INHIBITION OF IRON CORROSION USING TWO NEWLY SYNTHESIZED SCHIFF BASE COMPLEXES IN ETHANOLIC HYDROCHLORIC ACID MEDIA

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Abstract

Two different Schiff base complexes were tested as corrosion inhibitors for iron in hydrochloric acid medium (prepared in ethanol) at different temperatures using potentiodynamic polarization measurements. The obtained results reveal that increasing HCl concentration at 35°C increased the anodic and cathodic current density values. Moreover, anodic current density peak was observed at concentrations >1M HCl. However, the magnitude of corrosion rate C_R in presence of complexes is suppressed as its tendency to increase with acid concentration. On the other hand, the values of corrosion potentials (around −300 mV(SCE)) were not affected by the addition of any complex. The inhibition efficiency values increase with an increase in complex concentrations in which Hg- complex achieves higher protection efficiency than Zn-complex. The adsorption processes follow the Langmuir isotherm. Concerning the effect of temperature, results demonstrate that increasing the temperature leads to an increase in the corrosion rate of iron and a decrease in the inhibition efficiencies of the complexes. The rise in activation energy E_a values in presence of the complexes explains the corrosion inhibition obtained through physical adsorption. Also, higher ΔH° values indicate higher protection efficiency. ΔS° has negative value for the blank and the complexes solutions indicating that the system passes from a more to a less orderly arrangement.

Introduction

Organic solvents cause quite important modifications of corrosion phenomena on metallic materials. Due to environmental concerns, the use of alcohol of all kinds as an automotive fuel in engine industry is increasing. So that, it is very important to investigate the corrosion of iron in alcohol solutions [1], as well as ways to prevent it. Previous workers have used furfural [2], octynol and propynol[3] as corrosion inhibitors of iron in ethanol. The mechanism of dissolution of metals in organic solvents is still not completely known [4]. Iron corrosion studies in organic solvents of some glycols, methanol and ethanol [5-8] showed that dissolution mechanism of iron is similar to that one in pure acidic aqueous solutions if the relative amount of water in the medium was taking into account. The kinetics of the oxidation reactions, are a function of the specific alcohol. This has been interpreted in terms of the different protic and stereo chemistry properties of the alcohols considered [9]. The

situation is more complex when the solvent is an organic compound, comparatively to pure aqueous environments. This is not only due to the different electric and bond interaction between the metal and solvent, but also because of the physicochemical properties of the solvent itself, i.e., its dielectric constant, dipole moment, dynamic viscosity, electrical conductivity, protic nature of the solvent, etc, that have a direct effect on the ionic transport process at the metal electrode [8].

The use of inorganic inhibitors in acid solutions is a very common way in metals protection. Some Schiff base compounds have recently been reported as effective corrosion inhibitors for mild steel, aluminum, copper, and zinc in acid media [10-14]. Due to the presence of the >C=N group in the Schiff base molecules, they should be good corrosion inhibitors [15]. The difference in the efficiency of inhibitors against corrosion might be due to π -electron and donating electron group such as Cl^- and CH_3 [16]. On the other hand, the surface adsorption of the Schiff bases has led to a decrease in the double layer capacitance and to an increase in polarization resistance [17].

Acid media were widely used in the industry and it is very important to study basic aspect concerning the relationship among type of metal, molecular structure of the inhibitors and its adsorption and protection against corrosion in this media.

This paper is to throw some lights on the ability of two different Schiff base complexes to inhibit the corrosion processes of iron in ethanolic HCl solutions.

Experimental

The specimen of iron (99.99% purity, Alfa Ventron) with 1.643 cm^2 exposed area was made of massive cylindrical rod mounted into glass tube by epoxy resin. A copper wire was employed for an electrical contact. The iron surface was polished mechanically using emery papers of Grade Nos. 220, 400, 600, 800 and 1200, washed thoroughly with distilled water and degreased with acetone. Then, it was immersed in the acid solution.

Two coordinated compounds of the transition metal ions; Zn^{+2} and Hg^{+2} with Schiff base ligand derived from thiophene 2- carboxaldehyde and 4-aminoantipyrine have been synthesized [18] and tested as inhibitors for iron electrode. The solid compounds of Schiff base ligand were dissolved in different concentrations of HCl (1 to 5M) prepared in ethanol. The effects of inhibitor concentration were studied within the concentration range of 10^{-6} to 10^{-2} M for both inhibitors in 1M HCl solution. 4 and 2 mmol of Zn- and Hg- complexes respectively

was used to study the effect of HCl concentration on the inhibition efficiency. The effect of temperature was applied on 4mmol of each complex dissolved in 0.1MHCl. All solutions were prepared using pure ethanol (99% ethanol, 1% water with conductivity of 42.37 µS/cm).The aggressive solution of HCl was prepared by dilution of AR grade HCl (35.4%, density 1.18 g/cm^3) in ethanol.

Figure (1) gives the preparation equation of Schiff base ligand while the chemical structures of the investigated inhibitor compounds are shown in Figure (2). The physical and analytical data of prepared complexes are demonstrated in Table (1).

