

# Corrosion Behavior of Carbon Steel in HCl Solution by Fe and Cr Complexes with a Schiff-Base Ligand Derived from Salicylaldehyde and 2-(2-aminoethylamino)ethanol

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A comparative study of Fe and Cr complexes with a Schiff-base ligand (1-[(2-hydroxyethyl)amino]-2-(salicylideneamino)ethane) as inhibitors for carbon steel corrosion in 0.5M HCl solution at 25°C was carried out. Corrosion measurements based on the weight loss method, potentiodynamic polarization curves, and electrochemical impedance spectroscopy (EIS) indicate that Fe complex, in most cases, accelerates carbon steel corrosion in HCl while Cr complex act as moderately inhibitor. The UV-visible and the attenuated total reflectance–Fourier transform infrared spectroscopy (ATR-FTIR) studies of the electrode surface confirmed existence of an adsorbed film of the complexes on the electrode surface. Adsorption of Cr complex obeys the Langmuir adsorption isotherm with a very low value of free energy of adsorption  $\Delta G^\circ$  (physisorption). Cr complex acts as mixed type inhibitor, with the dominating effect on the anodic dissolution of iron. The mechanism of adsorption is discussed and it is concluded that the adsorbed chloride ions on the metal surface could be stabilized in their anionic form by hydrogen bonding of oxygen and nitrogen atoms in the tail of the complexes, like a crab-claw. The accelerating properties of Fe complex could be due to the formation of non adherent and/or soluble complex that is readily removed from the metal surface.

*Keywords: acid corrosion inhibitors, adsorption isotherms, Schiff-base complex, carbon steel.*

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## INTRODUCTION

Recently, researchers attentions have been often focused on inter-disciplinary areas. This has been partially the result of reports concerning interaction of various chemicals, including molecules and their properties. These properties can be important in understanding some activities or efficiency on molecule structure. In the last decade, various hetero atom substances were studied extensively, among them a good number of Schiff bases [1–3]. As is known, nitrogen and oxygen containing ligands and their complexes have a number of potential technological applications as catalysts of chemical reactions [4], as well as with the account of their biological [5], antifungal [6], anti tumor and anti HIV activities [7]. The main results showed that some mechanical properties depend on the electronic and structural properties of the inhibitor molecule such as aromatic and functional groups, electron density on donor atoms and  $\pi$  orbital character of donor electrons [8, 9].

Inhibitor is a keyword in the case of corrosion prevention by changing the chemistry of corrosive media. The use of inhibitors is one of the most practical methods for protection against corrosion especially in acidic conditions [10, 11]. A Schiff base is an organic compound having general formula  $R-C=N-R'$  where  $R$  and  $R'$  are aryl, alkyl or cycloalkyl, or heterocyclic groups formed by the condensa-

tion of an amine and a carbonyl group; it is a potential inhibitor for different metallic surfaces. Several Schiff bases were reported as effective corrosion inhibitors for carbon steel in HCl media [12–14]. The existing data show that those inhibitors act by adsorption on the metal/solution interface. This phenomenon could take place via: (i) electrostatic attraction between the charged metal and the charged inhibitor molecules, (ii) dipole-type interaction between unshared electron pairs in the inhibitor with the metal, (iii)  $\pi$  electron interaction with the metal, and (iv) combination of all of the above [15]. On the other hand, some organic inhibitors could react with metal ions resulting from corrosion process to form analogous complexes spontaneously that may decrease the corrosion rate. However, studies about metal complexes as corrosion inhibitors for carbon steel in acid solutions are extremely limited in literature [16, 17]. Abdel-Gaber et al. [18] proposed corrosion inhibition through a bulky Co(III) Schiff-base complex molecule that could cover more than one active site where carbon steel was immersed in HCl solution. Some metal complexes of a Schiff base are suggested as effective corrosion inhibitors for Cu and Al [19, 20].

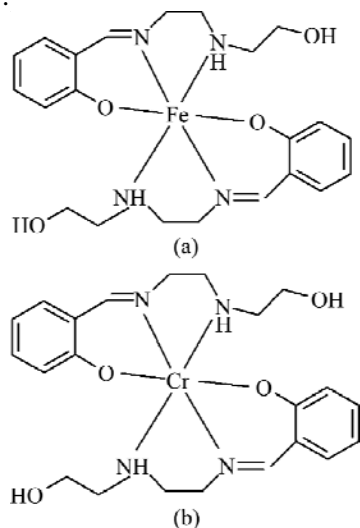
In continuation of our ongoing programme to develop the inhibitive properties of metal complexes in acidic media [21, 22], we present here the inhibitive properties of two Schiff-base complexes, namely, Bis(N-(2-(2-hydroxyethylamino)ethyl)-sali-

cylideneimine)chromium(III) chloride (Cr complex) and Bis(N-(2-(2-hydroxyethylamino)ethyl)-salicylideneimine)iron(III) chloride (Fe complex) on CK10 carbon steel in HCl solution studied by gravimetric and electrochemical techniques. It is worth mentioning that these compounds are quite stable in aerated HCl solutions where no change in color or no precipitation was observed during the run of the experiments.

