

## Surface Protection of Carbon Steel in Acidic Solution Using Ethylenediaminetetraacetic Disodium Salt

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The influence of ethylenediaminetetraacetic acid disodium (EDTA) on the corrosion behavior of carbon steel in 0.5M HCl solution has been investigated using open circuit potential (OCP), potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and weight loss measurements. The surface of the carbon steel samples was also analyzed by scanning electron microscopy (SEM) in the absence and presence of inhibitor. Polarization curves indicate that EDTA is a mixed-type inhibitor in 0.5M HCl solution and the inhibition efficiency (*IE*%) is temperature-dependent. Adsorption of EDTA on the carbon steel surface follows the Langmuir isotherm model. The thermodynamic parameters of dissolution and adsorption processes are calculated from experimental polarization data and interpretation of the results are given.

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**Keywords:** Carbon steel; EDTA; Corrosion of iron; Activation energy; Adsorption isotherms

### 1. INTRODUCTION

Acid solutions are often used in industry for cleaning, descaling and pickling of metallic structures, processes which are normally accompanied by considerable dissolution of the metal [1-5]. A useful method to protect metals and alloys deployed in service in aggressive environments against corrosion could be achieved by the addition of organic and/or inorganic species to the solution in contact with the surface in order to inhibit the corrosion reaction(s) and hence reduce the corrosion rate [6-11]. Several categories of compounds have been investigated and showed effective inhibition for the corrosion of steel in acidic environments. Most of the organic inhibitors contain nitrogen, oxygen, sulfur atoms, and multiple bonds thus facilitating their adsorption on the metal surface [12-15]. The process of adsorption of inhibitors are influenced by the nature and surface charge of the metal, the chemical structure of organic inhibitors, the type of aggressive electrolyte and the type of interaction between the organic molecules and the metallic surface [16-18].

Most of the organic inhibitors are expensive and health hazardous. Their toxic properties limit their application. Thus, it remains an important issue to find alternative low-cost and non-hazardous inhibitors for the protection of metals against corrosion [19]. Ethylenediaminetetra-acetic acid disodium (abbreviated as EDTA) is benign to the environment which is readily soluble in aqueous medium. For these and other reasons, EDTA is used in several industrial applications owing to its high ability to bind to most of metal cations. For instance, EDTA prevents metal ion impurities from changing colors of dyed products. It is also used as a preservative to some foods to prevent oxidative decoloration, which is catalyzed by metal ions [20] and is added to ascorbic acid-disodium benzoate containing soft drinks to mitigate the formation of benzene [20].

In view of the well-documented ability of EDTA to sustain iron oxidative dissolution [21-23], The corrosion behavior of several Fe-based structures has been studied in the presence of EDTA to avoid the formation of oxide-film on Fe<sup>0</sup>. For instance, the corrosion behavior of cold rolled steel has been studied in the presence of EDTA-benzotriazole (BTA) blends [24]. in which EDTA+BTA blends acted as a mixed type inhibitor whereas, EDTA alone acted as an anodic type inhibitor [24]. Also the dissolution behavior of Mg/Zn-ferrites in citric acid—EDTA formulations has been reported [25], in which the dissolution rate of single phase oxides is hindered significantly. Furthermore, the chemical reactivity and dissolution rate of Fe<sup>0</sup> materials (mostly of similar particle size) has been studied in the presence of EDTA [26]. EDTA was found to minimize the formation of oxide-film on the metal surface [26]. A blend of EDTA-Hydroxylamine Sulfate-Fe<sup>2+</sup> has been suggested as an efficient corrosion inhibitor for 316L type stainless steel in an aqueous solution of ammonium and sodium sulfates [27].

Using the virtues of EDTA, it is selected herein as a corrosion inhibitor for carbon steel in hydrochloric acid medium. The influence of adding a few ppm concentrations of Fe(III) ions on the protection efficiency of EDTA against the corrosion of steel has been investigated as well. This was done in view of the high chelating affinity of EDTA to Fe(III) with a very high stability constant at low pH [24,27].

## 2. METHODS AND MATERIALS

### 2.1. Materials

The present study was carried out using carbon steel samples. Its chemical composition was analyzed by X-ray fluorescence and is shown in Table 1.

**Table 1.** Chemical composition (wt %) of the investigated steel sample

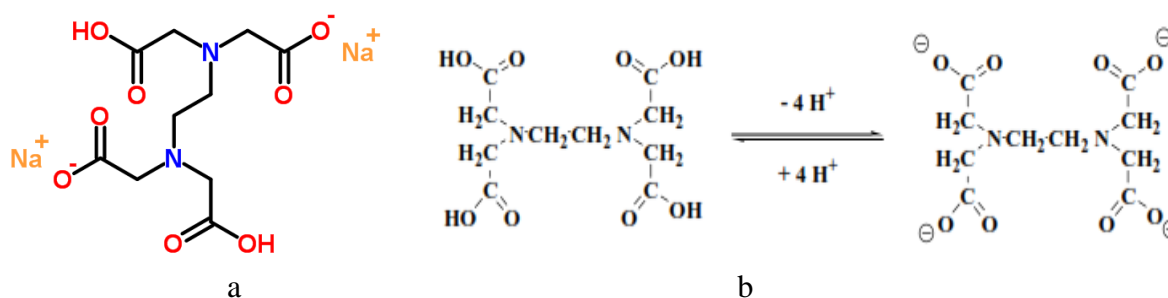
C	Mn	S	P	Fe
0.22	0.9	0.03	0.03	Balance

The used samples were mechanically cut into different dimensions: 2.0 cm, 1.0 cm and 0.5 cm. They were polished using SiC abrasive papers from 320, 500, 800 and 1200 grit, respectively, then

washed with absolute ethanol and acetone and finally dried at room temperature and stored in a moisture free desiccators before their use in corrosion studies. The carbon steel samples were impeded into a Teflon jacket leaving an exposed surface area of 1.0 cm<sup>2</sup>.

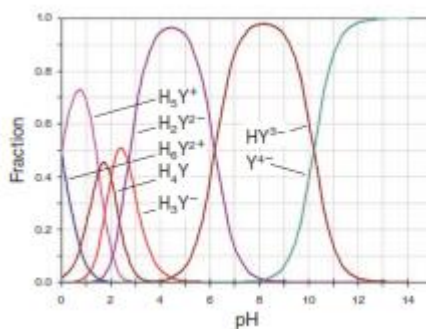
## 2.2. Electrolytes

Solution of 0.5 M HCl was prepared by a proper dilution of analytical grade 37% HCl with bidistilled water. Analytical grade (>99%) Ethylenediamine tetraacetic acid disodium (EDTA) was used. The solution in the absence of EDTA was taken as blank for comparison. A freshly prepared acid solution was used for each experiment. The experiments were carried out under unstirred naturally aerated conditions. The chemical structure of the inhibitor molecule is given in Fig. 1(a). And protonation of EDTA Fig. 1(b).



