ortho-Chlorophenyl-2-imidazoline as Corrosion Inhibitor for Mild Steel in Acidic Media

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Present study involved the synthesis of *o*-chlorophenyl-2-imidazoline (OCP2I) and its inhibition behaviour on mild steel corrosion in sulphuric acid and hydrochloric acid media, using weight loss method and electrochemical methods. The results of weight loss method revealed that the inhibitor shows a maximum efficiency of 84.55 % in H_2SO_4 at 200 ppm and 91.42 % in HCl medium at 120 ppm of concentration. Thermodynamic parameters indicated physisorption mode of adsorption of *o*-chlorophenyl-2-imidazoline follows Langmuir and Temkin adsorption isotherms. Potentiodynamic polarization and impedance studies were conducted to investigate the mechanism of the inhibition and the present system follows mixed mode of inhibition.

Key Words: Mild steel, *o*-Chlorophenyl-2-imidazoline, Hydrochloric acid, Sulphuric acid, Inhibitor, Corrosion.

INTRODUCTION

Mild steel is one of the most important widely used engineering materials particularly for the structural and automobile applications. However it undergoes rusting easily in the humid atmosphere and its rate of corrosion is quite high in acidic environment. Thus protection of mild steel from corrosion is an important topic of research. Out of several methods, use of chemical inhibitors is one of the practical methods for the prevention of corrosion particularly in acidic media. Acid solution are widely used in chemical laboratories and in several industrial processes such as acid pickling, acid cleaning, acid descaling and oil wet cleansing *etc*.[1,2].

Corrosion inhibitors are generally used to reduce the corrosion rates. Most of the well known acid inhibitors are organic compounds containing electron donor atoms particularly nitrogen, sulphur, oxygen in their functional groups with aromatic and heterocyclic rings. These compounds have been reported by several workers[3-6].

EXPERIMENTAL

Synthesis of *o*-chlorophenyl-2-imidazoline: *ortho*-Chlorophenyl-2-imidazoline was synthesized using the procedure described by Midori Ishihara and Hideo Togo[5] and the compound was characterized by IR spectral data. IR spectral data shows broad singlet at 3346 cm⁻¹ for N-H stretching, aromatic C-H stretching at 2904 cm⁻¹, aliphatic stretching at 2851 cm⁻¹, C=N stretching at 1622 cm⁻¹ and for C-Cl stretching at 750.13 cm⁻¹.
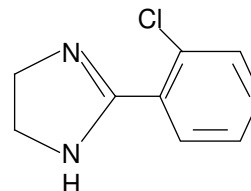
Weight loss measurements: Mild steel specimens of composition C = 0.098 %, Mn = 0.201 %, P = 0.020 %, S = 0.016 %, Ni = 0.012 % and Fe = 99.653 % used for the measurement of the corrosion rates. Rectangular specimens of working surface area 5 cm × 1 cm were used for weight loss measurements and 1 cm × 1 cm with 5 cm long stem (isolated with Teflon tape) for the electrochemical methods. The specimens were polished mechanically using emery papers and worked thoroughly with triple distilled water, degreased with acetone and dried using air flow at room temperature. The weight loss experiments were carried our for an immersion time of 0.5, 1, 3, 6, 12 and 24 h at room temperature and the temperature variation studies from 303-343 K in sulphuric acid solution and hydrochloric acid solution in the absence and presence of various concentration of *o*-chlorophenyl-2-imidazoline.

Electrochemical measurements: Electrochemical studies were carried out using Solartron Electrochemical Analyzer Model (1280B). Platinum electrode was used as auxillary electrode and a saturated calomel electrode (SCE) was used as reference electrode and mild steel was used as working electrode. All potentials were measured *versus* saturated calomel electrode. The impedance measurements were carried out in the frequency

range of 10 kHz to 10 mHz at the rest potential by applying a 5 mV sine wave AC voltage. The same cell and instrument as in the polarization method were used. The double layer capacitance (C_{dl}) and charge transfer resistance (R_{ct}) were obtained from Nyquist plots[7].

Most of the well known acid inhibitors are organic compounds containing electron donor atoms particularly nitrogen, sulphur, oxygen in their functional groups with aromatic and hetero-cyclic rings. These compounds have been reported by several workers[3-6]. Hence in this direction, the present investigation is conducted to study the inhibitive action of *o*-chlorophenyl-2-imidazoline on mild steel acid corrosion.