## EXPERIMENTAL

### *Synthesis of Schiff-base metal complexes*

The Schiff-base Fe complex was synthesized by the reaction of the precursor compound N-(2-(2-hydroxyethylamino)ethyl)salicylideneimine (L) with  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ . The precursor compound L was synthesized by the reaction of equimolar salicylaldehyde (0.84 mmol, 103 mg) and 2-(2-aminoethylamino)ethanol (1.2 mmol, 122 mg) in anhydrous ethanol (5 ml). Also,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (0.12 mmol, 33 mg) in anhydrous ethanol (5 ml) was added to the previous solution. After keeping the solution in air to evaporate about half of the solvent, dark brown prisms of the complex compound were formed. The crystals were isolated, washed with ethanol three times and dried in a vacuum desiccator using silica gel. The Schiff-base Cr complex was synthesized in the same procedure [23]. All chemicals chosen for our study were of analytical grade, double distilled water was used throughout the experiment. The chemical structure of synthesized inhibitors is shown in Figure 1.



**Fig. 1.** Chemical structures of Schiff-base metal complexes: (a) Fe complex and (b) Cr complex.

### *Electrodes*

Prior to all measurements, the carbon steel specimens, having the composition (in wt%) 0.099 C, 0.166 Si, 0.346 Mn, 0.131 Cr, 0.040 Mo and the remainder iron, were abraded successively with fine grade emery papers (600–1200 grade). The speci-

mens were washed thoroughly with double distilled water and finally degreased with acetone and then dried at room temperature. For weight loss measurements, carbon steel specimens with dimensions: 26 mm in diameter and 2 mm thickness, were used. For polarization and electrochemical impedance studies, the metal was embedded in epoxy resin so as to expose a geometrical surface area of  $1 \text{ cm}^2$  to the electrolyte. The aggressive solution 0.5M HCl was prepared by dilution of analytical grade HCl (37%) with double distilled water and all experiments were carried out in unstirred solutions.

### *Weight loss measurements*

Gravimetric corrosion measurements were carried out according to the standard procedure described in the Annual Book of the American Society for Testing and Materials [24]. In brief, carbon steel specimens in triplicate were immersed for a period of 4 h in 50 ml HCl 0.5M containing various concentrations of studied inhibitors. After immersion, the surface of the specimen was cleaned by double distilled water followed by rinsing with acetone. The mass of the specimens before and after immersion was determined using an analytical balanced accurate to 0.1 mg. In the present study, for the specified experimental conditions, relative differences between replicate experiments were found to be less than 6% indicating good reproducibility. For further data processing, the average of the three replicate values was used. For each experiment, a freshly prepared solution was used and the solution temperature was controlled thermostatically at a desired value.

### *Electrochemical techniques*

Electrochemical impedance (EIS) measurements and potentiodynamic polarization studies were carried out using an electrochemical unit (model PARstat 2273). A three electrode setup was employed using graphite of a convenient area as counter electrode and a saturated calomel electrode (SCE) as reference electrode. The working electrode carbon steel (7.5 cm long stem) with the exposed surface of  $1.0 \text{ cm}^2$  was immersed into aggressive solutions with and without an inhibitor; the open circuit potential was measured after 30 min, (the stable potential time). EIS measurements were performed at corrosion potentials,  $E_{corr}$ , over a frequency range of 100 kHz to 10 mHz, with an AC signal amplitude perturbation of 10 mV peak to peak. Potentiodynamic polarization studies were performed with a scan rate of  $1 \text{ mVs}^{-1}$  in the potential range from 250 mV below the corrosion potential to 250 mV above the corrosion potential. All potentials were recorded with respect to the SCE. All measurements were done at  $25 \pm 0.1^\circ\text{C}$ . Impedance fitting was performed using Z-View software.

### Surface examination

The attenuated total reflectance–Fourier transform infrared spectroscopy (ATR–FTIR) was used to investigate the coupon surface after 24 h immersion in the test solutions. A JASCO, V-570, Rev. 1.00 FTIR fitted with an ATR stage was used for surface infrared measurements. Spectrophotometer technique was employed in this study to investigate the stability and adsorption of the complexes under study. Spectra were achieved using a UV–visible double beam ratio recording, spectrophotometer JASCO model V-670.

## RESULTS AND DISCUSSION

### Weight loss measurements

The weight loss method of monitoring corrosion rate is useful because of its simple application and reliability [25]. Therefore, a series of weight loss measurements were carried out with and without changes in of the complexes. The behavior of corrosion inhibition for carbon steel by both Cr and Fe complexes was investigated by the corrosion weight loss measurements in 0.5M HCl solution and is summarized in Table 1.

The weight loss, surface coverage ( $\theta$ ), and inhibition efficiency ( $IE_w(\%)$ ) for different Cr and Fe complexes concentrations were reported. The inhibition efficiency ( $\%IE_w$ ) was calculated from the equation:

$$IE_w \% = \frac{W_u - W_i}{W_i} \times 100,$$

where  $W_u$  and  $W_i$  are the corrosion rates of iron without and with inhibitors, respectively. It is indicated that the inhibition efficiency of carbon steel increases with the increase of Cr complex concentration up to 60% at 25°C. However, the inhibition efficiency decreased with rise in concentration, suggesting that an increase in concentration resulted in desorption of some Cr complex molecules adsorbed from the metal surface.

