

## Inhibition of Carbon Steel Corrosion by Iron(III) and Imidazole in Sulfuric Acid

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The inhibitive action of iron(III), imidazole and mixture of them on the corrosion of carbon steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution was investigated using galvanostatic, potentiodynamic anodic polarization and weight loss techniques. It was found that the percentage inhibition efficiency was found to increase with increasing concentration of each compound. However, the combination of iron(III) with the imidazole increases the values of inhibition efficiency compared with individual compound. It was found that iron(III), imidazole and mixtures of them inhibit the pitting corrosion of carbon steel in chloride containing solutions by shifting the pitting potential into more positive direction. The inhibiting solutions were analyzed using UV-Visible spectrophotometric before and after polarization measurements. The inhibition was explained on the basis of a complex formation between the two components, which was much more effective than the inhibiting action of each additive separately. The inhibition mechanism was discussed depending on the results derived from corrosion and UV-visible spectrophotometric measurements as well as conductometric investigations.

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**Keywords:** Carbon steel, Fe<sup>3+</sup> cation, Imidazole, Corrosion inhibitors.

### 1. INTRODUCTION

Acid solutions are widely used in industry, some of important fields of application being acid pickling, industrial cleaning, acid descaling, oil-well acidizing and petrochemical processes [1–3]. The use of inhibitors is the most economical and practical methods of reducing corrosive attack on metals [4, 5]. During the past decade, the inhibition of mild steel corrosion in acid solutions by various types of organic inhibitors has attracted much attention [6–8], many researchers report that the inhibiting effect mainly depends on some physicochemical and electronic properties of the organic compound molecule which related to its functional groups, steric effects, electronic density of donor atoms, and p

orbital character of donating electrons, and so on[9,10]. It is well known that the organic inhibitors contain sulphur, nitrogen, oxygen, phosphorous and aromatic rings or multiple bonds in their molecular structure [11]. On the other hand, the effect of various metal cations on the corrosion of metals has been reported earlier [9-13]. Several mechanisms have proposed to explain both the accelerating and inhibiting effect of metal cations. It was found that [14] the accelerating effect is due to the formation of soluble compounds while the inhibiting effect was attributed to the formation of insoluble compounds adhering to the metal surface [15, 16]. Recently, it was found that the formation of donor – acceptor surface complex between free or  $\pi$ -electron of an organic inhibitor and vacant d-orbital of a metal is responsible for the inhibition of the corrosion process [17].

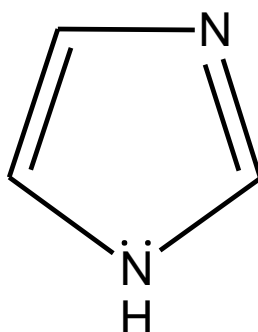
The aim of this work is to study the inhibiting effect of iron(III)and imidazole as well as a mixture from them on the corrosion behavior of carbon steel type (L-52) used in petroleum pipe lines (Egypt) in 0.5 M  $H_2SO_4$  solutions using galvanostatic polarization, potentiodynamic polarization and weight loss measurements, Moreover the ability of these compounds to provide a protection against pitting corrosion.

## 2. EXPERIMENTAL

### 2.1. Materials

The carbon steel specimen (L-52) used for this study has the following composition (wt. %); C = 0.26; Mn = 1.35, P = 0.04, S = 0.05, Nb = 0.005, V = 0.02, Ti = 0.03, and Fe to balance. The galvanostatic polarization measurements were performed using specimens in the form of rods of 1 cm<sup>2</sup> exposed surface area as a working electrode. For weight loss tests, small rectangular coupons of the dimensions 1.0 x 2.0 x 0.3 cm<sup>3</sup> were used.

The testing media were aqueous aerated 0.5M  $H_2SO_4$  solutions without and with different concentrations from  $Fe_2(SO_4)_3$  ( as a source for iron(III)), imidazole and  $Fe_2(SO_4)_3$  + imidazole mixture, respectively. All chemicals used in this study were analytical grade (Aldrich chemicals) and the desired temperature of each experiment was adjusted to  $\pm 1$  C<sup>o</sup> using air thermostat. The structural formula of imidazole is represented as follows in figure



**Figure 1.** (chemical formula of imidazole)

## 2.2. Apparatus

The weight loss measurements were carried out in large test tubes ( $20 \times 2.5$  cm<sup>2</sup> diameter) suspended in a thermo stated water bath. Each tube was open to air. The galvanostatic cathodic and anodic polarization measurements were carried out using three-compartment glass cell and EG&G model 363 Potentiostat/galvanostat corrosion measurement system. Platinum electrode was used as a counter electrode (separated from the cell solution by a sintered glass frit) and a saturated calomel electrode (inside a luggin's probe) as a reference electrode.

The potentiodynamic anodic polarization measurements were performed using a Wenking potentiostane, type POS 73. The X-Y recorder, type advanced, HR 2000.

The UV-visible spectrophotometric experiments were carried out using JASCO UV-VIS 530 spectrophotometer and 10 mm matched silica cell.

The conductance measurements were carried out using YSI model 32 conductance meter of cell constant equal to 1.6.

## 2.3. Procedures

### 2.3.1. Galvanostatic polarization

The working electrode was polished and pre-polarized prior to recording the cathodic and anodic polarization curves at each concentration of the tested solution. All the polarized curves were obtained using the direct technique at regular intervals. The duration of potential stabilization at each current density value was between 3 and 5 min.