**Figure 1.** Chemical structure of inhibitor molecules and protonation

Figure 2 shows a distribution diagram for the EDTA system. At the pH of normal waters, the predominant species have one or both of the nitrogen atoms protonated. Complexation, however, requires that both nitrogens be deprotonated and it is generally assumed that the form that complexes with metal ions is Y<sup>4-</sup> [28]



**Figure 2.** A distribution diagram for the EDTA system. At the pH of normal waters, the predominant species have one or both of the nitrogen atoms protonated.

Gravimetric experiments were carried out at  $25 \pm 1^\circ\text{C}$  in 0.5 M HCl with and without the addition of EDTA. The weight loss experiments were performed for 7 days immersion time by weighing the cleaned samples before and after hanging the coupon into 100 ml of the solution. Each test was carried out three times and the mean weight loss was reported and recorded.

### 2.3. Electrochemical Measurements

#### 2.3.1. Open circuit potential measurements

The potential of carbon steel electrodes in 0.5M HCl was measured against saturated calomel electrode in the absence and presence of various concentrations of EDTA at  $25^\circ\text{C}$  for 30 min. All measurements were carried out using Gamry PCI300/4 Potentiostat/Galvanostat/Zra analyzer.

The impedance measurements were carried out at the open circuit potential (OCP) in the frequency range from 100 kHz to 0.01 Hz with a signal amplitude perturbation of 5 mV

#### 2.3.2. Potentiodynamic polarization study

Polarization study was also carried out using a three-electrode cell composed of carbon steel as the working electrode, platinum and saturated calomel electrode (SCE) as the counter and the reference electrodes, respectively. Polarization measurements were carried out at a sweep rate of 0.5 mV/s. Prior to electrochemical tests, the carbon steel electrode was cathodically cleaned for 15 min at  $-0.90\text{ V}$  (SCE) to remove the air-formed oxide film. The Echem Analyst 5.21 statistically fits the experimental data to the Stern-Geary model for a corroding system. The routine automatically selects the data that lies within the Tafel region ( $\pm 250\text{ mV}$  with respect to the corrosion potential). It then calculates the corrosion current and the corrosion rate. Inhibition efficiency ( $IE\%$ ) was calculated from corrosion current density values by using Eq. (1):-

$$IE\% = \left( \frac{i_0 - i}{i_0} \right) * 100 \quad (1)$$

where  $i_0$  and  $i$  are the corrosion rates of carbon steel in the absence and presence of inhibitor, respectively.

### 2.4. Surface Examination Study

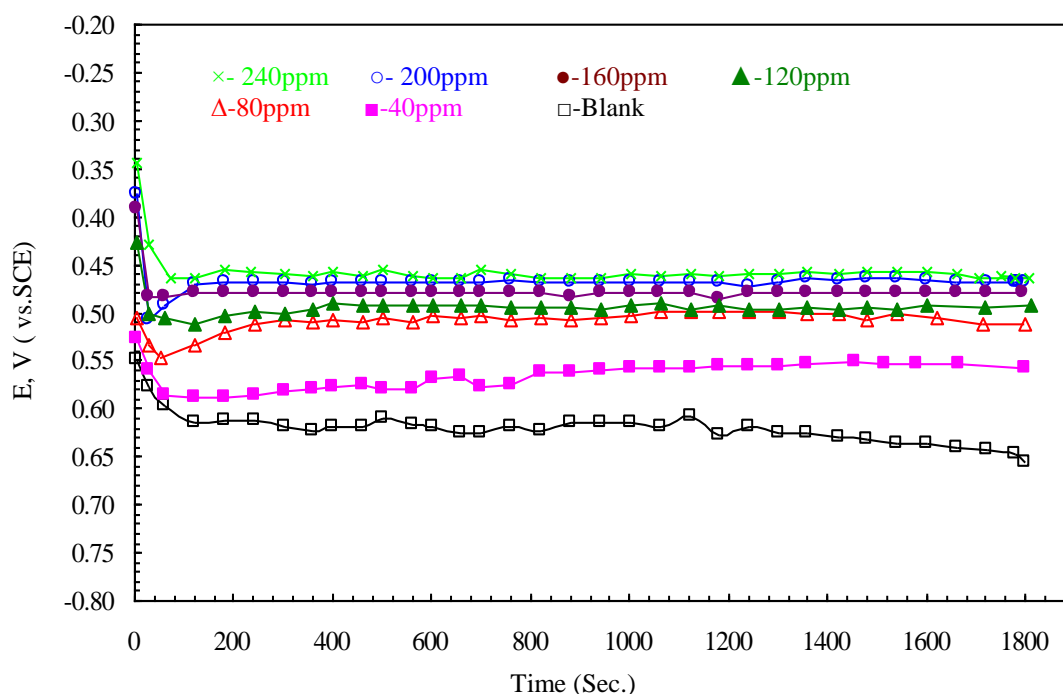
The carbon steel samples were immersed in the test solution (0.5 M HCl with/without EDTA) for a period of 24 hours. After that, the samples were dried and their surfaces were examined by scanning electron microscope (SEM, Joel-JXA-840A).

### 3. RESULTS AND DISCUSSION

#### 3.1. Open circuit potential measurements

The electrochemical behavior of carbon steel in 0.5M HCl solution containing different concentrations of EDTA was studied by monitoring the change in open circuit potential (OCP) with time. Fig. 3 shows that in the absence of EDTA, the OCP shifts towards more negative value due to the breakdown of the pre-immersion, air formed oxide film on the carbon steel surface [29].

However, in the presence of EDTA, the OCP shift towards more noble potentials with EDTA concentration. This behavior is attributed to the adsorption of EDTA onto the steel surface.