Table 1: The physical and analytical data of prepared Schiff's bases complexes

Complexes	Formula	Molecular Mass g/mol	Melting Point °C	Geometry	Molar conductance $\Omega^{-1}cm^2mol^{-1}$
Zn- complex	[ZnLBr]Br.½H$_2$O	531.61	>300	Square planar	65
Hg- complex	[Hg(L)$_2$(Br)$_2$]	955.21	177	Octahedral	11.6

L: Schiff base ligand: C$_{16}$ H$_{15}$N$_3$OS   Mwt = 297.41 g/mol
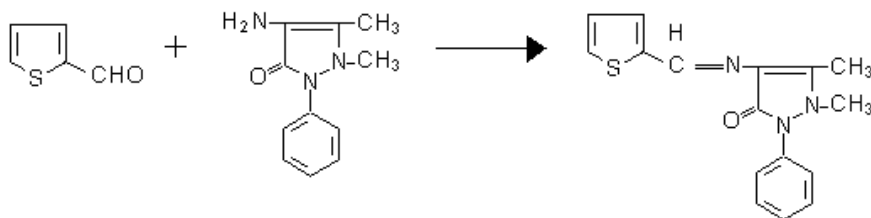
.Figure (1): The preparation equation of Schiff base ligand (L) used
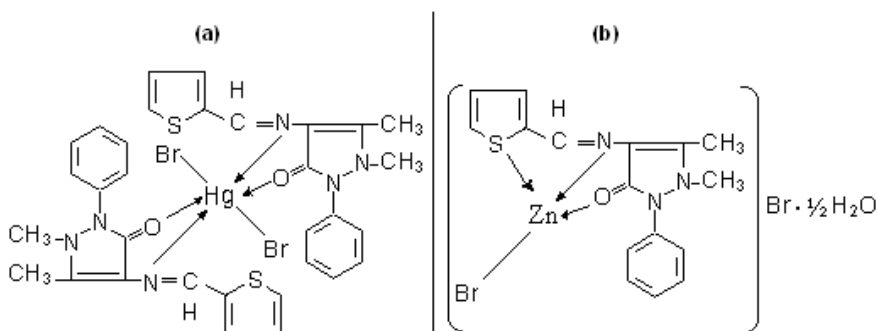
Figure (2): Schematic representation of studied metal complexes of Schiff base ligand(L),
(a) Hg- complex   and   (b) Zn- complex.

Potentiodynamic polarization measurements were performed using an instrument Wenking Electronic Potentioscan (model 73) with the aid of a double– walled glass cell (30 ml solution) containing three openings for electrodes. A saturated calomel electrode (SCE) provided with a Luggin capillary probe and a platinum sheet (4cm^2) were used as the reference and the counter electrodes, respectively. The liquid junction potential was not taken in account since the experiments were performed comparatively in absence and in presence of the corrosion inhibitor. As the experiments were performed in short time interval the reference electrode was immersed directly into the alcoholic solutions. This strategy was necessary in order to get diagrams without noise from the equipment. The E/ Log I curves for all solutions were swept from negative to positive potential at scan rate of 10mV/sec. The potential range was chosen to obtain the reduction and oxidation processes of the metal during the potential sweeps. The potentiodynamic curves were recorded after keeping the electrode polarized for 30 sec. at the initial potential. The inhibition efficiency, IE (%), was calculated from the following equation [19]:

$$ IE \% = \left[1 \; - \; \frac{I_{corr}}{I^{o}_{corr}} \right] \times 100 \quad (1) $$

where $\tilde{I}_{corr}$ and I_{corr} are the corrosion current densities obtained in uninhibited and inhibited solutions. While the corrosion current density is converted to a corrosion rate by using the equation [20]:

$$ C_R = 0.13 \; I_{corr} \; e/\rho \qquad (2) $$

where C_R is the corrosion rate in mmpy, I_{corr} is the corrosion current density in mAcm^{-2}, e is the equivalent weight of metal in g/ mol, and ρ is the density of metal in gcm^{-3}. The results are quite reproducible and the indicated results are the mean of four experiments.

Results And Discussion
1- Effect of HCl concentration
1-1- Effect of free HCl concentration on the corrosion of iron electrode

When the electrode potential changed from −1.5 to +1.0 V(SCE), anodic current density peaks were observed at concentrations >1M HCl (Figure 3- a). These peaks represent the charge transfer processes associated with the oxidation of the anode surface which is probably due to the compositional change of the oxide film on the electrode surface [21]. Increasing the concentration of HCl in ethanol at 35°C

increased the anodic and cathodic current density values associated with the electrooxidation and evolution of hydrogen on the metal. Consequently, the corrosion rates increase with increasing acid concentration (Figure 3- b). The corrosion potentials were negligibly shifted to more negative values.