### 2.3.2. Potentiodynamic anodic polarization

The working electrode is the same as that used before in galvanostatic polarization techniques; the electrode surface was polished and left for 10 min. as a pre-steady state prior to scanning rate (100 mV/s) at each concentration of the tested solution.

### 2.3.3. Weight loss measurements

The coupons were successively abraded with SiC paper to a final finish using 1200 grade paper. Before immersion in the test solution (50 ml), the dimensions of each coupon were ascertained. They were then degreased in AR grade acetone, etched in HCl for 30 S, washed with double distilled water, followed by acetone, dried and weighed.

The cleaned carbon steel coupons were weighed before and after immersion in 50 ml of the test solution for a period of time up to 8 hr. The average weight loss for each to identical experiments was taken and expressed in mg cm<sup>-2</sup>.

### 2.3.4. UV-visible spectra

Using UV-visible spectrophotometric method, some experiments were carried out on the electrolyte solution of the inhibited system before and after polarization measurements.

### 2.3.5. Conductometric titration

Conductometric investigation was carried out typical to the following:[18] The titration of  $5 \times 10^{-4}$  M iron(III)dissolved in 0.5 M  $H_2SO_4$  solution using 0.5 M  $H_2SO_4$  solution containing  $5 \times 10^{-3}$  imidazole as a titrant .

## 3. RESULTS AND DISCUSSION

### 3.1. Galvanostatic polarization measurements

Figure 2 represents the anodic and cathodic polarization curves of carbon steel in 0.5 M  $H_2SO_4$  in the absence and presence of different concentrations of imidazole. Similar curves were obtained in case of  $Fe^{+3}$  cation and mixtures of iron(III)and imidazole (not shown). Some corrosion parameters e.g. corrosion current density ( $I_{corr}$ ) corrosion potential ( $E_{corr}$ ), and Tafel slopes ( $b_c$  and  $b_a$ ) and the percentage inhibition efficiency (%I.E)was calculated from the galvanostatic polarization curves and given in Table 1.

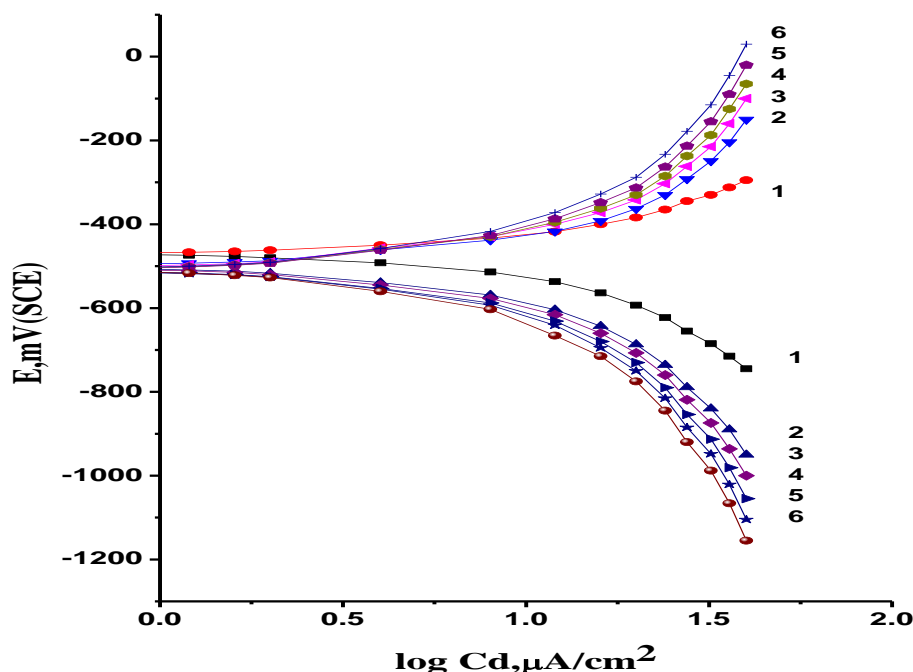
The percentage inhibition efficiency (%I.E) was calculated and listed in Table 1 using the following equation:

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

where,  $I_{corr}^o$  and  $I_{corr}$  are the uninhibited and inhibited corrosion current densities, respectively. The corrosion current densities are calculated from the intersection parts of the cathodic curves with stationary corrosion potentials ( $E_{corr}$ ).

An inspection of Fig.2. and Table 1, illustrate that as the additives concentration increases the values corrosion current density ( $I_{corr}$ ) decreases and the percentage inhibition efficiency increase indicating the inhibiting effect of these compounds. The values of corrosion potential ( $E_{corr}$ ) is shifted slightly toward negative direction .These results would indicate that the additives provide an inhibition effect on the corrosion of carbon steel electrodes in 0.5M  $H_2SO_4$  solutions and behave as mixed inhibitor type effectiveness.

This effect is predominately anodic, cathodic



**Figure 2.** Cathodic and anodic polarization curves of carbon steel in 0.5M H<sub>2</sub>SO<sub>4</sub> solution with Imidazole: (1) blank, (2) 5.0 × 10<sup>-4</sup>, (3) 1.0 × 10<sup>-3</sup>, (4) 2.0 × 10<sup>-3</sup>, (5) 3.0 × 10<sup>-3</sup>, (6) 5.0 × 10<sup>-3</sup>M.