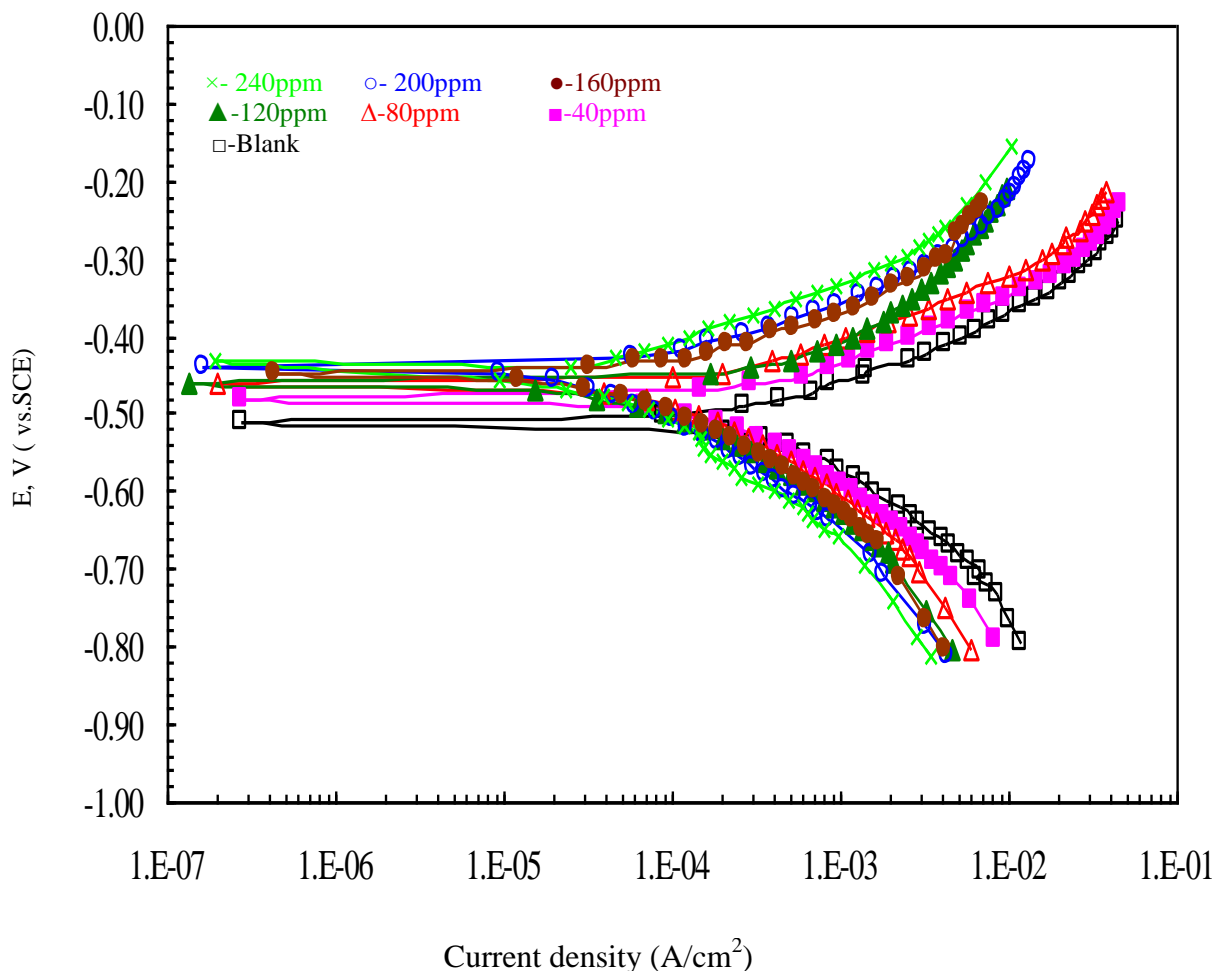
**Figure 3.** Potential–time curves for carbon steel in 0.5M HCl solution in absence and presence of different concentrations of the inhibitor at 25 °C.

#### 3.2. Polarization and weight loss measurements

The potentiodynamic polarization curves of carbon steel measured in 0.5M HCl (containing various concentrations of EDTA) are shown in Fig. 4. Note that the electrode was immersed in the test solution for 30 min prior to measurements. This Fig. depicts a progressive decrease of the cathodic and anodic currents with increasing EDTA concentration from 0 to 240 ppm. The electrochemical parameters including corrosion potential ( $E_{\text{corr}}$ ), corrosion current density ( $i_{\text{corr}}$ ), corrosion rate, anodic and cathodic Tafel slopes ( $b_a$  and  $b_c$ ), and inhibition efficiency ( $IE$  %) were calculated from the corresponding Tafel plots, and are summarized in Table 2. Inspection of this table reveals several points:

- (i) The addition of EDTA decreases the corrosion rate of carbon steel.
- (ii)  $IE$  increases with EDTA concentration.

- (iii) The changes in both the anodic and cathodic Tafel slopes observed upon the addition of EDTA indicates that both anodic and cathodic reactions are retarded.
- (iv) EDTA shifts the  $E_{\text{corr}}$  values toward more positive potential.



**Figure 4.** Potentiodynamic polarization curves of carbon steel in 0.5M HCl solution in absence and presence of different concentrations of inhibitor

**Table 2.** Electrochemical parameters obtained from potentiodynamic polarization measurements for the corrosion of carbon steel in the presence of different concentrations of EDTA at different temperatures

Temp. °C	Conc. Inhib.(ppm)	$E_{\text{cor.}}$ (mV)	$i_{\text{cor}}$ (A/cm <sup>2</sup> )	$m_{\text{my}}$	$\beta_{\text{c}}$ (mV/dec)	$\beta_{\text{a}}$ (mV/dec)	IE %
25	0	-480	$1.34 \times 10^{-3}$	15.49	140	150.3	--
	40	-451	$5.05 \times 10^{-4}$	5.84	126.2	144.2	62.31
	80	-445	$6.75 \times 10^{-5}$	0.78	126.6	144.3	94.96
	120	-450	$3.00 \times 10^{-5}$	0.35	126.8	144.5	97.76
	160	-442	$2.53 \times 10^{-5}$	0.29	127.7	144.6	98.11
	200	-434	$2.12 \times 10^{-5}$	0.25	127.7	144.5	98.42

40	240	-420	$2.01 \times 10^{-5}$	0.23	127.8	144.6	98.50
	0	-495	$1.76 \times 10^{-3}$	20.34	140.9	155.8	--
	40	-440	$8.39 \times 10^{-4}$	9.70	133.5	150.3	52.33
	80	-440	$1.93 \times 10^{-4}$	2.23	133.3	150.2	89.03
	120	-435	$9.98 \times 10^{-5}$	1.15	134.4	150.3	94.33
	160	-430	$9.66 \times 10^{-5}$	1.12	134.4	150.2	94.51
	200	-430	$6.21 \times 10^{-5}$	0.72	136.5	150.3	96.47
	240	-428	$5.11 \times 10^{-5}$	0.59	137.7	150.4	97.10
50	0	-505	$4.25 \times 10^{-3}$	49.12	145.4	157.2	--
	40	-457	$8.66 \times 10^{-4}$	10.01	127.4	157.2	49.00
	80	-460	$4.88 \times 10^{-4}$	5.64	132.2	157.3	88.53
	120	-460	$2.15 \times 10^{-4}$	2.48	133.3	158.2	94.94
	160	-462	$1.79 \times 10^{-4}$	2.07	134.5	158.6	95.79
	200	-470	$1.47 \times 10^{-4}$	1.70	134.9	158.9	96.54
	240	-480	$1.37 \times 10^{-4}$	1.58	134.9	159.2	96.78
	60	0	-512	$6.65 \times 10^{-3}$	76.85	147.8	143.1
40		-475	$3.48 \times 10^{-3}$	40.22	136.1	143.3	47.69
80		-480	$9.55 \times 10^{-4}$	11.04	136.3	143.4	85.64
120		-515	$4.66 \times 10^{-4}$	5.39	137.4	143.3	92.99
160		-515	$4.32 \times 10^{-4}$	4.99	137.6	143.5	93.50
200		-520	$4.11 \times 10^{-4}$	4.75	137.8	143.6	93.82
240		-525	$4.01 \times 10^{-4}$	4.63	137.8	143.6	93.97

It has been reported that if the displacement in  $E_{corr}$  (inhibited) is more than  $\pm 85$  mV compared to  $E_{corr}$  (uninhibited), the inhibitor can be considered as a distinctive cathodic or anodic type [30-32]. In the present study, though a small deviation in the  $E_{corr}$  is observed, the average displacement is effectively less than 85 mV, which suggests that EDTA is a mixed type inhibitor.