It is probable that ethanolic HCl can form soluble products with iron and tend to stimulate the dissolution of metal as Fe^{+2}. This behavior is similar to that of carbon steel in cyclohexane propionic acid[22-24]. The Potentiodynamic behavior of iron in ethanolic HCl is to some extent similar to that in aqueous HCl solutions [25]. According to Heitz [26], ethanol is protic medium capable of sustaining electron transfer and ionization of the hydrogen atom. Therefore, in most cases, corrosion processes and galvanic interactions would be expected to be thermodynamically similar in water, methanol and ethanol.
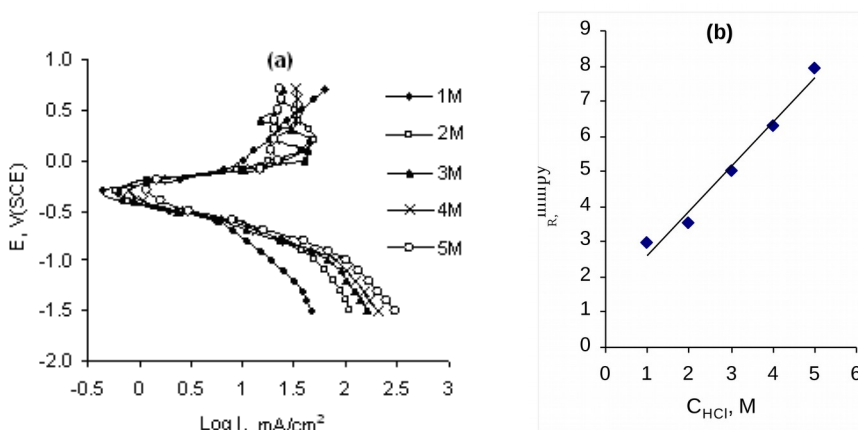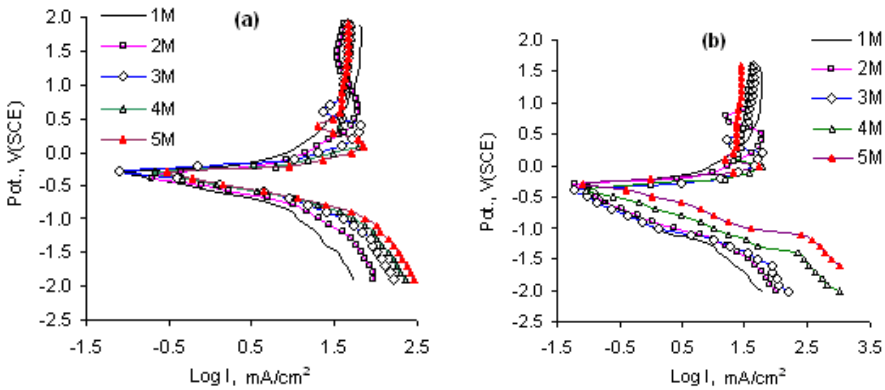

Figure (3): **(a) E– Log I curves of iron electrode in different concentrations of ethanolic HCl acid solutions,**

(b) Variation of corrosion rate of iron electrode with different concentrations of ethanolic HCl at 35 °C.

### 1-2- *Effect of HCl concentration on the inhibition efficiency of complexes on the corrosion of ironelectrode*

The potentiodynamic behavior of iron in presence of Hg- and Zn- complexes is similar to that in uninhibited ethanolic HCl solutions. The anodic peaks were observed at 0.4 and 0.2V(SCE) for 2 and 3M HCl and at zero potential for 4 and 5M in presence of 2mmol Hg- complex. Also, at 0.7and 0.4V(SCE) at 2and 3 M

HCl and at 0.1V(SCE) for 4 and 5 M in presence of 4mmol Zn- complex (Figure 4). The positivity of peaks potential decrease with increasing HCl concentration in which Zn- complex achieves higher values in all concentrations than Hg- complex. In organic media, corrosion phenomena should be linked to physicochemical parameters of these media such as dielectric constant, viscosity or acidity [5,7]. The inhibitory effect of tested compounds could be attributed to the adsorption of the Square planar (1:1) electrolyte Zn- complex and the octahedral non electrolyte Hg- complex over the iron surface via the free adsorption centers in the compounds.


Figure(4):E-Logi polarization curves of Fe elect rode in the two complexes soluble in different concentrations of ethanolic HCl solutions. (a) 4mmol Zn –complex, (b) 2mmol Hg- complex.

The reaction from the first step of the corrosion process of iron in HCl solution with inhibitor is:

$$\text{Fe} + \text{Inh} \leftrightarrow \text{Fe(Inh)}_{ads} \leftrightarrow \text{Fe}^{n+} + ne^- + \text{Inh} \qquad (3)$$
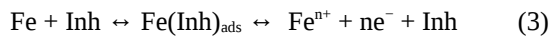
At first, when there is not enough Fe(Inh)$_{ads}$ to cover the metal surface, (because the inhibitor concentration is low or because the adsorption rate is slow) metal dissolution takes place on sites on the iron surface free of Fe(Inh)$_{ads}$. With high inhibitor concentrations, a compact and coherent inhibitor layer is formed on iron that reduces chemical attacks of the metal [20]. On the contrary, with high acid concentration, the reverse was observed. The effect of acid concentration on the inhibition efficiency of complexes was investigated and presented in Figure (5).