A comparison of the corrosion inhibition effect afforded by Cr and Fe complexes revealed that Cr complex is a much better inhibitor than Fe complex for the acid-induced corrosion of carbon steel. The corrosion rates in different concentrations of inhibitors are shown in Table 1. An average corrosion rate of steel in 0.5M HCl is 30.2 mpy but, in the presence of 50 ppm of Cr complex, the corrosion rate goes down to 12.1 mpy.

### Polarization measurements

The effect of concentrations of Cr and Fe complexes on the values of  $E_{corr}$  obtained in HCl solution is depicted in Figure 2. It shows that a value of  $E_{corr}$  obtained in HCl solution is shifted in the noble

(positive) direction. This behavior indicates that this compound is mainly adsorbed on the anodic sites of the surface. On the other hand, Fe complex does not shift  $E_{corr}$  in HCl solution. No shift of  $E_{corr}$  indicates that this compound is not mainly adsorbed on the cathod and anodic sites of the steel surface.

Both anodic and cathod polarization curves for carbon steel in 0.5M HCl at various concentrations of Cr and Fe complexes are shown in Fig. 3a,b.

The respective kinetic parameters, including the corrosion current density ( $i_{corr}$ ), corrosion potential ( $E_{corr}$ ), cathodic Tafel slope ( $\beta_c$ ) and anodic Tafel slope ( $\beta_a$ ), are listed in Table 2.

The degree of the surface coverage ( $\theta$ ) and the percentage of the inhibition efficiency ( $IE\%$ ) were calculated using the following equations [26]:

$$\theta = \frac{i_{corr}^0 - i_{corr}}{i_{corr}^0},$$

$$IE\% = \theta \times 100,$$

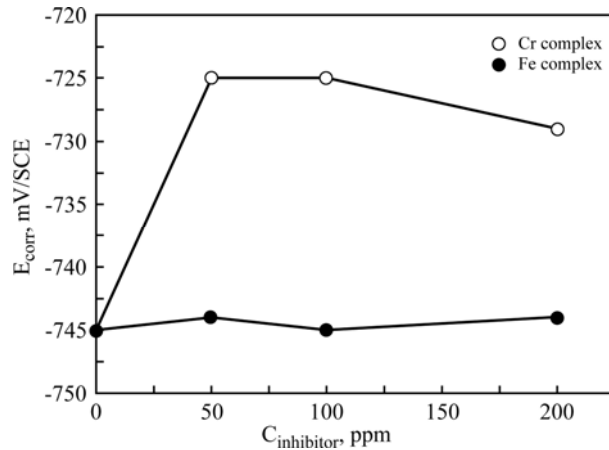
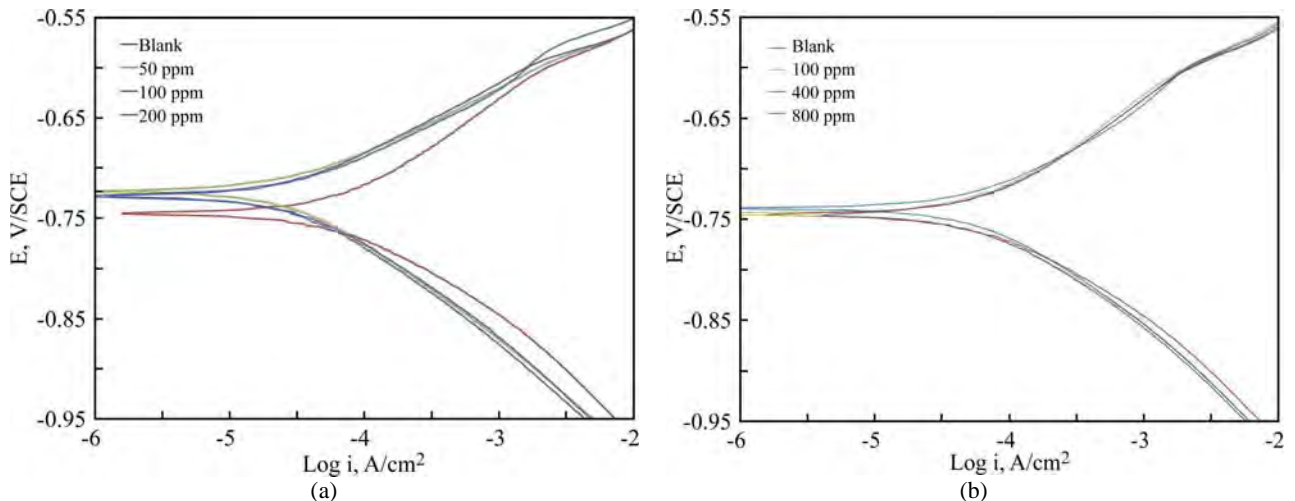
where  $i_{corr}^0$  and  $i_{corr}$  are corrosion current densities in the absence and presence of inhibitors, respectively. Values of  $\beta_a$  and  $\beta_c$  obtained in the additive-free medium were found to be 96.2 and -88.9 mV/decade, respectively. Comparison of curves showed that with respect to the blank, increasing the concentration of Cr complex gave rise to a consistent increase in the cathod current density but addition of Cr complex did not modify the mechanism of this process [27]. Cr complex acts as a mixed-type inhibitor with the predominant effect on the anodic reaction. The value of  $i_{corr}$  obtained in pure HCl solution was found to be 63.8  $\mu\text{A}/\text{cm}^2$ . This value decreases by 54–56% in the presence of 50–200 ppm of Cr complex. At the lowest examined concentration (50 ppm), Cr complex inhibits the anodic reaction (Fe dissolution) and accelerates the cathod reaction (hydrogen evolution). The overall corrosion process is slightly retarded. Further addition of Cr complex results in the displacement of the anodic branches to a low corrosion current density, while the cathod branch remains approximately unaffected. The values of the maximum inhibitor efficiency are lower than in the gravimetric tests because they are recorded at a much shorter time interval and reflect the corrosion behavior at the initial stage. The results obtained for Fe complex indicated the acceleration effect of these additives towards the corrosion of carbon steel in HCl solution. The potentiodynamic data confirm the conclusions of the gravimetric tests, giving some additional information about the type of inhibition.