The inhibition efficiency of EDTA against the corrosion of carbon steel is also evident from the results of the weight loss tests that are listed in Table 3. It shows a significant reduction in the corrosion rate in the presence of EDTA is observed consistently with the observed behavior obtained from the analysis of the potentiodynamic polarization experiments.

**Table 3.** Inhibition efficiencies for different concentrations of EDTA for the corrosion of carbon steel in 0.5 M HCl obtained from weight loss measurements

[EDTA] / ppm	0	40	80	120	160	200	240
IE%	0.00	87.88	89.32	89.01	88.74	89.70	92.25
mmy	22.1432	2.6843	2.3647	2.4326	2.4926	2.2818	1.7153
$\theta$	0.00	0.8788	0.8932	0.8901	0.8874	0.8970	0.9225

3.3. EIS measurements

EIS is a powerful technique in the investigation of the corrosion behaviour of metals and alloys as well as the study of adsorption phenomena [33-39]. The impedance data of steel in 0.5 M HCl in the absence and/or the presence of EDTA are presented as Nyquist plots in Fig. 5. The Nyquist plots show slightly depressed arcs with their centres below the x-axis. This is a characteristic behaviour of solid electrodes with a large number of surface defects such as kinks, jags and ledges, inhomogeneities and variations in composition resulting from the corrosion of the metal surface [40-42].

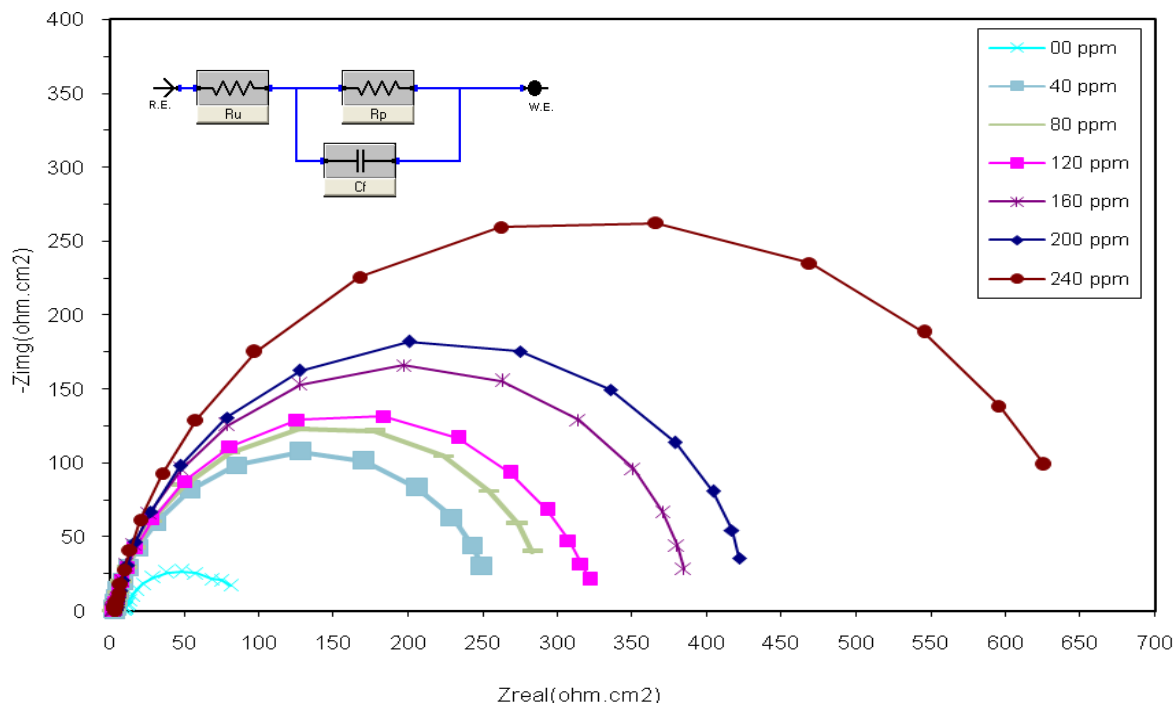


Figure 5. EIS of the corrosion of carbon steel in 0.5M HCl solution in absence and presence of different concentrations of inhibitor

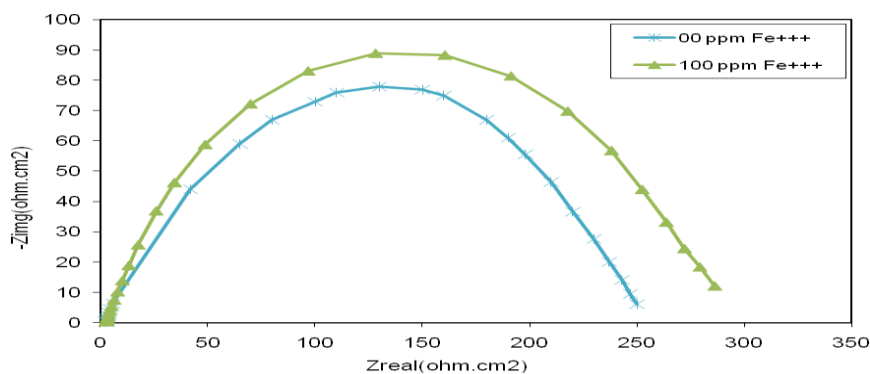


Figure 6. Nyquist plots of mild steel in 0.5M HCl solution containing 80 ppm EDTA in the absence and presence of 100 ppm Fe<sup>3+</sup> ions



Fig. 5 shows that, increasing the concentration of EDTA from 40 to 240 ppm increases the diameter of the semicircle indicating that the surface is increasingly more protected. These increases are more pronounced in the presence of a few ppm amounts of Fe(III) ions (shown in Fig. 5) indicating that Fe(III) ions caused a paramount enhancement of the inhibiting efficiency of EDTA, possibly due to the formation of a very stable 1:1 Fe(III)-EDTA complex (stability constant  $K \cong 10^{22}$ ).