The values of anodic and cathodic Tafel slopes remain almost unchanged, indicating that [19,20] the presence of these compounds in the solution has no effect on the mechanism of the dissolution process of the metal and the adsorbed molecules mechanically screen the coated part of the electrode and therefore protect it from the action of the corrosion medium.

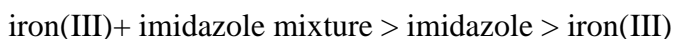
The reaction mechanism of the corrosion process in 0.5M H<sub>2</sub>SO<sub>4</sub> solution free from inhibitor is different from that in presence of additives. Inspection of data given in table 1, it is clear that in presence of inhibitors the value of b<sub>c</sub> is more than in free acid solution.

This behavior should be due to the decrease of the cathodic transfer coefficient, which can be ascribed to the thickening of the electric double layer or the formation of multi-molecular layers on the metal surface [21].

Also, the anodic Tafel slope (b<sub>a</sub>) in the inhibited solution is higher than that obtained in the acid inhibitor free solutions.

This increase in anodic Tafel slope suggests a mode of inhibition involving an interposition of the additives into the charge transfer process for the anodic reaction [22], which may lead to a morphological change of the electrode surface brought about by the anodic dissolution [23].

The values of %I.E reveal that the order of inhibition efficiency decreases in the following order:

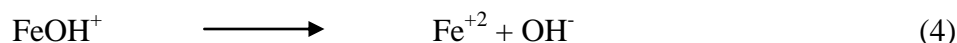


**Table 1.** Corrosion parameters for carbon steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions in absence and presence of different concentrations of inhibitors at 30 °C

Inhibitor system	Conc. (M)	b <sub>a</sub> mV dec <sup>-1</sup>	b <sub>c</sub> mV dec <sup>-1</sup>	E <sub>corr</sub> mV (SCE)	I <sub>corr</sub> (mA cm <sup>-2</sup> )	%I.E	
						Polarization	Weight loss
-----	0.0	115	101	-462	0.625	-----	-----
iron(III)	5.0 × 10 <sup>-4</sup>	123	121	-495	0.475	24.00	24.54
	1.0 × 10 <sup>-3</sup>	144	156	-493	0.38	39.00	40.90
	2.0 × 10 <sup>-3</sup>	133	135	-492	0.45	28.00	29.00
	3.0 × 10 <sup>-3</sup>	116	118	-493	0.510	18.50	19.00
	5.0 × 10 <sup>-3</sup>	108	112	-491	0.525	16.00	16.36
Imidazole	5.0 × 10 <sup>-4</sup>	111	136	-499	0.45	28	29
	1.0 × 10 <sup>-3</sup>	123	151	-500	0.362	42	43.63
	2.0 × 10 <sup>-3</sup>	133	178	-502	0.30	52	52.72
	3.0 × 10 <sup>-3</sup>	151	191	-505	0.223	64	65.45
	5.0 × 10 <sup>-3</sup>	186	258	-504	0.113	81.95	82.72
Imidazole+ iron(III)	5.0 × 10 <sup>-4</sup> + 5.0 × 10 <sup>-4</sup>	181	275	-533	0.101	83.80	82.50
	1.0 × 10 <sup>-3</sup> + 5.0 × 10 <sup>-4</sup>	209	283	-533	0.076	87.80	86.36
	2.0 × 10 <sup>-3</sup> + 5.0 × 10 <sup>-4</sup>	218	298	-531	0.073	88.30	88.18
	5.0 × 10 <sup>-4</sup> + 1.0 × 10 <sup>-3</sup>	186	263	-533	0.116	81.44	81.81
	5.0 × 10 <sup>-4</sup> + 2.0 × 10 <sup>-3</sup>	178	258	-535	0.119	80.96	80.00

### 3.2. Potentiodynamic polarization measurements

Fig.(3) represents the effect of addition of increasing concentrations of imidazole on the potentiodynamic anodic polarization curves of carbon steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at a scan rate 50 mVs<sup>-1</sup>. Similar curves were obtained in case of iron(III)and mixtures of iron(III)and imidazole (not shown).The curves in Figs. (3)illustrate the presence of one anodic anodic peak. This peak may be corresponding to the active dissolution of Fe to Fe<sup>+2</sup> ion according to the following mechanism:

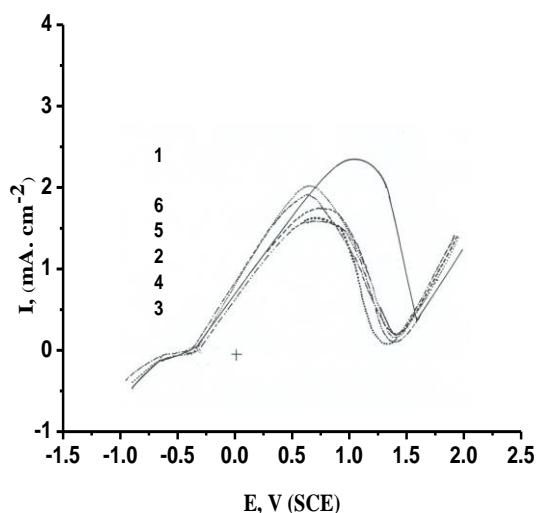


As the concentration of the additives increases the corrosion current peak (I<sub>p</sub>) decreases and the values of peak potential E<sub>p</sub> is shifted the more positive values which suggest the inhibiting effect of these additives. The percentage inhibition efficiency (%I.E) was calculated using the following equation:

$$\% I.E = \left[ 1 - \frac{I_{P (add)}}{I_{P (free)}} \right] \times 100 \quad (5)$$

where,  $I_{p( add)}$  and  $I_{p (free)}$  are the peak current densities in the presence and absence of inhibitors. The values of  $I_p$ ,  $E_p$  and %I.E are listed in Table 2. It is obvious from Table 2, the order of inhibition efficiency decreases in the following order.

iron(III)+ imidazole mixture > imidazole > iron(III)



**Figure 3.** Potentiodynamic anodic polarization curves of carbon steel in 0.5M H<sub>2</sub>SO<sub>4</sub> solution with Imidazole: (1) blank, (2) 5.0 × 10<sup>-4</sup>, (3) 1.0 × 10<sup>-3</sup>, (4) 2.0 × 10<sup>-3</sup>, (5) 3.0 × 10<sup>-3</sup>, (6) 5.0 × 10<sup>-3</sup>M.

**Table 2.** Corrosion parameters for carbon steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions without and with different concentrations of inhibitors at 30 °C

Inhibitor system	Conc. (M)	$I_p$ (mA cm <sup>-2</sup> )	$E_p$ , V(SCE)	%I.E
-----	0.0	2.4	1.049	-----
iron(III)	5.0 × 10 <sup>-4</sup>	1.83	0.54	23.80
	1.0 × 10 <sup>-3</sup>	1.68	0.59	30.00
	2.0 × 10 <sup>-3</sup>	1.74	0.55	27.50
	3.0 × 10 <sup>-3</sup>	2.01	0.52	16.50
	5.0 × 10 <sup>-3</sup>	2.10	0.51	12.50
Imidazole	5.0 × 10 <sup>-4</sup>	1.74	0.47	27.5
	1.0 × 10 <sup>-3</sup>	1.41	0.467	41.25
	2.0 × 10 <sup>-3</sup>	1.2	0.469	50
	3.0 × 10 <sup>-3</sup>	0.84	0.471	65
	5.0 × 10 <sup>-3</sup>	0.54	0.472	77.5
Imidazole+ iron(III)	5.0 × 10 <sup>-4</sup> + 5.0 × 10 <sup>-4</sup>	0.54	0.69	77.50
	1.0 × 10 <sup>-3</sup> + 5.0 × 10 <sup>-4</sup>	0.42	0.72	82.50
	2.0 × 10 <sup>-3</sup> + 5.0 × 10 <sup>-4</sup>	0.44	0.70	81.70
	5.0 × 10 <sup>-4</sup> + 1.0 × 10 <sup>-3</sup>	0.66	0.67	72.50
	5.0 × 10 <sup>-4</sup> + 2.0 × 10 <sup>-3</sup>	0.68	0.65	71.70

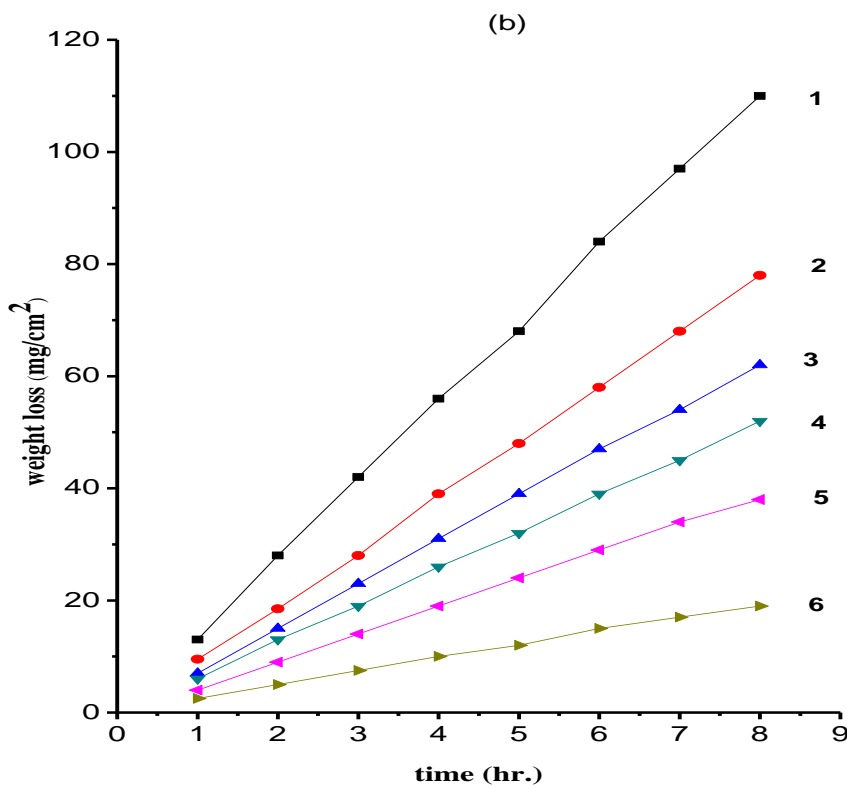
3.3. Weight loss measurements

Fig. 4 shows the relation between time and weight loss of carbon steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions in absence and presence of different concentrations of imidazole as an example. Similar curves also were obtained in case of iron(III) and mixtures of iron(III) and imidazole (not shown). An inspection of this figure reveals that the weight loss of the inhibitor, varied linearly with time and much lower than that obtained in the blank solution. The linearity obtained indicates the absence of insoluble film during corrosion and that the inhibitors were first adsorbed onto the metal surface and thereafter, impede corrosion either by merely blocking the reaction sites (anodic and cathodic)