Figure (5): Effect of HCl concentration on the inhibition efficiency of 2mmol Hg- and 4mmol Zn- complexes for iron electrode at 35°C.
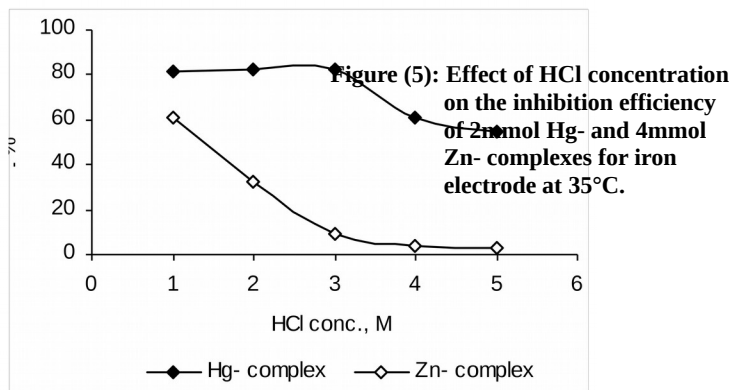
Apparently, the adsorption between the surface atoms of the iron metal and the Hg- complex is strong at concentrations up to 3MHCl thus inhibiting the oxidation process. At high concentration levels of acid, the adsorbed complex ions could be expected to be desorbed by the retardation action of Cl⁻ ions. Adsorbed Zn- complex is not as strong as adsorbed Hg- complex. This may be due to increasing number of the attached ligands in Hg- complex, consequently, the electronic charge density on the Hg atom in the complex will increase, and the greater will be the forces of attraction and hence inhibition.

The following rate equation was set up to describe the relationship between the natural logarithm of the corrosion rate (C_R) of complexes versus the molar concentration of HCl [27].

$$\ln C_R = \ln k + BC \qquad (4)$$

Where k, is the specific reaction rate constant, B, is a constant for a reaction and C, is the molar concentration of the acid.

In the presence of the complexes, the magnitude of C_R is suppressed as its tendency to increase with acid concentration (Figure 6). Such effect of HCl concentration can be explained by the stronger chemisorptions of Cl⁻ ions on the electrode surface, facilitating dissolution of iron metal [28]. The greater increase in C_R observed above 3M HCl in the presence of Hg- complex may be due to interaction of Cl⁻ ions with the adsorbed film to produce a less protective film than that observed at lower HCl concentrations [29]. Calculated kinetic parameters of equation (4) are listed in Table (2).

Figure (6): Variation of ln C_R with concentration of HCl in absence and presence of 2mmol Hg- and 4mmol Zn- complexes for iron electrode at 35°C.

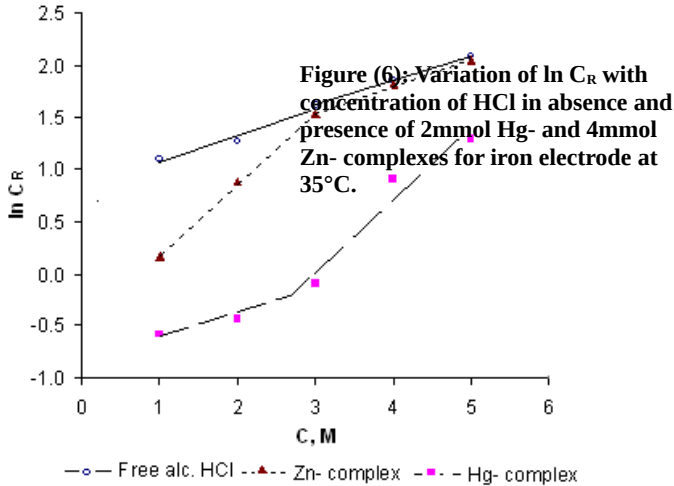—o— Free alc. HCl --▲-- Zn- complex -■- – Hg- complex

Table (2): Calculated values of kinetic parameters for the corrosion of iron electrode in HCl solutions in absence and presence of additive complexes

Medium	B mg m^{-2}s^{-1} M^{-1}		k mg m^{-2}s^{-1}	
	B$_1$	B$_2$	k$_1$	k$_2$
Blank	0.26	0.23	2.23	2.50
HCl solutions containing 2mmol Hg	0.24	0.69	0.43	0.12
HCl solutions containing 4mmol Zn	0.68	0.26	0.61	2.08

Subscript 1 refers to concentration range from 1 to 3M,
Subscript 2 refers to concentration range from 3 to 6M

2-1- Effect of inhibitor concentration

The corrosion current density (I_{corr}) obtained by extrapolation of the anodic and cathodic Tafel lines to the corresponding corrosion potential, decreases with increasing complexes concentration (Figure 7 and Table 3). Early Stern [30] has shown that the corrosion rates obtained by this method check well with those determined by analysis of the amount of dissolved iron. The decrease in the current density values I_{corr} may suggest that the iron dissolution was inhibited by the presence of the complexes on the electrode surface.