The impedance data of carbon steel were analyzed and fitted to a simple equivalent circuit (represented in the inset of (Fig. 5) consisting of a parallel combination of a capacitor ( $C_{dl}$ , representing the double layer capacity of the interface) and a resistor ( $R_p$ , representing the polarization resistance) in a series with the solution resistance component ( $R_s$ ). The impedance of this circuit,  $Z$ , is related to the frequency of the a.c. signal ( $f$ ),  $R_p$ ,  $C_{dl}$ , and  $R_s$ , [43].

$$Z = R_s + [R_p / (1 + (j2\pi f C_{dl} R_p)^\alpha)] \quad (2)$$

where  $\alpha$  is an empirical parameter ( $0 \leq \alpha \leq 1$ ) which measures the extent of deviation from the ideal RC-behaviour of the electrode/electrolyte interface. Eq. (2) is a Cole–Cole type frequency distribution which is frequently used to describe the occurrence of depressed semicircular arcs [40]. The corrosion of iron in 0.5 M HCl turns the surface rough and inhomogeneous. Thus, the capacitance is presented through a constant phase element (CPE). The calculated equivalent circuit parameters are presented in Table 4.  $IE$  of the inhibitor was, then, calculated using the following correlation [44].

$$IE\% = [1 - (R_p^{(b)} / R_p^{(in)})] \times 100 \quad (3)$$

where  $R_p^{(b)}$  and  $R_p^{(in)}$  are the polarization resistances in the absence and the presence of the inhibitor, respectively. Table 4 lists the values of  $IE$  obtained under various conditions. Inspection of this table reveals a significant enhancement of  $IE$  in presence of EDTA and Fe(III) ions. For instance, 80 ppm EDTA (without Fe(III) ions) has a  $IE$  value of 77% compared to 85% (with 100 ppm Fe(III) ions). Further increase of the concentration of EDTA causes a monotonic increase in  $IE$ .

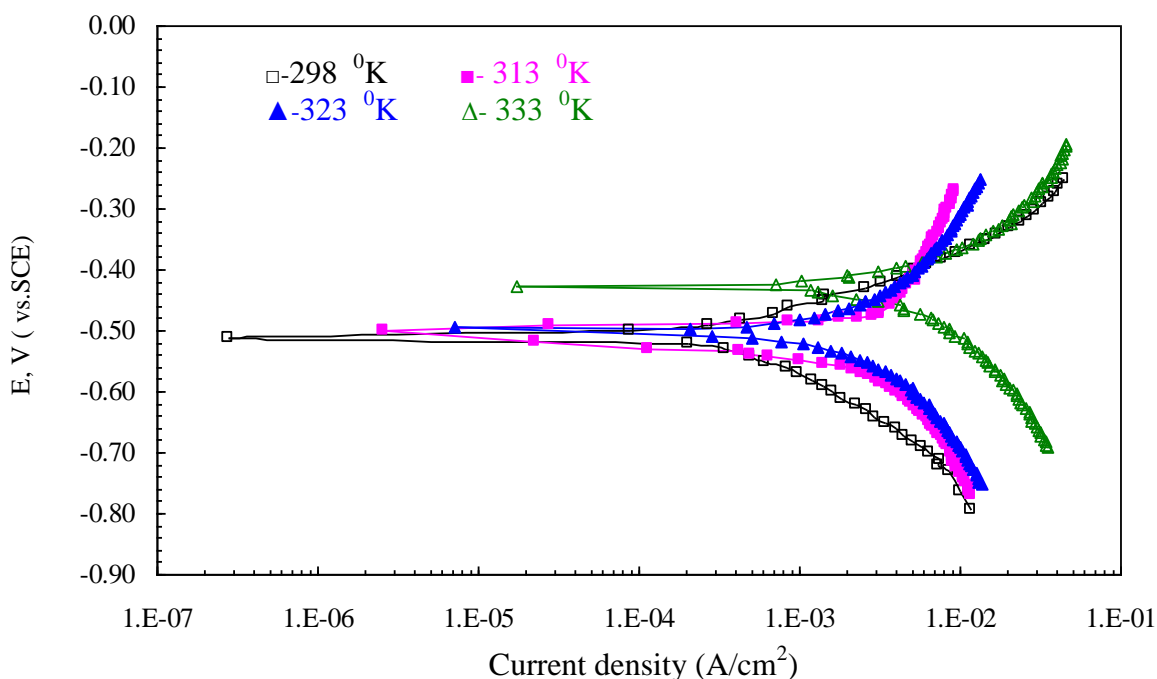
**Table 4.** Impedance parameters and inhibition efficiency for the corrosion of carbon steel in the presence of different concentrations of EDTA at 25°C

[EDTA] / ppm	$R_p$ (ohms)	$R_s$ (ohm)	$C_{dl}$ (F)	$IE$ %	$\theta$
0	59.96	4	6.44E-04	0	0.00
40	223.70	3	3.21E-05	73	0.73
80	256.10	3	3.33E-05	77	0.77
120	285.00	3	3.19E-05	79	0.79
160	348.90	4	3.25E-05	83	0.83
200	383.00	3	3.29E-05	84	0.84
240	548.90	3	3.80E-05	89	0.89
80 ppm EDTA +100 ppm Fe <sup>3+</sup>	341	3	3.25E-05	82	0.82

### 3.3. Effect of Temperature

The effect of temperature on the corrosion behavior of carbon steel was studied by polarization measurements in the absence and presence of EDTA. The data are shown in Fig. 7, Fig. 8 respectively. The  $IE$  and other parameters are listed also in Table 2 at different temperatures and concentrations of EDTA. Inspection of Fig. 7, Fig. 8 and Table 2, reveals the following points:

- (i)  $E_{\text{corr}}$  shifts toward more negative potentials in the absence and presence of EDTA with temperature.
- (ii)  $IE\%$  decreases considerably with the increase of temperature.