The percentage inhibition efficiency (%I.E) was calculated from the weight loss measurements and listed in Table 1 using the following relation:

$$\%I.E = [1 - W/W_0] \times 100 \tag{6}$$

where, W<sub>0</sub> and W are the weight loss per unit area in the absence and presence of inhibitor, respectively. Inspection of Table 1 reveals that the percentage efficiency (%I.E) increases with increasing the additive concentration. Moreover, the percentage inhibition efficiency (%I.E) is found to decrease in the following order: iron(III)+ imidazole mixture > imidazole > iron(III)



**Figure 4.** Weight loss as a function of time of carbon steel in 0.5M H<sub>2</sub>SO<sub>4</sub> solution without and with Imidazole: (1) blank, (2) 5.0 × 10<sup>-4</sup>, (3) 1.0 × 10<sup>-3</sup>, (4) 2.0 × 10<sup>-3</sup>, (5) 3.0 × 10<sup>-3</sup>, (6) 5.0 × 10<sup>-3</sup> M.



### 3. INHIBITION OF PITTING CORROSION

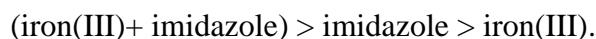
Potentiodynamic anodic polarization curves of carbon steel were traced in solutions of 0.5M H<sub>2</sub>SO<sub>4</sub>+0.5M NaCl (as a pitting corrosion agent) devoid of and containing different concentrations of iron(III), Imidazole and mixture of them at a scanning rate of 1mV/sec.

The potential was swept from negative potential towards anodic direction up to the pitting potential, no any anodic oxidation peaks are observed in all anodic scan. The pitting potential ( $E_{pitt.}$ ) was taken as the potential at which the current flowing along the passive film increases suddenly to higher values denoting the destruction of passive film and initiation of visible pits. The effect of addition of increasing concentration of iron(III),imidazole and mixture of them on the values of the pitting potential is represented in Fig.(6). This figure represents the relationship between  $E_{pitt.}$  and logarithmic of molar concentrations of additives. It is clear that from this figure that, as the concentration of these additives increases the pitting potential shifted to more positive values according to the following equation:

$$E_{pitt.} = a + b \log C_{add.} \quad (6)$$

where ,a and b are constants depending on the type of additives used and the nature of the metal. The positive shift of  $E_{pitt.}$  indicates the decrease the pitting attack.

At one and the same inhibitor concentration, the marked shift of potential in the positive (noble) direction decrease in the following sequence.



The different techniques used in this study gave the same order of inhibition efficiency but yielded different absolute values, probably due to the different experimental conditions.

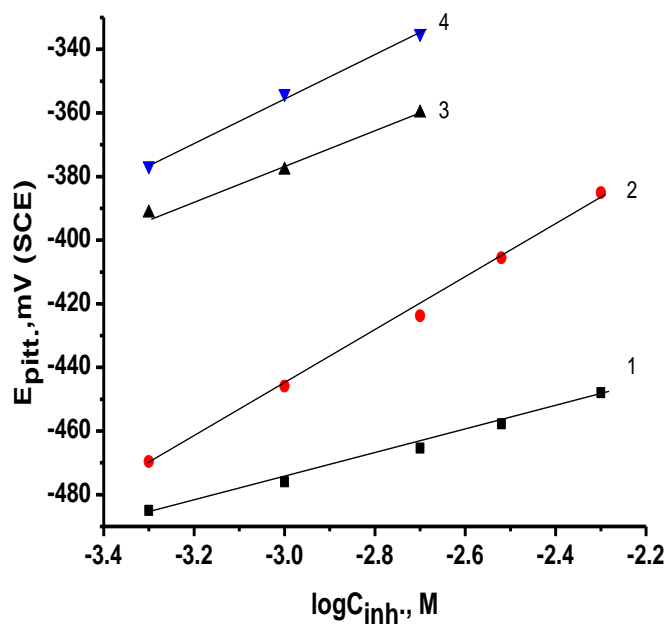
#### 3.5. Some qualitative analysis for the inhibited media

In order to clarify the inhibition mechanism of carbon steel corrosion in 0.5M H<sub>2</sub>SO<sub>4</sub> solutions containing additives, the UV-visible spectroscopy investigations on the testing solutions before and after some corrosion experiments were made. Also, the conductometric titration of Fe<sup>+3</sup> cation using imidazole as a titrant was performed.