### Electrochemical impedance measurements

EIS measurements of a steel electrode at its open circuit potential after 0.5 h of immersion in 0.5M HCl solution alone and in the presence of various inhibitor concentrations were performed over the frequency range from 100 KHz to 10 MHz. The

**Table 1.** Weight loss results of carbon steel corrosion in 0.5M HCl with various concentrations of inhibitor at 25°C

C/ (mg/L)	Cr Schiff- base complex				Fe Schiff- base complex			
	Weight loss ( $\text{mg}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$ )	$\theta$	$IE_W$ (%)	Corrosion Rate (mpy)	Weight loss ( $\text{mg}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$ )	$\Theta$	$IE_W$ (%)	Corrosion Rate (mpy)
0	8.8	–	–	30.2	8.8	–	–	30.2
50	3.5	0.6	60.0	12.1	8.6	0.02	2.3	29.6
100	3.9	0.55	55.3	13.6	8.4	0.04	4.3	29.1
200	4.0	0.54	54.2	13.9	8.7	0.02	1.5	29.9

**Fig. 2.** Variations of corrosion potential with concentrations of Cr and Fe complexed in 0.5M HCl solution.**Fig. 3.** Polarization curves of carbon steel in 0.5M HCl with and without changes in concentrations of inhibitors: (a) Cr complex and (b) Fe complex.**Table 2.** Kinetic parameters of carbon steel in 0.5M HCl at  $25 \pm 1^\circ\text{C}$  containing different concentrations of Fe complex and Cr complex

Inhibitor	C/(mg/L)	$-E_{corr}/\text{mV}$	$I_{corr}/\mu\text{Acm}^{-2}$	$-\beta_c/\text{mV}$	$\beta_a/\text{mV}$	$\theta$	$IE$ (%)	mpy
Blank	0	-745	63.8	85.9	93.8	–	–	29.4
Cr complex	50	-725	28.2	91.8	67.5	0.56	55.8	13.0
	100	-725	28.3	90	70.5	0.56	55.6	13.0
	200	-729	29.6	92.8	70.3	0.54	53.6	13.6
Fe complex	100	-744	65.4	94.2	98.3	0.02	1.9	30.1
	400	-745	70.7	98.5	99.5	-0.06	-6.0	32.5
	800	-739	67.8	99.2	90.0	-0.07	-1.6	31.2

recorded EIS spectrum for steel in 0.5M HCl, Fig. 4, shows one depressed capacitive loop at higher frequency range (*HF*) followed by an inductive loop that is observed in the lower frequency region (*LF*). The equivalent circuit of Fig. 5 fits well our experi-

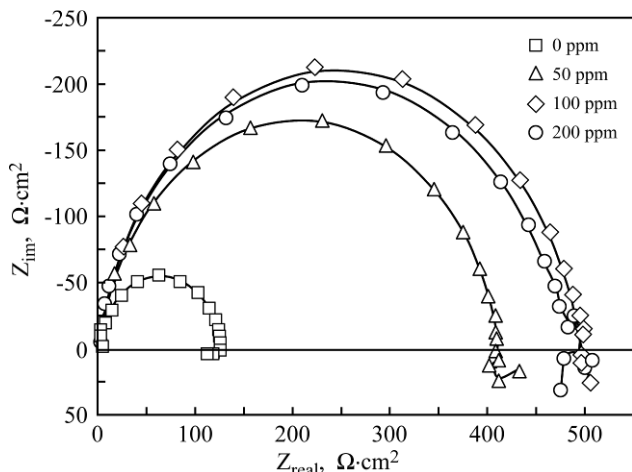
mental results; simulated points originated from the fitting process are also given in Figure 4.