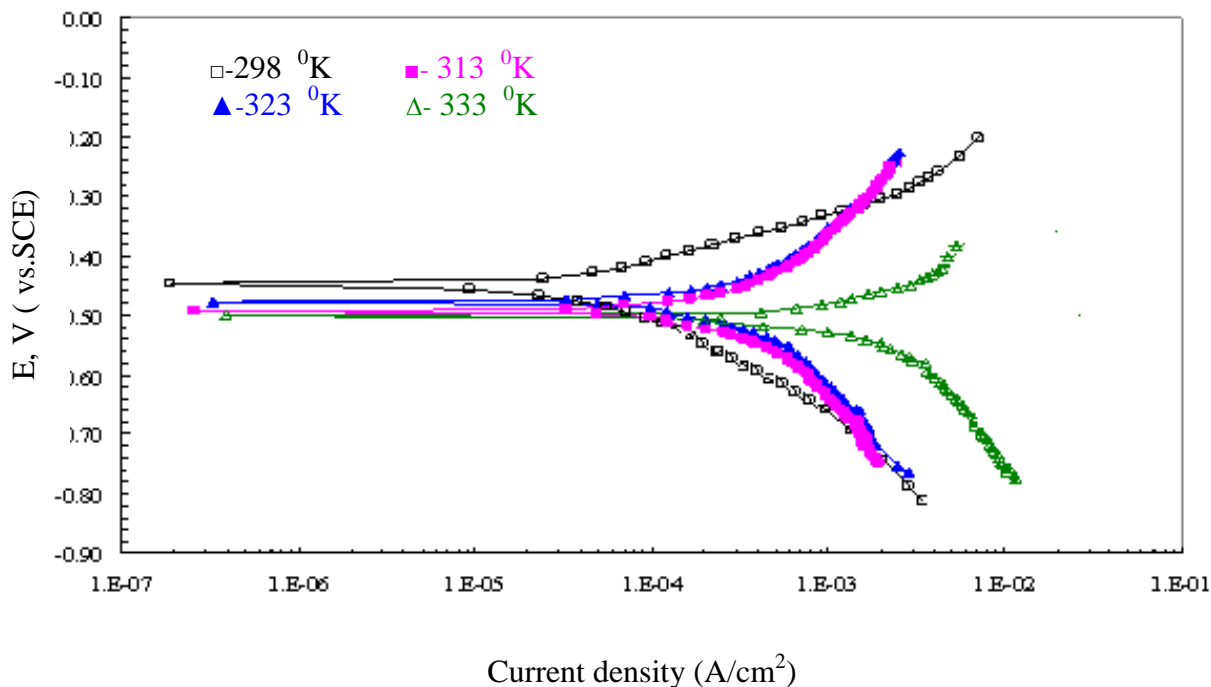


**Figure 7.** Anodic and cathodic polarization curves of carbon steel in 0.5M HCl at different temperatures

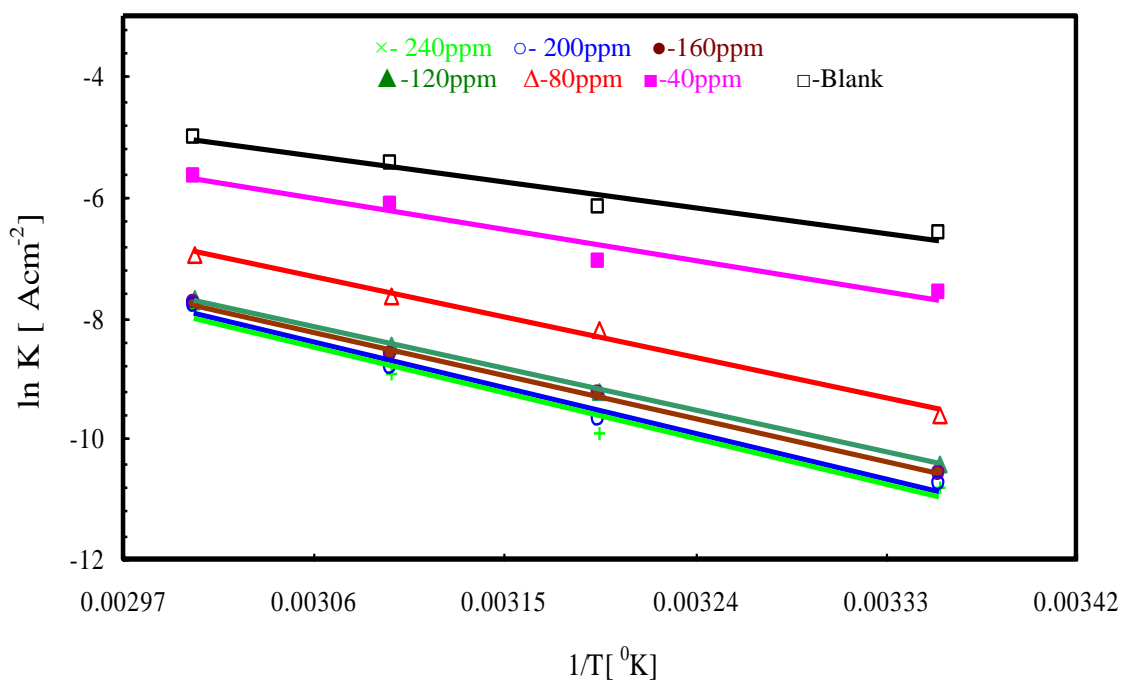
The activation parameters for the corrosion process were calculated from Arrhenius-type plot according to the following equation[45]:

$$k = A \text{Exp}(-E_a/RT) \tag{4}$$

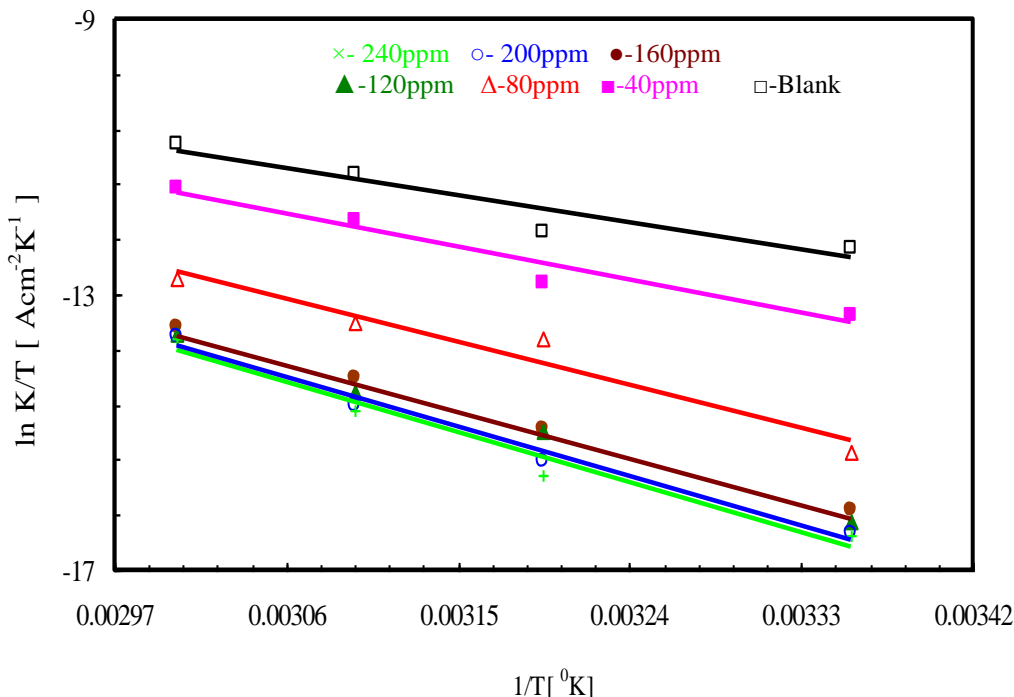
Where:  $E_a$  is the apparent activation energy,  $k$  is the corrosion rate,  $R$  is the universal gas constant and  $A$  is the Arrhenius pre-exponential constant. By plotting  $\ln(k)$  versus  $(1/T)$ , as shown in Fig. 9, a straight line with a slope equals  $-E_a/R$  is obtained. The values of  $E_a$  are shown in Table 5.