##### 3.5.1. UV-visible spectroscopic investigation

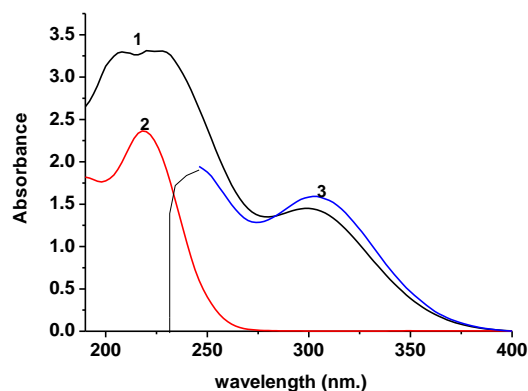
Fig. 6a (curves 1-3) represents the spectrum of iron(III) (curve 1). imidazole (curve 2) and a mixture of them (curve 3) before anodic and cathodic polarization measurements. It is obvious that the spectrum of imidazole shows a shoulder band at 215 nm, corresponding to the  $\pi$ - $\pi^*$  of the aromatic system. This band is shifted to a higher value (230 nm) in case of iron(III)+imidazole mixtures. In the

mean time, the intensity of the band obtained in case of iron(III)+imidazole mixtures is lower than that obtained for imidazole in 0.5M H<sub>2</sub>SO<sub>4</sub> solutions.

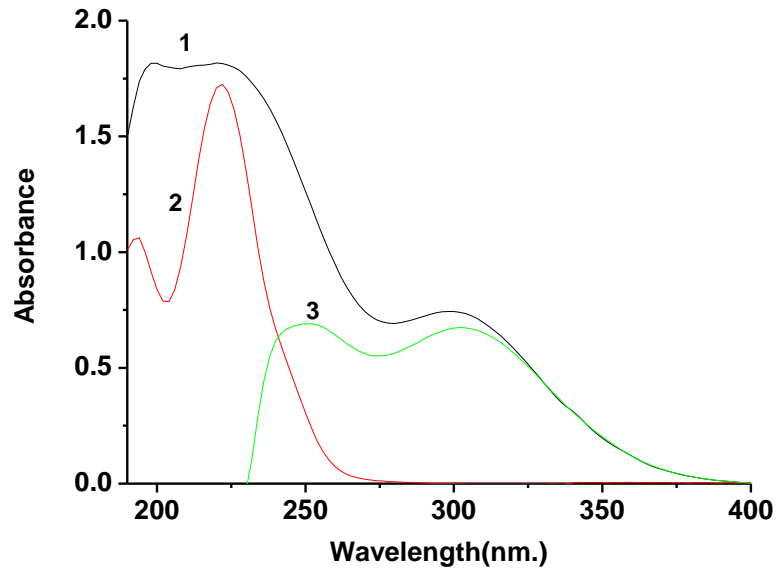


**Figure 5.** The relationship between pitting potential of C-steel and logarithm the concentration of (1) Fe<sup>3+</sup>, (2) Imidazole, (3) Imidazole+ iron(III) and (4) iron(III)+ Imidazole mixtures

For otherwise identical conditions, the spectra of both imidazole and iron(III)+imidazole mixture after polarization measurements (Fig.6b, curves 2 and 3) show the same absorption band values as obtained from those before polarization measurements but at lower intensities. This means that some of imidazole as well as iron(III)+imidazole complex that formed in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution is adsorbed on the carbon steel

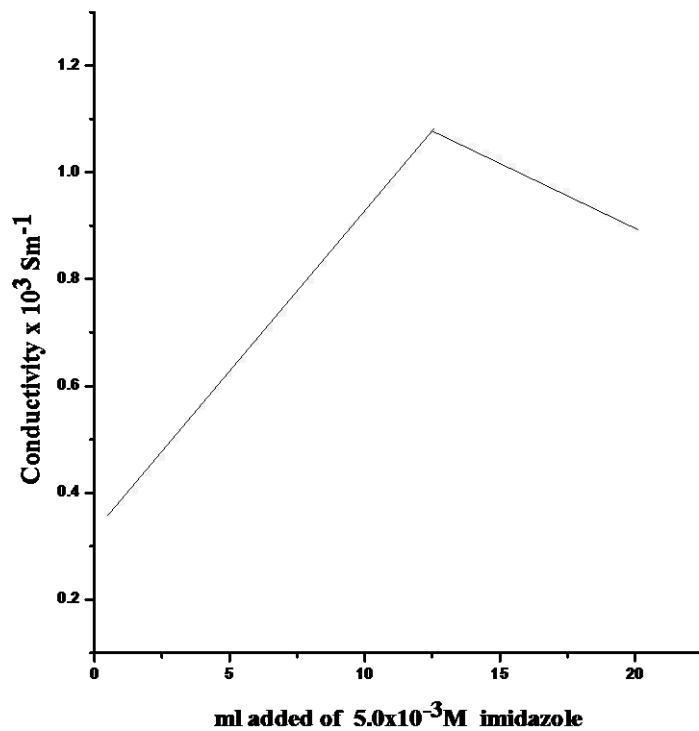


**Figure 6a.** UV-spectra of the additives used as inhibitors for carbon steel corrosion in 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions before measurements: (1) 5.0 × 10<sup>-4</sup>M iron(III), (2) 5.0 × 10<sup>-4</sup>M Imidazole, (3) 5.0 × 10<sup>-4</sup>M iron(III)+ 5.0 × 10<sup>-4</sup>M Imidazole.