The intersection of the capacitive loop with the real axis represents the ohmic resistance of the corrosion product films and the solution enclosed

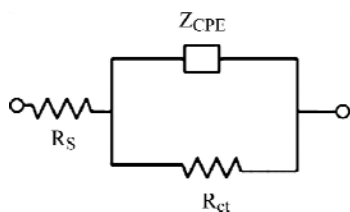
between the working electrode and the reference electrode,  $R_s$  [28, 29].  $R_{ct}$  represents the charge-transfer resistance whose value is a measure of electron transfer across the surface and is inversely proportional to corrosion rate [30]. The constant phase element (*CPE*) is introduced in the circuit instead of a pure double layer capacitor to give a more accurate fit [31]. The impedance of the *CPE* is expressed as:

$$Z_{CPE} = \frac{1}{Y_0(j\omega)^n},$$

where  $Y_0$  is the magnitude of the *CPE*,  $-1 \leq n \leq 1$ . The *HF* loops have depressed semicircular appearance,  $0.5 \leq n \leq 1$ , which is often referred to as frequency dispersion as a result of the non-homogeneity or the roughness [32] of the solid surface. The *HF* capacitive loop,  $R_{ct}$ -*CPE*, can be attributed to the charge-transfer reaction. The presence of the *LF* inductive  $R_L$ -*L* loop may be attributed to the relaxation process obtained by adsorption species like  $Cl_{ads}^-$  and  $H_{ads}^+$  on the electrode surface [33]. It may be also attributed to the re-dissolution of the passivated surface at *LF* [34].



**Fig. 4.** Nyquist plot of the steel electrode in 0.5M HCl without and with changes of concentrations of Cr complex after immersing the electrode in working solutions for 1 h under open circuit conditions.



**Fig. 5.** Equivalent circuits used to fit EIS data of steel in 0.5M HCl + xM inhibitor.

The effect of addition of increasing concentrations of Cr complex on the EIS of steel in 0.5M HCl solution has been studied at the respective open circuit potentials; some of the obtained results are shown in Figure 4. The electrochemical parameters obtained from fitting the recorded EIS data using

equivalent circuit of Fig. 4 are listed in Table 3. The inhibition efficiencies,  $IE\%$ , of the tested inhibitors were calculated from the  $R_{ct}$  values at different concentrations using the following equation [35]:

$$IE\% = \left[ \frac{R_{ct(free)}^{-1} - R_{ct(inh)}^{-1}}{R_{ct(free)}^{-1}} \right] \times 100,$$

where  $R_{ct(free)}$  and  $R_{ct(inh)}$  are the charge-transfer resistance values in the absence and presence of inhibitor, respectively. Increasing the concentration of Cr complex increases the corresponding  $IE\%$  values till  $C_{inh} = 100$  ppm, Fig. 4 above and Table 3.

We can note from Fig. 4 that the characteristic frequencies of the inductive loop diminish with increasing the magnitude of the electrode impedance whatever the inhibitor concentration is. In the high impedance Nyquist plots, the growing up inhibiting film delays the charge transfer processes to lower frequencies. The high impedance EIS curves were fitted to the one time constant equivalent circuit shown in Fig. 5 where the induction loops shifted below the studied *LF* limit. The protection layer resistance and the diffuse charge capacitance in it are not separated in this approximation rather they are conceived to be included in the elements of the used circuits.

Inspection of the data reveals that addition of the inhibitors increases the capacitive loop diameter of the Nyquist plots without affecting their characteristic features. This means that the inhibition action of the inhibitor in Fig. 5 above is due to its adsorption on the metal surface without altering the corrosion mechanism. In addition, the double layer capacitances,  $C_{dl}$ , for a circuit including a *CPE* were calculated from the following equation [36, 37]:

$$C_{dl} = Y_0(\omega_{max})^{n-1},$$

where  $\omega_{max} = 2\pi f_{max}$ ,  $f_{max}$  is the frequency at which the imaginary component of the impedance is maximal. The data in Table 3 show that the magnitude of  $C_{dl}$  decreases with increasing  $C_{inh}$ . The decrease in  $C_{dl}$  could be attributed to the adsorption of the inhibitors forming protective adsorption layers [38]. The thickness of the protective layer ( $d$ ) is related to  $C_{dl}$  according to the following equation [39]:

$$C_{dl} = \frac{\epsilon\epsilon_0}{d},$$

where  $\epsilon$  is the dielectric constant of the protective layer and  $\epsilon_0$  is the permittivity of free space ( $8.854 \times 10^{-14} \text{ F}\cdot\text{cm}^{-1}$ ).

#### Adsorption isotherms

Adsorption isotherms provide information about the interaction of the adsorbed molecules with the electrode surface [40, 41]. The adsorption of an

**Table 3.** Electrochemical impedance parameters for carbon steel corrosion in 5.0M HCl solution with and without changes in concentrations of inhibitor

Inhibitor	$C_{inh}$ (ppm)	CPE-T ( $\mu\text{F}\cdot\text{cm}^{-2}$ )	$R_s$ ( $\Omega$ )	$R_{ct}$ ( $\Omega$ )	IE%
Blank	0	104.5	2.56	119.2	–
Cr complex	50	72.4	2.23	384.1	68.9
	100	80.1	2.13	465.1	74.4
	200	87.3	1.78	454.2	73.8

organic adsorbate at the metal–solution interface can be presented as a substitution adsorption process between the organic molecules in aqueous solution ( $\text{Org}_{(sol)}$ ) and water molecules on a metallic surface ( $\text{H}_2\text{O}_{(ads)}$ ) [13]:



where  $\text{Org}_{(sol)}$  and  $\text{Org}_{(ads)}$  are the organic species dissolved in an aqueous solution and adsorbed onto the metallic surface, respectively;  $\text{H}_2\text{O}_{(ads)}$  is the water molecule adsorbed on the metallic surface; and  $x$  is the size ratio representing the number of water molecules replaced by one organic adsorbate.