Increasing the concentrations of complexes in 1M ethanolic HCl has a slight effect on the anodic branch associated with the oxidation of the metal, and a pronounced inhibitive effect on the cathodic branch of the polarization curves during the potential sweep. This indicates that these complexes can be classified as cathodic

type inhibitors and the rate of hydrogen evolution reaction on iron surface occurs under activation control. The pronounced inhibitive effect on the cathodic curve suggests that the inhibiting action occurred by retardation of cathodic reduction rate by simple blocking of the available cathodic sites on the iron surface, which lead to a decrease in the exposed area necessary for hydrogen evolution and lowered the dissolution rate with increasing complexes concentration [31,32].
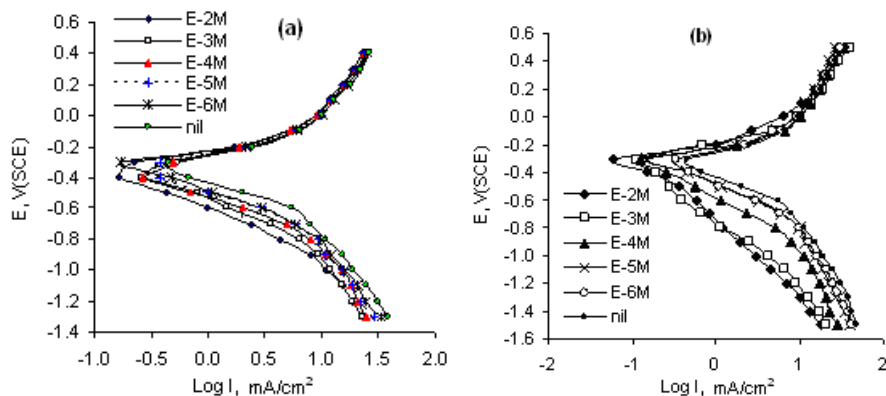
Figure (7): E- LogI curves of iron electrode in 1MHCl containing different concentrations of complex at 35°C   (a) Zn- complex, (b) Hg- complex.

The values of corrosion potential, E_{corr}, which were around −300 mV(SCE) were not affected by the addition of any complex indicating that these compounds could act as pickling inhibitors which in spite of leaving the corrosion potential virtually unaffected, cause a significant decrease in the corrosion rate [33].
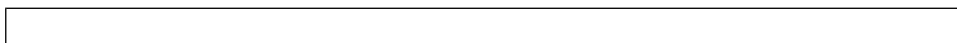
Table (3): Electrochemical parameters of Fe electrode in 1M ethanolic HCl solution containing different concentrations of Hg- and Zn- complexes at 35°C

Additive	Conc. M	E_{corr} (mV/SCE)	I_{corr} (mA/cm^2)	b_a (mV/dec.)	$-b_c$ (mV/dec.)	C_R mmpy
Hg- complex	nil	-300	5.31	1000	1000	2.89
	E-6	-296	4.00	1000	947	2.24
	E -5	-296	3.44	909	1153	1.93
	E -4	-294	2.90	1000	1250	1.63
	E -3	-290	1.66	909	811	0.93
	E -2	-287	0.89	1000	606	0.50
Zn- complex	nil	-300	5.31	1000	1000	2.89
	E -6	-290	3.80	1034	968	2.13
	E -5	-295	3.55	1025	952	1.99
	E -4	-315	3.31	952	1363	1.85
	E -3	-305	2.51	909	1026	1.41
	E -2	-310	2.14	937	869	1.20

E_{corr}, corrosion potential $\qquad$ I_{corr}, corrosion current density b_a, b_c anodic and cathodic Tafel slopes $\qquad$ C_R, corrosion rate

The inhibition efficiency values increase markedly with increasing the complexe concentrations, except for a minor deviation within the range of Zn-complex concentrations from 10^{-6} to 10^{-4}M (Figure 8). At lower concentrations (10^{-4} to 10^{-6}), the IE% is very low for the two complexes. While at higher concentrations (10^{-3} and 10^{-2}), the IE% values increase in which Hg- complex achieve higher protection efficiency than Zn-complex. These results reveal that, the inhibition efficiency of Schiff's base metal complexes under test increase with increase of inhibitor concentration. In many cases the adsorption of the inhibitor molecules on the iron surface is the result of the donor acceptor interaction between π electrons of aromatic rings of the inhibitors and the vacant d orbitals of iron surface atoms [34] or the presence of electronegative atoms (O or N) in the inhibitor molecular structures [35].