**Figure 6b.** UV-spectra of the additives used as inhibitors for carbon steel corrosion in 0.5 M  $\text{H}_2\text{SO}_4$  solutions after measurements: (1)  $5.0 \times 10^{-4}\text{M}$  iron(III), (2)  $5.0 \times 10^{-4}\text{M}$  Imidazole, (3)  $5.0 \times 10^{-4}\text{M}$  iron(III)+  $5.0 \times 10^{-4}\text{M}$  Imidazole.

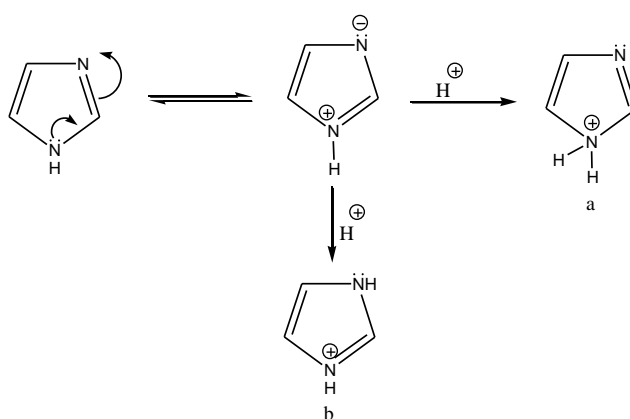
### 3.5.2. Conductometric titration of iron(III) using imidazole



**Figure 7.** Conductometric titration curve for 50 ml  $5.0 \times 10^{-4}\text{M}$  iron(III) titrated with different volumes of  $5.0 \times 10^{-3}\text{M}$  Imidazole solution.

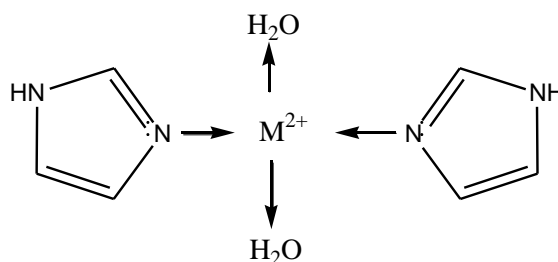
The conductometric titration curve obtained for iron(III) with imidazole as a titrant is shown in Fig.7. It is illustrated that the conductometric titration of  $5.0 \times 10^{-4}$  M iron(III) with  $5.0 \times 10^{-3}$  M imidazole shows an obvious maximum in the conductometric curve, which corresponds to a molar ratio of 1.0 metal cation 2.0 additive. This observation would give a strong indication for the formation of a complex compound between the two additives by a molar ratio of 1.0 (iron(III)): 2.0 (imidazole).

It is known that [24], the shape of the conductometric curve depends on the concentrations of all the species present during the titration process as well as some other factors such as viscosity, dielectric constant, solvation, complexation and proton transfer. On the other hand and as given below imidazole [25] is organic compound with two nitrogen atoms in the heterocyclic ring. One of them is of pyrrole type, and the other of pyridine-like nitrogen atom. Consequently, imidazole is basic, which become protonated in the acid solution in the following manner (Fig.8)



**Figure 8.** Protonation of imidazole in acidic medium.

In the present work, the conductance of the titrated solution is mainly due to iron(III) and partially to the hydrogen ions resulting from the dissociation of the protonated imidazole in the acidic medium. After the complete formation of 1.0 (iron(III)) 2.0 : (imidazole) complex, the conductance values remain constant. This would indicate that no liberation of hydrogen ions from the protonated imidazole added after complete complexation. Consequently it can be concluded that the iron(III)- Imidazole complex compound ( Fig. 9) is of the following type



**Figure 9.** 1:2 complex formation between metal cation and imidazole

It is shown that the protonated –N-heteroatom center of the imidazole molecules is assumed to participate in the complex formation with iron(III). Generally, the participation of the –N-heteroatom center (i.e. the nitrogen of pyridine type) of some organic compounds like imidazole and phenylazo-hydroxy quinoline in the complex formation with iron(III) in  $\text{H}_2\text{SO}_4$  solutions is reflected in many publications [26,27].

### 3.6. Inhibition mechanism

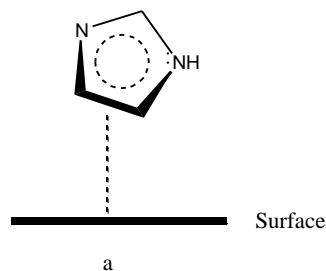
The results discussed above indicate that the influence of the additives as inhibitors for carbon steel corrosion in 0.5 M  $\text{H}_2\text{SO}_4$  solutions depends on the nature and size of the additives. The inhibition action of iron(III) is ascribed to the plating of the corresponding metal on the carbon steel surface [28], which forms a protective layer with consequent more complete anodic passivation of the anodic sections of the substrate.

The inhibition of carbon steel corrosion by imidazole compound is attributed to the adsorption of the inhibitor molecules on the metal surface. As shown above, imidazole molecule shows three different anchoring sites suitable for surface adsorption, the nitrogen atom with its lonely  $\text{sp}^2$  electron pair, the active hydrogen atom attached to the nitrogen atom and the  $\pi$ -bond of the aromatic ring. As previously stated [28], most of the organic compounds containing nitrogen atoms have an electron donating ability and could be adsorbed by electron donating of the N-atom and by bridging with the active hydrogen atom attached to the N-atom. On the other hand, the  $\pi$ -bond of the aromatic ring is considered as the center for adsorption process [29, 30], in which the great adsorption of some organic compounds is attributed to the interaction of the  $\pi$ -electrons with surface, atoms of the adsorbent.