In an attempt to find the most suitable adsorption isotherm ( $s$ ), the fraction of the surface coverage ( $\theta$ ) was calculated from the equation:

$$\theta = [1 - (i_{corr}/i_{corr}^0)]$$

and was subjected to various adsorption isotherms. For Cr complex, the experimental results were found to fit the Langmuir adsorption isotherm where  $\theta$  and  $C$  (inhibitor's concentration in the bulk of the solution) are related to each other via the equation:

$$\frac{\theta}{1-\theta} = K_{ads} \cdot C.$$

Rearranging gives:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C,$$

where  $K$  is the equilibrium constant of the adsorption process. Figure 6 shows plots of  $C/\theta$  against  $C$  for Cr complex.

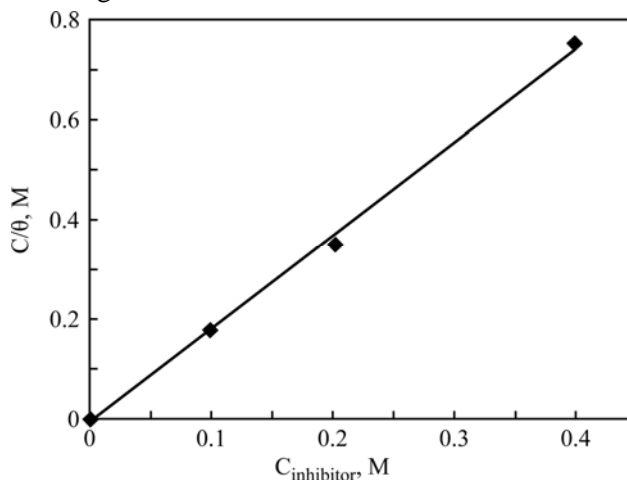
The data fit straight lines of slopes more than unity, thus indicating that this inhibitor is adsorbed according to the Langmuir isotherm. A deviation from unity of the slope of the line in Fig. 4 can be explained in terms of mutual repulsion or attraction of adsorbed species adjacent to each other, a fact which was ignored during the derivation of the Langmuir isotherm [42]. Similar results were obtained by many authors [43, 44].

The constant  $K$  is related to the standard free energy of adsorption ( $\Delta G^\circ$ ) by the equation:

$$K = (1/55.5)\exp(-\Delta G^\circ / RT).$$

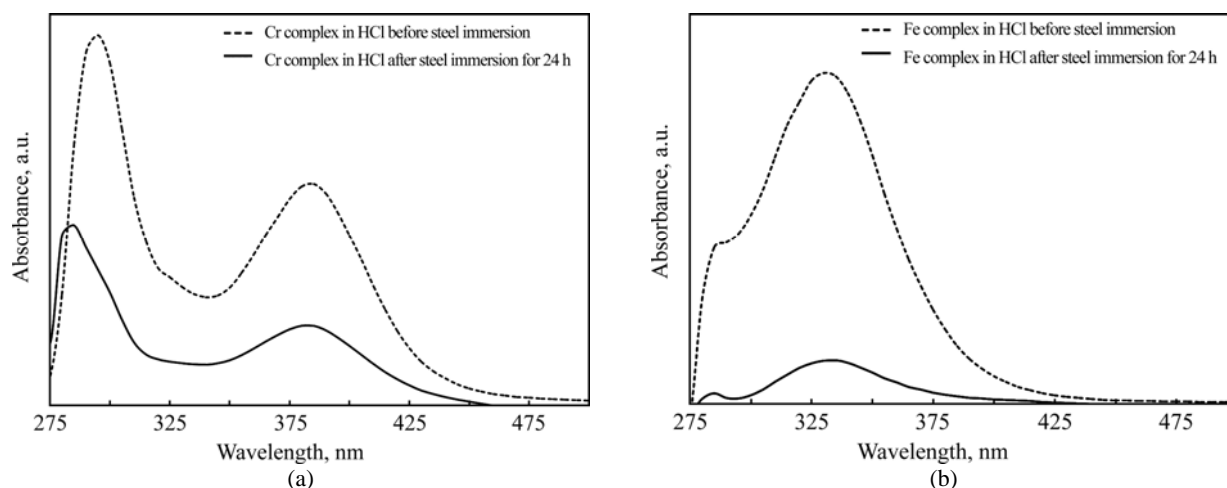
For Cr complex, values of  $K$  and  $\Delta G^\circ$  were found to be  $200 \text{ M}^{-1}$  and  $-23.1 \text{ kJ}\cdot\text{mol}^{-1}$ . The negative sign of

$\Delta G_{ads}^0$  indicates that the inhibitors are spontaneously adsorbed onto the metal surface [45]. Generally, the magnitude of  $\Delta G_{ads}^0$  around  $-20 \text{ kJ/mol}$  or a less negative value make it possible to suppose that there is an electrostatic interaction between the inhibitor and the charged metal surface (i.e., physisorption). Those around  $-40 \text{ kJ/mol}$  or more negative values indicate that the charge sharing or transferring from organic species to the metal surface to form a coordinate type of a metal bond (i.e., chemisorption) [45]. In the same work, the author interpreted the reported values of  $\Delta G_{ads}^0$  (less negative than  $-40 \text{ kJ/mol}$ , for physical adsorption) as indicators of the formation of an adsorptive film with an electrostatic character. In our experiments, the calculated  $\Delta G_{ads}^0$  values for Cr complex show that an electrostatic interaction, i.e., physisorption, is presented between the inhibitor and the charged metal surface, as in Figure 6.