RESULTS AND DISCUSSION

Weight loss studies: The values of percentage inhibition efficiency (IE %) obtained from weight loss method for different concentrations of *o*-chlorophenyl-2-imidazoline in sulphuric acid and hydrochloric acid are presented in Figs. 1 and 2, respectively. From the figure it is clear that the inhibition efficiency increases with increase in concentration of *o*-chloro-phenyl-2-imidazoline in both examined media.
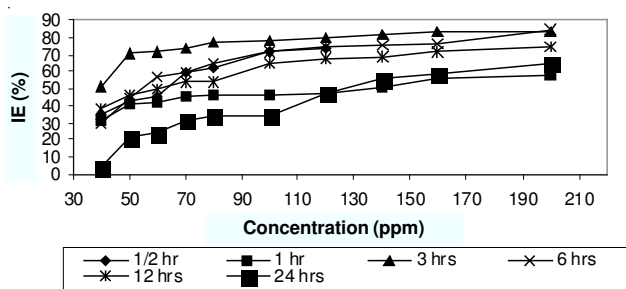

Fig. 1. Weight loss of *o*-chlorophenyl-2-imidazoline in 0.5 M H_2SO_4
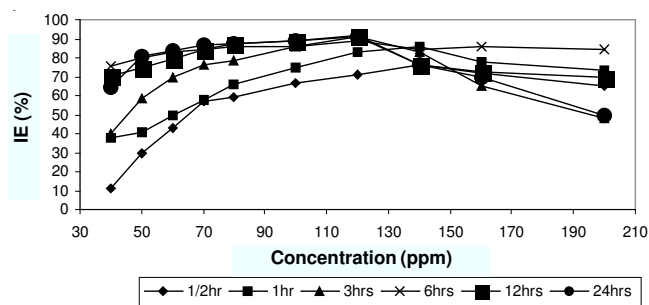

Fig. 2. Weight loss of *o*-chlorophenyl-2-imidazoline in 1 M HCl

The maximum efficiency of *o*-chlorophenyl-2-imidazoline in sulphuric acid medium was 84.55 % at 200 ppm concentration for an immersion time of 6 h and in hydrochloric acid medium 91.42 % for an immersion time of 3 h at 120 ppm concentration.

This result may be attributed due to the increase in the surface area of adsorbed molecules of *o*-chlorophenyl-2-imidazoline on mild steel surface. Figs. 1 and 2 also reflect the effect of period of immersion of mild steel in the absence and presence of the *o*-chlorophenyl-2-imidazoline in both examined media. inhibition efficiency increases from 3 h upto 6 h and after that there is decrease in inhibition efficiency .

Initially inhibition efficiency increase from 0.5 to 3.0 h and then there is a decline in inhibition at 6 h. This behaviour can be discussed on the following basis. Prolonged immersion of steel in acidic solution allows the cathodic or hydrogen evolution kinetics to increase presumably as more cathodic or carbon containing sites are exposed by the corrosion process[8] and increase the concentration of ferrous ion which is known for its stimulation of corrosion attack of the acid on the base metal[9].

o-Chlorophenyl-2-imidazoline works out as a promising inhibitor in HCl medium, furnishing 91.4 % inhibition efficiency at 120 ppm concentration for a period of 3 h immersion. In H_2SO_4 bath, maximum of 84.55 % at 200 ppm concentration for a period of 6 h immersion. This fact may explained by many research workers. Enhanced inhibition efficiency in HCl medium is due to the synergistic effect of chloride ions and also due to the chloro substituted product as inhibitor. This chloro substituted product forms a protective layer on mild steel surface[10-12].

Effect of temperature: To test the stability of the inhibitor at higher temperature, experiments were performed at different temperature in the range 303-343 K Fig. 3.
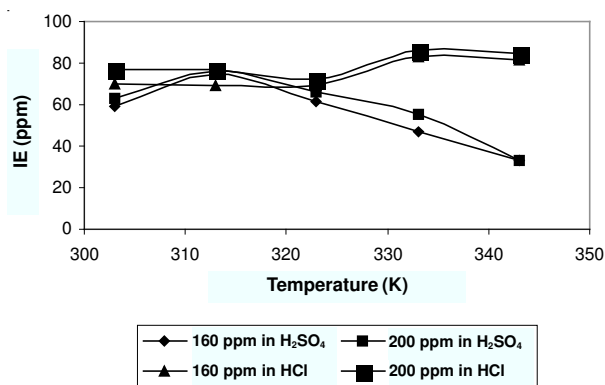

Fig. 3.   Effect of temperature on IE of *o*-chlorophenyl-2-imidazoline in HCl and H_2SO_4 medium

From the Fig. 3, it can be deduced that an increase in the temperature range of 303-343 K enhanced the inhibition efficiency of the inhibitor upto 333 K for HCl medium and 313 K for sulphuric acid medium. This inhibitor under study is found to be highly effective in HCl medium than H_2SO_4 medium.

The behaviour of *o*-chlorophenyl-2-imidazoline at 303 K may be attributed to the adsorption of the inhibitor upto 313 K and after that further increase in temperature brings about desorption of the *o*-chlorophenyl-2-imidazoline under study. This may be explained as follows. Adsorption and desorption of inhibitor molecules continuously occur at the metal surface and the equilibrium exists between theses two processes at a particular temperature. With the increase of temperature, the equilibrium between adsorption and desorption process is shifted leading to a higher desorption rate than adsorption until equilibrium is again established at a different value of equilibrium constant. It explains the lower inhibition efficiency at higher temperature[13].

Adsorption isotherms: Surface coverage data play an important role in assessment of inhibitor characteristics and

are useful for fitting experimental data into adsorption isotherms which give detailed in sight into the inhibition mechanism. *ortho*-Chlorophenyl-2-imidazoline obeys Langmuir and Temkin adsorption isotherms by giving a straight line for a plot of log C *versus* $\log\left[\dfrac{\theta}{(1-\theta)}\right]$ and log C *versus* θ, respectively. These straight lines obtained reveal that the main process of inhibition is adsorption.