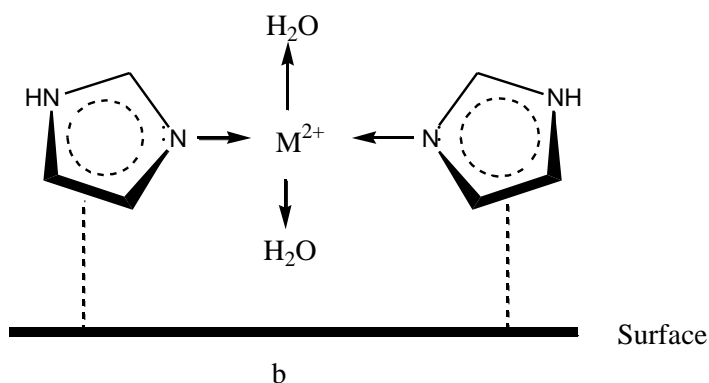
The adsorption of the imidazole molecules through its  $\text{N}^+\text{-H}$  protonated center onto the carbon steel surface is omitted. This is because the carbon steel surface is assumed to be positively charged in sulfuric acid solution [29], in which positively charged centers of the organic molecules are not attached to the same positively charged metal surface. Also, the fact that participation of the active hydrogen atom attached to the N atom in the inhibition processes is omitted could be due to its ability to form an intermolecular hydrogen bonding with another imidazole molecule and/or with  $\text{H}_2\text{O}$  from the medium [25]. Consequently, it can be concluded that the adsorption of the imidazole molecules onto the carbon steel surface is arisen by one anchoring site that is the  $\pi$ -bond of the aromatic ring. Thus, it is reasonable to assume that the imidazole molecule is adsorbed onto the carbon steel surface in a flat orientation through a monodentate form as shown from the model presented in Fig. 10a. The flat model for adsorption is stable and preferred [31] since the covered fraction surface is high, even at, low inhibitor concentration.

In the case of addition of iron(III)+ imidazole mixture, the results demonstrated the complex formation between the two components, which was much more effective than the inhibiting action of each additive separately (Table 1). The conductometric studies revealed the participation of two imidazole molecules in the complex formation with iron(III). This finding would suggest that the molecular size of the complex formed and consequently the number of adsorption centers play an important role in the enhancement of the protection of carbon steel against corrosion. Thus, it is

reasonable to suggest that the adsorption of the complex molecule onto the carbon steel surface occurs in a flat orientation through the  $\pi$ -bond of the aromatic rings in a bidentate form (Fig. 10b), which cover a large fraction surface as compared to the case of imidazole additive.



**Figure 10a.** Schematic representation of the mode of adsorption of Imidazole.



**Figure 10b.** Schematic representation of the mode of adsorption of iron(III)-Imidazole.

It is of interest to remark that when the iron(III)+ imidazole mixture is added to the corrosive medium with higher stoichiometric amount from iron(III) than that required to form a complex with imidazole by a ratio of 1.0 (iron(III)) : 2.0 (imidazole), the value of percentage inhibition efficiency is decreased (Table 1). The same results are obtained from the weight-loss experiments

(Fig.4 and Table 1). This behavior could be explained on the basis that although the presence of a high stoichiometric amount of iron(III) permits a formation of the complex compound by 1 (iron(III)) : 2 (Imidazole) ratio, some of the iron(III) are still free in the acid solution. So it is expected that there is a competition between iron(III) and the complex ions to form a protective layer onto the carbon steel surface. This competition may slow down the rate of film formation and consequently reduce the percentage inhibition efficiency (I.E %). However, the experimental results revealed that (Table 1), although the percentage inhibition efficiency is decreased when the ratio of iron(III) is higher than the ratio of imidazole, its value is still high as compared with those obtained in case of using different concentrations from iron(III) separately. This finding suggests that the carbon steel surface is protected by layer most probably composed from adsorbed iron(III)-imidazole complex ions. This

assumption is further confirmed from the nearly constancy of the  $E_{\text{corr}}$  value obtained in case of adding iron(III)+ imidazole mixtures of various ratios from the two component.

#### 4. CONCLUSION

1- The corrosion of carbon steel in 0.5M  $\text{H}_2\text{SO}_4$  solution is inhibited by addition of iron(III),imidazole and mixture of them

2- The percentage inhibition efficiency increases with increase of the inhibitor concentration

3- The results revealed a complex formation between iron(III)and imidazole, which has much more inhibition effect than the inhibiting action of each additive separately.

4- The inhibition action of iron(III)is ascribed to the plating of the corresponding metal on the carbon steel surface. In contrast, the corrosion inhibition by imidazole as well as its complex compound with iron(III)is attributed to the adsorption of the additives onto the carbon steel surface. The adsorption is assumed to arise from the  $\pi$ -bond of the imidazole rings and the carbon steel surface.

5- Iron(III), imidazole and mixture of them prevent the pitting corrosion of carbon steel in presence of chloride ions by shifting of pitting corrosion into the noble direction.

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