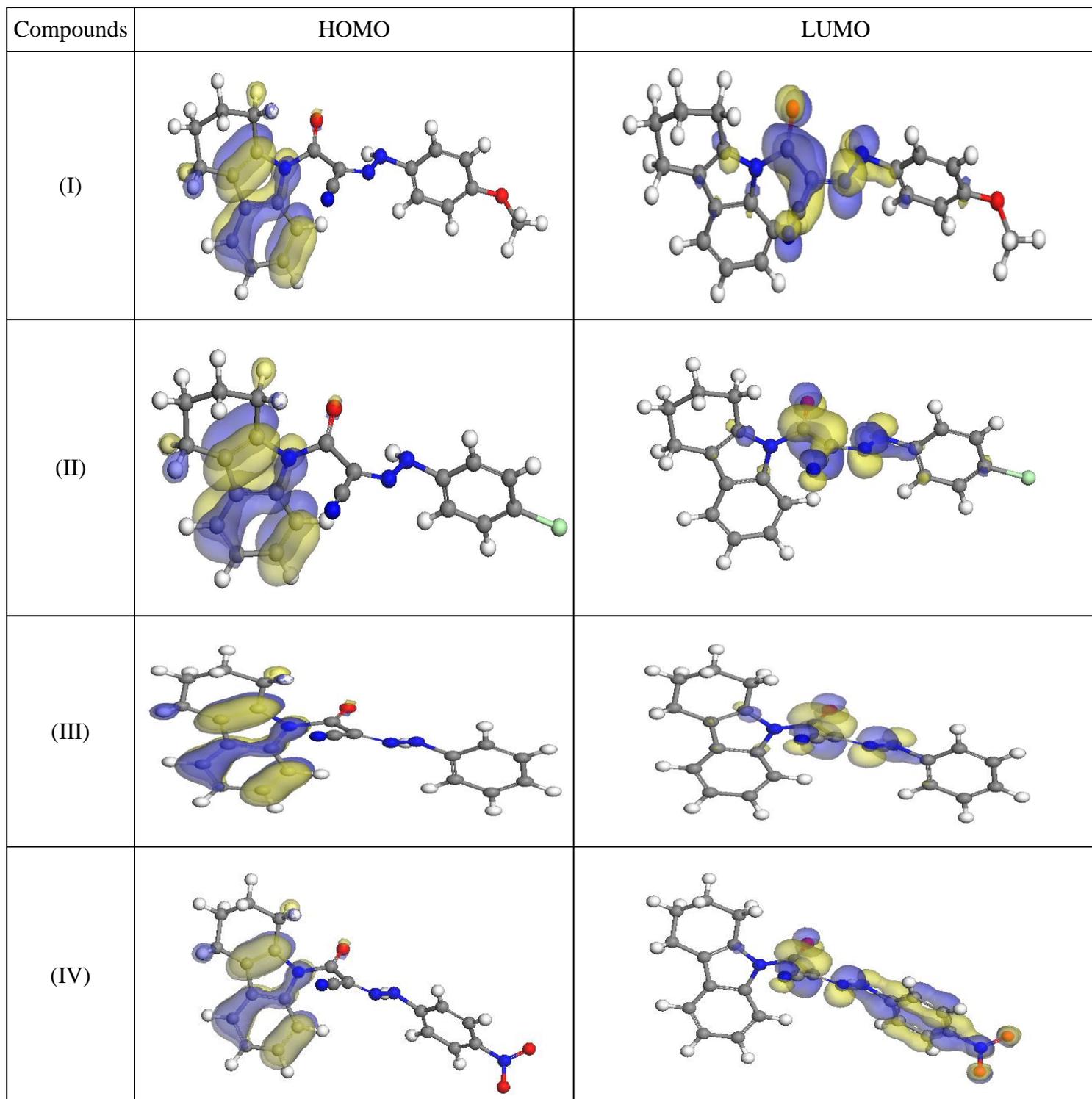


Figure 14. The frontier molecular orbital density distribution of the investigated compounds (HOMO and LUMO).

4. CONCLUSIONS

- 1-The tetrahydrocarbazole derivatives are considered as corrosion inhibitors for zinc in 0.4 M HCl act as efficient inhibitor. The inhibition efficiency increases with the increase of inhibitor concentration.
- 2-The addition of KI, KCl and KBr to these compounds improve the values of inhibition efficiency due to synergistic effect
- 3-The inhibitive effect is due to the adsorption of the inhibitor molecule on the zinc surface
- 4-The adsorption process follows Langmuir isotherm.
- 5- Tetrahydrocarbazole derivatives provide protection against pitting corrosion of zinc in presence of chloride ions by shifting the pitting potential into positive direction.
- 6-The values of inhibition efficiencies calculated using weight loss, potentiodynamic anodic polarization and quantum chemical calculation were in good agreement.

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