Figure (8):
The relationship between inhibition efficiency IE%, and logarithmic concentration of additive complexes on iron electrode.
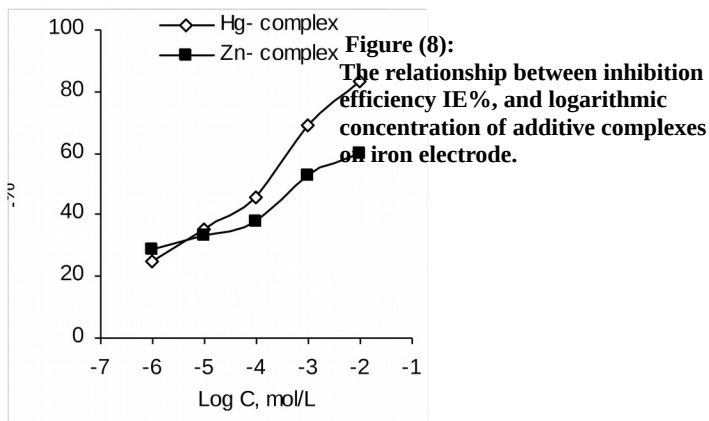
The Hg- complex has two Schiff base ligands (L) in its structure containing the electron rich N, O and aromatic rings. N and O atoms are electron donating (strongly activating) by virtue of presence of lone pair of electrons on the atoms [19, 36] so, electron density increases. Hence more binding of Hg- complex with the metal and thereby more inhibition efficiency is observed. However, to quantify the effect of inhibitor concentration on the corrosion rate theoretical fitting of different isotherms are tested.

2-2-Adsorption Isotherms

2-2-1-The Langmuir isotherm

The Langmuir equation was chosen for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface. The linearized Langmuir equation as reported by Eligwe *et al.* [37], was used to analyze the data. The equation is given as:

$$C_{inh}/\Theta = 1/KB_s + C_{inh}/B_s \qquad (5)$$

Where C_{inh} is the molar concentration of inhibitor, Θ is the surface coverage by inhibitor molecules, B_s is the sorbent binding capacity (mmol/mol), that is, the maximum sorption upon complete saturation of adsorbent surface and K_{ads} (L mol^{-1}) is the binding constant representing the interaction of the additives with metal surface and is defined as [38]:

$$K_{ads} = \frac{1}{C_{solvent}} \exp\left(\frac{-\Delta G_{ads}}{RT}\right) \quad (6)$$

Where $C_{solvent}$, is the molar concentration of the solvent, which in case of ethanol is 17.13 mol L^{-1}[21]. R is the universal gas constant, 8.314 J/mol K, T is the thermodynamic temperature and ΔG_{ads} is the adsorption free energy.

The present results were fitted into equation 5 for linearization by plotting C_{inh}/Θ against C_{inh}, (Figure 9). The figure yield straight lines and indicates a good fit of the isotherm to the experimental data which reflects monolayer adsorption [39]. The calculated equilibrium constant K_{ads} of the adsorption reaction leads to $\Delta G_{ads} = -31.6$ and -32.7 kJ mol^{-1} for Hg- and Zn- complexes respectively. The negative and low value of ΔG_{ads} indicates the spontaneous and physical nature of adsorption [19]. The regression coefficient (R^2) and the different constants for this model are given on Table 4. From this table, it was observed that the regression coefficients are very good for the Langmiur isotherm. This isotherm gave a very good description of the sorption process over the range of concentrations studied.

Figure 9: Langmuir plots for different concentrations of Schiff base complexes in 1MHCl.
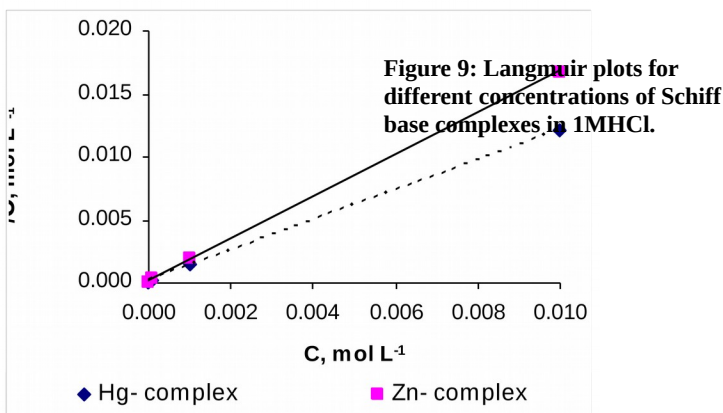
2-2-2-Freundlich isotherm

The Freundlich isotherm model was chosen to estimate the adsorption intensity of the sorbent towards the adsorbate. The linearized form is given as [39]:

$$\text{Log } \Theta = \text{Log } K_{ads} \quad + \quad 1/n \text{ Log } C_{inh} \quad (7)$$

Where, K_{ads} (the binding constant) and n (the exponent) are the Freundlich empirical constants, C_{inh} is the additive concentration (mol/L) and Θ is the surface coverage. The values of K_{ads} and n determine the steepness and curvature of the isotherm [40].

Application of the Freundlich equation to analyze the equilibrium isotherms of the two additives gave linear plots (Figure 10).