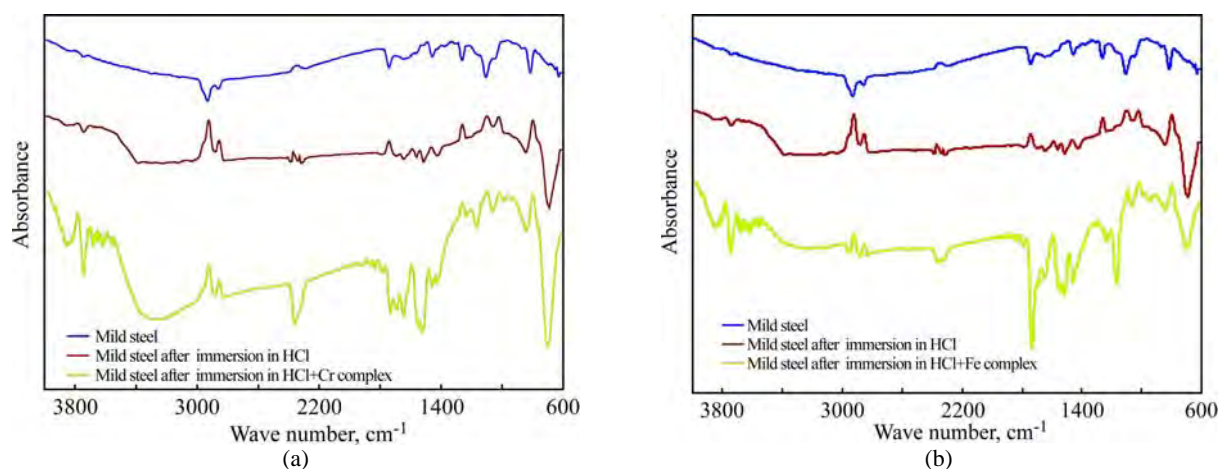
**Fig. 6.** Langmuir adsorption isotherm of Cr complex in 0.5M HCl solution at 25°C.

It is worth investigating the stability and absorbability of the entitled complexes in the test solution in the presence of carbon steel samples. The stability of Cr and Fe complexes at 25°C was studied using spectrophotometry technique in which the UV–visible absorption spectra were measured for the complexes in the test solution before and after carbon steel immersion (Fig. 7a and 7b).

Cr and Fe complexes are of a similar trend before and after carbon steel immersion in HCl acid solution. Therefore, it should be concluded that the



**Fig. 7.** UV-visible absorption spectra for synthesized complexes: (a) Cr complex and (b) Fe complex in HCl solution before and after carbon steel immersion for 24 h.



**Fig. 8.** FTIR reflectance spectra of carbon steel before and after immersion in 0.5M HCl solution without inhibitors and after immersion for 24 h in 0.5M HCl solution containing inhibitors: (a) Cr complex and (b) Fe complex.

Schiff-base ligand could stabilize higher oxidation states of Cr(III) and Fe(III). Hence, the reduction of Cr(III) and Fe(III) on the steel surface could be affected by the ligands surrounding them and these complexes are thermodynamically stable. The complex-acid solution bands after carbon steel immersion have lower intensity than the complex-acid solution bands before carbon steel immersion, which may be attributed to absorbance of the complex in such media. This shows that the interaction of Cr and Fe complexes with the carbon steel surface is due to physical adsorption.

Attenuated total reflection (ATR) is a sampling technique used in conjunction with infrared spectroscopy, which enables samples to be examined directly in the solid state without further preparation [46]. Corrosion inhibition of Cr and Fe complexes on the metal steel is evaluated in the present research by the ATR-FTIR method. Fig. 8a and 8b shows the FTIR reflection of the pure carbon steel and carbon steel samples in the HCl solution with and without corrosion inhibitors. The ATR-FTIR curve of the carbon steel sample after 1 day aging in HCl solution shows the corrosion products stretching modes

but the samples, which are aged in the presence of Cr and Fe complexes, show stretching modes of the Schiff-base complexes. The O–H and N–H bending FT-IR peaks appeared in  $1020\text{ cm}^{-1}$  to  $1200\text{ cm}^{-1}$  wave numbers. Also, O–H stretching modes appeared in  $2800\text{--}3000\text{ cm}^{-1}$ . Both modes are directly related to displacements of the hydrogen atoms in the crab-claw site, which are bonded by hydrogen bonding with chloride ion. Another important FTIR peak, which appears in  $1400\text{ cm}^{-1}$ , is related to C=N stretching of the imine bonds.