**Figure 8.** Anodic and cathodic polarization curves of mild steel in 0.5M HCl + 240 ppm EDTA at different temperatures



**Figure 9.** Ln k vs. 1/T for carbon steel dissolution in 0.5M HCl in the absence and presence of inhibitor



**Figure 10.** Transition state plots for carbon steel dissolution in 0.5M HCl in the absence and presence of inhibitor.

**Table 5.** The values of activation parameters  $E_a$ ,  $\Delta H$  a and  $\Delta S$  for carbon steel in 0.5M HCl in the absence and the presence of different concentrations of EDTA

[EDTA] / ppm	$E_a$ (kJmol <sup>-1</sup> )	$\Delta H$ (kJmol <sup>-1</sup> )	$\Delta S$ Jmol <sup>-1</sup> K <sup>-1</sup>
0	39.37	36.75	19.6
40	58.93	56.32	77.39
80	63.84	61.23	79.88
120	70.31	67.69	91.27
160	71.35	68.73	95.72
200	93.78	91.16	168.23
240	94.07	91.46	169.84

Table 5 shows that  $E_a$  increases with EDTA concentration. The values of which indicate that a physical adsorption mode of EDTA prevails on the carbon steel surface (*c.f.* section 3.4).

Another form of Arrhenius equation is [1,45]:

$$k = (RT/Nh) \text{Exp}(-\Delta H/RT) \text{Exp}(\Delta S/R) \quad (5)$$

By plotting  $\ln(k/T)$  versus  $(1/T)$ , the slope of the line is  $-\Delta H/R$  and the intercept is  $\Delta S/R$ . By evaluating the temperature dependence of the corrosion rate constant, the enthalpy and entropy of dissolution can be determined from Fig. 10 (data are shown in Table 5). The positive sign of  $\Delta H$

reflects the endothermic nature of the steel dissolution process. The increase of  $\Delta S$  reveals that an increase in disordering takes place on going from reactants to the activated complex [46].

### 3.4. Adsorption isotherm

Information on the interaction between the inhibitor molecules and the metal surface can be provided by adsorption isotherm. The degree of surface coverage ( $\theta$ ) for different concentrations of EDTA in 0.5 M HCl was evaluated from Tafel polarization using [17]:

$$\theta = \frac{i_0 - i}{i_0} \quad (6)$$

Table 6 shows the values of  $\theta$  at different conditions. Attempts were made to fit these values to various isotherms. The data were fitted to various isotherms such as the Langmuir adsorption isotherm, Temkin, Freundlich and Frumkin.

**Table 6.** The values of coverage obtained from the corrosion current for different concentrations of EDTA in 0.5M HCl at different temperatures

[EDTA] / ppm	$\theta$			
	298 K	313 K	323 K	333 K
40	0.62	0.52	0.49	0.48
80	0.95	0.79	0.89	0.86
120	0.98	0.94	0.95	0.93
160	0.98	0.95	0.96	0.94
200	0.98	0.96	0.97	0.94
240	0.99	0.97	0.97	0.94

The Langmuir's adsorption isotherm was found to represent the best fitting of the data in which EDTA is considered to form a physically adsorbed on carbon steel. The Langmuir's isotherm can be written as follows:

$$\theta = k' C / (1 + k' C) \quad (7)$$

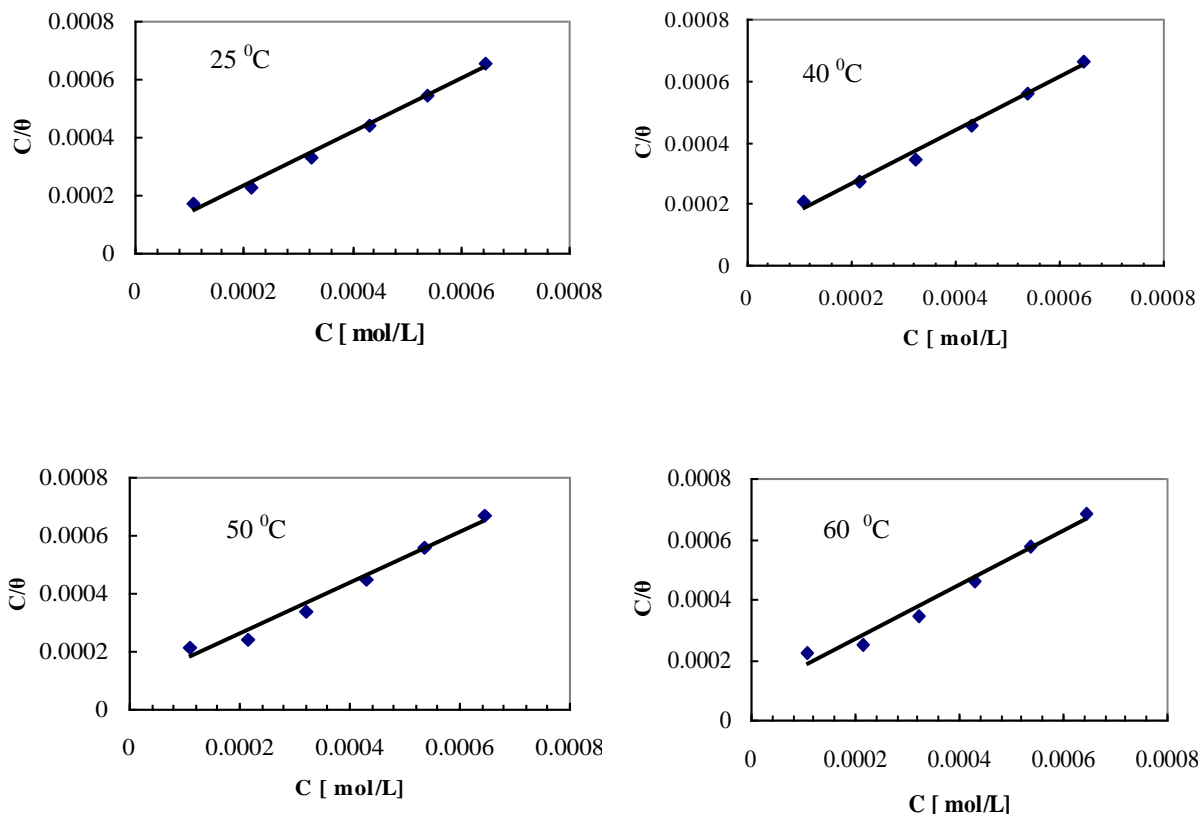
Where:  $k'$  is the equilibrium constant for the adsorption process.

Rearrangement of Equation 7 [45] gives:

$$\frac{C}{\theta} = \frac{1}{k'} + C \quad (8)$$

By plotting  $C/\theta$  vs.  $C$  for all the inhibitors at different temperatures, straight lines are obtained (Fig. 11). This indicates that EDTA is adsorbed on the metal surface through a physical adsorption made with negligible no interaction among the adsorbed species [47]. Values of equilibrium constant ( $k'$ ) ( $\text{mol}^{-1}$ ) deduced from the isotherms are presented in Table 7. It could be observed that  $k'$

decreases with increasing temperature indicating that the inhibitor is easily physisorbed onto the carbon steel surface at lower temperatures. But when the temperature is relatively higher, the adsorbed inhibitors tend to desorption.