Figure 10: Freundlich isotherm plots for Hg- and Zn- complexes of different concentrations on iron surface.
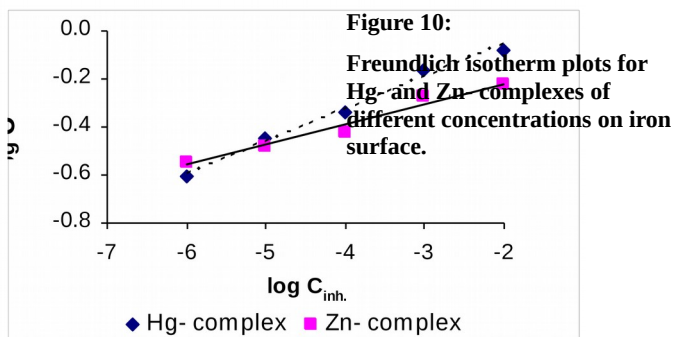
The values of 1/n, less than unity is an indication of that a significant adsorption takes place at low concentration but the increase in the amount adsorbed with concentration becomes less significant at higher concentrations and vice verse [39]. Also, the higher the K_{ads} value, the greater the adsorption intensity. In the present study, little adsorption occur at low concentrations. Generally, this model gave a poor fit to the experimental data due to its low constant values.

Table (4): Regression coefficient of determination (R^2) and the different constants for Langmuir and Freundlich isotherm models for the Schiff base metal complexes adsorption on iron surface

	Hg- complex	Zn- complex
Langmuire isotherm		
R^2	0.9996	0.9998
B_s	0.8372	0.5996
K	13271	20846
Freundlich isotherm		
R^2	0.9902	0.9716
K	1.6199	0.8877
1/n	0.1348	0.0847
n	7.4183	11.8063

3-

Effect of temperature

3-1- Effect of temperature on the corrosion of iron in 0.1MHCl solution

Analysis of the polarization curves shows that no active– passive transition up to high potentials at any given temperature was observed (Figure 13). This could be explained as follows: hydrochloric acid prevents the formation of passive film and enhances the process of anodic dissolution with increasing temperature. On the other hand, at low potential values, the Tafel relation is met with linear dependence, indicating that both anodic and cathodic reactions are controlled by activation. Corrosion current densities and corrosion rates were found to increase with the increase in temperature for 1M ethanolic acid solutions (Table 5).

Figure (11): E− Log I curves of iron electrode at different temperatures of ethanolic 0.1M HCl solutions.
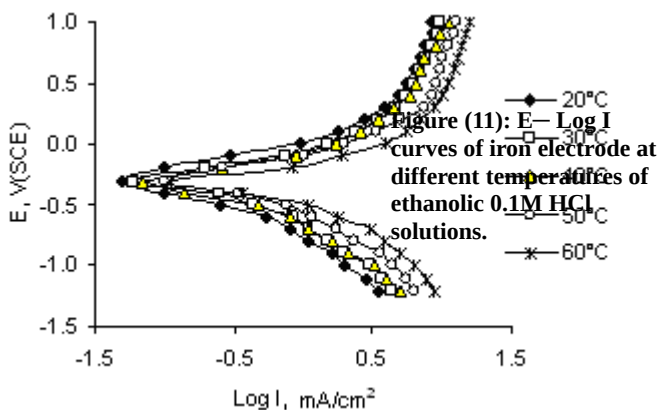
3-2- Influence of temperature on the corrosion of iron in presence of the additive complexes

Increasing the temperature leads to an increase in the corrosion rate of iron and a decrease in the inhibition efficiencies (IE%) of complexes (Figure 12 and Table 5) indicating the formation of an adsorptive film of a physical character [41]. Increasing the temperature of the medium may cause an addition to the agitation energy of the system [42] and as a consequence enhances the conducting of the solution and migration of Cl^- ions towards the metal surface. Corrosion potential in presence of the two complexes was unchanged with increasing temperature ≈ -300mV(SCE) supporting the proposed pickling inhibitor effect of these compounds.
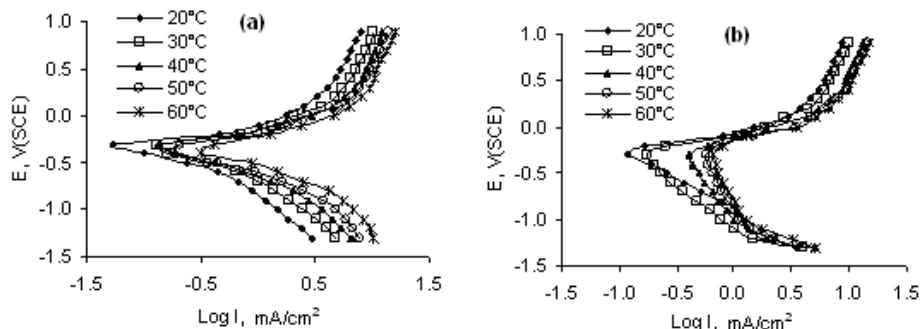
Figure (12): E— Log I polarization curves of iron electrode in 0.1MHCl containing 4mmol complex at different temperatures, (a) Zn- complex, (b) Hg-complex.