#### *Mechanism of inhibition or acceleration by the Schiff base complexes*

It is well known that the first step in the inhibition of acid corrosion is the adsorption of inhibitor molecules onto the metal surface. To elucidate the adsorption mechanism, it is necessary to reveal the mode of adsorption of compounds: whether it is physisorption (ionic) or chemisorption (molecular). The predominating mode of adsorption depends on several factors, such as the molecular structure of the inhibitor, type of the surface charge, i.e. position of

$E_{corr}$  with respect to the potential of point of zero charge (pzc) and the type of an acid anion.

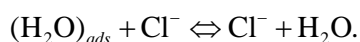
The surface charge of a metal, which is due to an electric field existing at the metal solution interface, is defined by the position of  $E_{corr}$  with respect to the pzc according to:

$$\varphi_c = E_{corr} - E_{q=0},$$

where  $\varphi_c$  is referred to as the Antropov's "rational" corrosion potential or potential on the correlative scale [47], and  $E_{q=0}$  is the potential of zero charge. If  $\varphi_c$  is negative, then the electrode surface has net negative charge and adsorption of cationic species is favoured. On the contrary, adsorption of anions is favored when  $\varphi_c$  becomes positive.

According to Benerijee and Mahotra [48], the carbon steel surface in HCl is positively charged at the corrosion potential. Therefore, the adsorption of the cationic Cr complex does not take place. Instead, adsorption of  $\text{Cl}^-$  ions occurs and the surface becomes negatively charged. Due to the electrostatic attraction, the cationic Cr complex molecules are adsorbed (physical adsorption) and a high inhibition effect is expected. Low values of  $IE\%$  of Cr complex (Tables 1 and 2) and a low value of  $\Delta G_{ads}$  indicate the physical nature of adsorption.

In the presence of  $\text{Cl}^-$  ions, the following rapid reaction proceeds on the iron surface:



The substitution of water molecules with  $\text{Cl}^-$  ions leads to the probability of the formation of adsorbed ion pairs and neutral molecules formed by the adsorbed  $\text{Cl}^-$  ions and Cr and Fe complex cations [13]. The molecular structures of these complexes were determined by the single-crystal X-ray structure analysis by Mikuriya et al. [23]. They showed that those two complexes are mononuclear with an octahedral metal (III) ion, and that two Schiff-base ligands act as meridional tridentate chelate forming hydrogen bonds with the chloride anion. Therefore, the adsorbed chloride ions on the metal surface could be stabilized in their anionic form by hydrogen bonding of oxygen and nitrogen atoms in the tail of the complexes, like a crab-claw. This molecular self-assembling not only stabilized the corrosive chloride ions but also improved the surface coverage by four medium-strength hydrogen bonding.

The accelerating properties of Fe complex in 0.5M hydrochloric acid could be due to the formation of non adherent and/or soluble complex that is readily removed from the metal surface. This removal of a soluble complex is clearly detrimental to the protection of the surface from continued corrosion.

## CONCLUSIONS

- Fe complex is a weak inhibitor or an accelerator for carbon steel corrosion in HCl solution, while Cr complex acts as moderate inhibitor.

- Adsorption of Cr complex obeys the Langmuir adsorption isotherm with a very low value of free energy of adsorption  $\Delta G^\circ$  (physisorption).

- Cr complex acts as mixed type inhibitor, with the predominant effect on the anodic dissolution of iron.

- The mechanism of adsorption is discussed and it is concluded that the adsorbed chloride ions on the metal surface could be stabilized in their anionic form by hydrogen bonding of oxygen and nitrogen atoms in the tail of the complexes, like a crab-claw.

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### Реферат

Выполнено сравнительное исследование Fe и Cr комплексов с лигандом Шифф-основания (1 - [(2-гидроксиэтил) амино]-2-(салицилденеимин)этан) в качестве ингибиторов коррозии углеродистой стали в 0,5M растворе HCl при 25°C. Измерения коррозии, основанные на методе потери веса, на потенциодинамических поляризационных кривых и электрохимической импедансной спектроскопии (ЭИС), показывают, что Fe комплекс, в большинстве случаев, ускоряет коррозию углеродистой стали в то время как в HCl Cr комплекс действует как умеренный ингибитор. Исследования поверхности электрода в УФ-видимом и при ослабленном отражения методом инфракрасной спектроскопии на основе преобразования Фурье подтвердили существование адсорбированной пленки комплексов на поверхности электрода. Адсорбция Cr комплекса подчиняется изотерме адсорбции Лэнгмюра с очень низким значением свободной энергии адсорбции  $\Delta G^\circ$  (физической адсорбции). Cr комплекс действует как ингибитор смешанного типа, с доминирующим влиянием на анодное растворение железа. Обсуждается механизм адсорбции и делается вывод о том, что ионы хлора адсорбированные на поверхности металла могут быть стабилизированы в их анионной форме водородной связью с атомами кислорода и азота в хвосте комплексов, как крабовой клешней. Ускоряющие свойства Fe комплекса могут быть связаны с образованием не сцепленного с субстратом и/или растворимого комплекса, который легко удаляется с поверхности металла.

*Ключевые слова:* ингибиторы кислотной коррозии, изотермы адсорбции, Шифф-основные комплексы, углеродистая сталь.