**Figure 11.** Curve fitting of the corrosion data for carbon steel in 0.5M HCl in the presence of EDTA according to Langmuir thermodynamic kinetic model at different temperatures

Values of  $k'$  were used to calculate the free energies of adsorption ( $\Delta G_{ads}$ ) of EDTA on carbon steel surface using the following equation [45],

$$\Delta G_{ads} = -RT \ln(55.5k) \tag{9}$$

where 55.5 is the molar concentration of the acid in the solution. The calculated values of  $\Delta G_{ads}$  at different temperatures and concentrations are shown in Table 8.

**Table 7.** Values of equilibrium constant (K) at different temperatures

Temp. / K	Equilibrium constant ( $k'$ ) (mol <sup>-1</sup> )
298	1.85x10 <sup>4</sup>
313	1.08x10 <sup>4</sup>
323	0.97x10 <sup>4</sup>
333	0.94x10 <sup>4</sup>

**Table 8.** Data from Langmuir's isotherms for EDTA on the carbon steel surface in 0.5M HCl at concentration and temperatures

[EDTA] / ppm	$\Delta G_{ads.}$			
	298 K	313 K	323 K	333 K
40	-30.16	-32.29	-33.50	-34.61
80	-23.47	-28.36	-27.65	-29.13
120	-20.46	-23.90	-24.36	-26.02
160	-19.32	-23.07	-23.09	-25.01
200	-18.33	-21.34	-21.97	-24.26
240	-17.75	-20.36	-21.28	-23.68

The values are negative and are less than the threshold value of  $-40$  kJ/mol required for chemical adsorption, hence the adsorption of EDTA on carbon steel surface is spontaneous and is consistent with the mechanism of physical adsorption [47]. as depicted from the values of  $E_a$  and  $k'$  change with temperature.

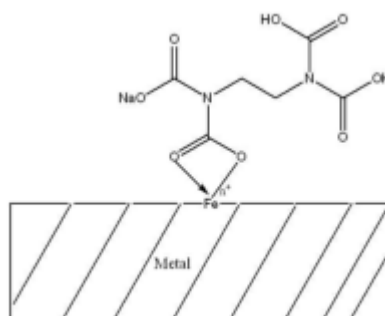
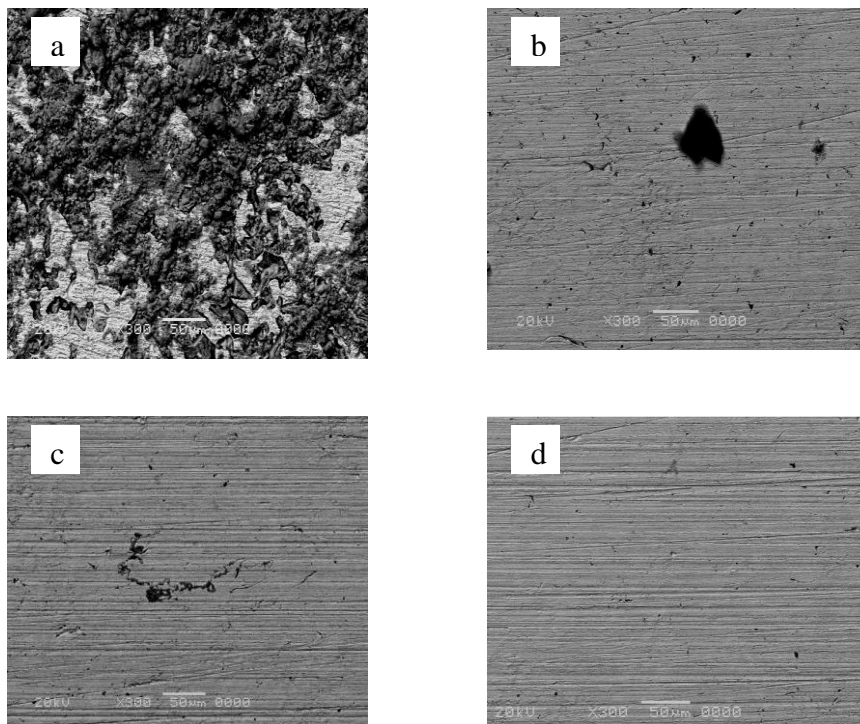
**Figure 12.** Interaction between carboxylate groups in EDTA with the metal

Fig.12 shows that the carboxylate groups in EDTA adsorbed on the steel surface through the lone pairs of electrons of the oxygen atoms forming a covering film. This arrangement of the oxygen atoms may lead to the conclusion that the carboxylate compound is forced to be adsorbed horizontally onto the steel surface. This adsorption gives rise to a large covered surface area with a small number of adsorbed molecules. Therefore, good inhibition efficiency could be obtained by relatively low concentrations of the inhibitor.

### 3.5. Scanning electron microscopy (SEM)

The scanning electron microscope images (Fig. 13) were recorded to monitor the change in carbon steel surface morphology in the presence and absence of EDTA.



**Figure 13.** Scanning electron micrographs of carbon steel samples after immersion in 0.5 M HCl solution for 24 h in (a) the absence and presence of (b) 100, (c) 200 and (d) 240 ppm of EDTA.

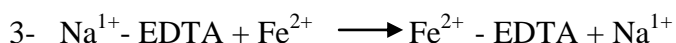
The SEM images show the features of carbon steel surface after being immersed for 24 hours in 0.5M HCl with and without different concentrations of EDTA. Fig. 13-a reveals that, the surface of carbon steel was strongly damaged and covered with corrosion products in absence of EDTA, but in presence of EDTA (Fig. 13b-d) the surface of carbon steel is more uniform without the observation of pits and/or adsorbed corrosion products. This indicates that dissolution of iron was hindered by the adsorption of EDTA molecules on the steel surface and thereby reduce the rate of corrosion.

### 3.6. Mechanism of corrosion inhibition

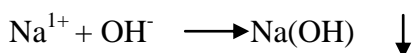
Based on the above results, the following mechanism of corrosion inhibition is proposed.

1- When carbon steel is immersed in the solution Na-EDTA, complexes diffuse from the bulk of the solution towards the metal surface.

2- On the metal surface  $\text{Na}^+$ -EDTA complexes are converted into  $\text{Fe}^{2+}$ -EDTA complexes on the anodic sites.



The released  $\text{Na}^+$  combines with  $\text{OH}^-$  to form Na(OH) on the cathodic site.





#### 4. CONCLUSIONS

The following points can be drawn from this study:

- 1- EDTA is found to reduce both the anodic and the cathodic reactions that are taking place during the corrosion of the carbon steel in 0.5M HCl.
- 2- The inhibition efficiency increase with EDTA concentration and/or the addition of a few ppm of Fe(III) ions.
- 3- The thermodynamic parameters reveal that the inhibition of carbon steel corrosion by EDTA is due to the formation of a physo-sorbed film on the metal surface.
- 4- Adsorption of EDTA was found to follow the Langmuir adsorption isotherm.
- 5- SEM examination of the steel surface confirms the good tolerance of the carbon steel against corrosion of the aggressive HCl solution in the presence of EDTA.

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