Table (5): Electrochemical parameters and the corresponding inhibition efficiencies of 4mmol complexes for iron electrode in 0.1M ethanolic HCl at different temperatures

T °C	0.1MHCl	0.1MHCl +Hg-Complex		0.1MHCl +Zn-Complex	
	C_R mmpy	C_R mmpy	IE %	C_R mmpy	IE %
20	0.202	0.056	72.2	0.102	49.4
30	0.320	0.098	69.3	0.244	23.5
40	0.426	0.145	65.8	0.354	16.9
50	0.782	0.325	58.3	0.644	17.4
60	1.044	0.505	51.6	0.975	06.5

The dependence of corrosion rate on temperature can be expressed by the Arrhenius equation [43]:

$$C_R = A \exp(-E_a/RT) \qquad (8)$$

where C_R is the reaction rate, A is a constant, E_a is the apparent activation energy of the iron dissolution reaction, R is the universal gas constant and T, is the absolute temperature. The activation parameters are obtained from an arrangement of equation (8) to Arrhenius-type plot (Eq. 9) [46]:

$$\text{Log } C_R = A - (E_a /2.303 \text{ RT}) \qquad (9)$$

while thermodynamic parameters are given by Eyring transition-state equation (Eq. 10) [47]:

$$\text{Log } C_R/T = \log (R/Nh) + \Delta S°/ 2.303 \text{ R} - (\Delta H° /2.303 \text{ RT}) \qquad (10)$$

Where N, is Avogadro's number, h is Planck's constant, $\Delta S°$ and $\Delta H°$ are the entropy and enthalpy of activation respectively. A plot of log C_R/T vs. $1/T$ gave straight line with slope of $[- \Delta H° /2.303 \text{ R}]$ and an intercept of $[\log (R/Nh) + \Delta S°/ 2.303 \text{ R}]$ (Figure 13). The calculated values obtained from these plots clearly show higher values of E_a and $\Delta H°$ in the inhibited solutions than those in the uninhibited ones (Table 6).
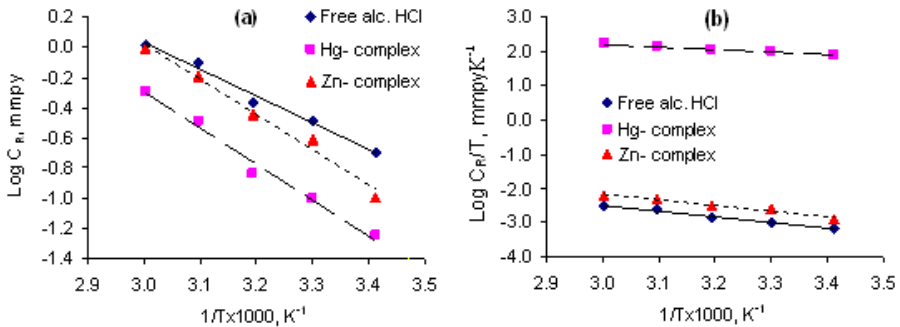
Figure (18): Corrosion rates of iron electrode in 0.1 M HCl in the absence and presence of 4mmol of additive complexes (a) Arrhenius plots, (b) Transition-state plots.

The rise in E_a values in the presence of the complexes could explain the corrosion inhibition obtained [46] through physical adsorption. Also, higher $\Delta H°$ values indicate higher protection efficiency due to the presence of an energy barrier for the reaction, that is, the process of adsorption leads to a rise in the enthalpy of the corrosion process [47].

Table (6): The values of activation parameters for iron in 0.1M HCl in the absence and presence of   complexes

Medium	A	E_a (kJmol^{-1})	$\Delta H°$ (kJmol^{-1})	$\Delta S°$ (JK^{-1} mol^{-1})
Blank	5.33	33.85	31.26	-151.58
Hg	7.01	44.61	38.52	-122.59
Zn	6.80	45.29	41.03	-113.42

The present data demonstrate that $\Delta S°$ has negative value for the blank and complexes solutions (Table 7). This may be discussed as follows, in the blank solution; the transition state of the rate determining recombination step represents a more orderly arrangement. Hence, a negative value for the entropy of activation is obtained. In the presence of complexes the surface is covered with the complexes molecules, this will retard the discharge of hydrogen ions at the metal surface which causing the system to pass from a more to a less orderly arrangement.

CONCLUSION

From the above mentioned results, it could be concluded that:

1-   The corrosion rates of iron increased with increasing concentration of HCl solutions prepared in ethanol at 35°C in absence or in presence of constant weight of complexes.

2-   The higher concentrations of complexes lead to a good adsorption on the iron surface, and reduce the chemical attack of HCl solution on iron. Besides, tested complexes could be classified as cathodic type inhibitors and could act as pickling inhibitors.

3-   Hg- complex achieve higher protection efficiency than Zn-complex due to the presence of greater numbers of electron rich N and aromatic rings.

4-   Increasing the temperature leads to an increase in the corrosion rate of iron and a decrease in the inhibition efficiencies of the complexes.

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