Thermodynamic parameters: The values of free energy of adsorption were calculated using the standard equation[14]. The results obtained are given in Table-1.

It was found that the ΔG$_{ads}$ value is less than -20 KJ/mol indicating that the *o*-chlorophenyl-2-imidazoline are physically adsorbed on the metal surface[15,19-21]. The negative value of ΔG$_{ads}$ shows a strong interaction of inhibitor molecules and a spontaneous adsorption of inhibitor on the surface of the mild steel[15,19]. Generally values of ΔG$_{ads}$ upto -20 KJ/mol are consistent with electrostatic interaction between charged molecule and a charged metal (which indicates physisorption) while those more negative than -40 KJ/mol involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond which indicated chemisorption[16-18]. Physical adsorption is a result of electrostatic attraction between charged species in the bulk of the solution. Adsorption of negatively charged species is facilitated if the metal is positively charged species at the same time the metal can also protect the positively charged metal surface acting with a negatively charged intermediated such as acid anions adsorbed on the metal surface[18]. The higher values of ΔH in the presence of inhibitor indicate higher protection efficiency of the inhibitor. The positive values of ΔH suggest that the dissolution process is an exothermic phenomenon and the dissolution of steel is difficult. This means the formation of an ordered stable layer of inhibitor on mild steel[22]. The values of entropy prove strong interaction of the inhibitor on the metal surface[23].

The activation energy of the inhibited solution decreases by increasing the concentration of the inhibitor. This finding indicates that *o*-chlorophenyl-2-imidazoline retards the corrosion of mild steel in both examined media[24,25].

Potentiodynamic polarization studies: Both the anodic and cathodic polarization curves of mild steel in 0.5 M sulphuric acid and 1 M HCl in the absence and presence of *o*-chlorophenyl-2-imidazoline were shown in Fig. 4. Electro-

TABLE-1
THERMODYNAMIC PARAMETERS OF MILD STEEL IN THE PRESENCE OF *o*-CHLOROPHENYL-2-IMIDAZOLINE IN ACIDIC MEDIA

Conc. (ppm)	H$_2$SO$_4$								HCl						
	-Ea	-ΔG Change in free energy					-ΔS (J/mol)	ΔH (kJ/mol)	Ea	-ΔG Change in free energy					-ΔS (J/mol)	ΔH (kJ/mol)
		303	313	323	333	343				303	313	323	333	343		
40	98.5	7	13	8	7	6	81	34	48.09	12	9	8	14	13	80	15
50	99.9	9	12	8	10	7	72	32	42.88	11	9	10	15	15	121	27
60	104.7	11	12	8	10	7	100	42	42.15	11	11	11	15	15	115	25
70	105.2	11	12	9	10	7	97	41	41.50	11	11	11	15	16	122	27
80	104.2	11	12	10	11	8	74	34	45.04	12	11	11	15	15	109	23
100	105.7	11	12	10	10	8	74	62	44.88	11	10	10	15	15	108	31
120	104.7	10	11	10	10	8	54	51	45.49	11	11	10	15	15	101	26
140	105.5	10	11	11	10	8	61	46	45.91	11	11	10	14	15	95	81
160	107.2	10	12	11	9	8	60	47	45.93	11	11	12	14	14	93	42
200	107.9	10	12	11	10	7	62	81	47.86	11	11	12	14	14	84	42

TABLE-2
POLARIZATION STUDIES OF MILD STEEL IN THE PRESENCE OF *o*-CHLOROPHENYL-2-IMIDAZOLINE IN H$_2$SO$_4$ AND HCl

	Conc. of OCP2I (ppm)	I$_{corr}$ × 10^{-4} (mA/cm^2)	E$_{corr}$ (mV/s)	b$_a$ (mV/dec)	b$_c$ (mV/dec)	IE (%)
H$_2$SO$_4$	Blank	12.63	487	78.2	207	–
	40	6.17	460	62.7	168	51.14
	50	5.58	464	62.3	150	55.82
	60	4.77	463	61.4	131	62.23
	70	4.73	464	62.0	127	62.55
	80	2.64	461	55.7	98	79.09
	100	2.20	467	54.6	118	82.58
	120	1.94	461	90.4	146	84.63
	140	1.92	457	52.9	109	84.79
	160	1.80	489	52.2	503	85.75
	200	1.16	467	47.7	146	90.81
HCl	Blank	10.04	519	99.0	150	–
	40	5.40	508	136.0	123	45.52
	50	5.06	509	158.0	131	49.60
	60	4.95	507	162.0	136	50.69
	70	4.89	504	159.0	142	51.29
	80	4.44	514	175.0	123	55.77
	100	2.23	473	78.0	195	78.08
	120	0.67	454	62.0	119	93.32

chemical parameters such as corrosion current density I_{corr}, corrosion potential E_{corr}, Tafel constants and inhibition efficiency % are listed in Table-2.
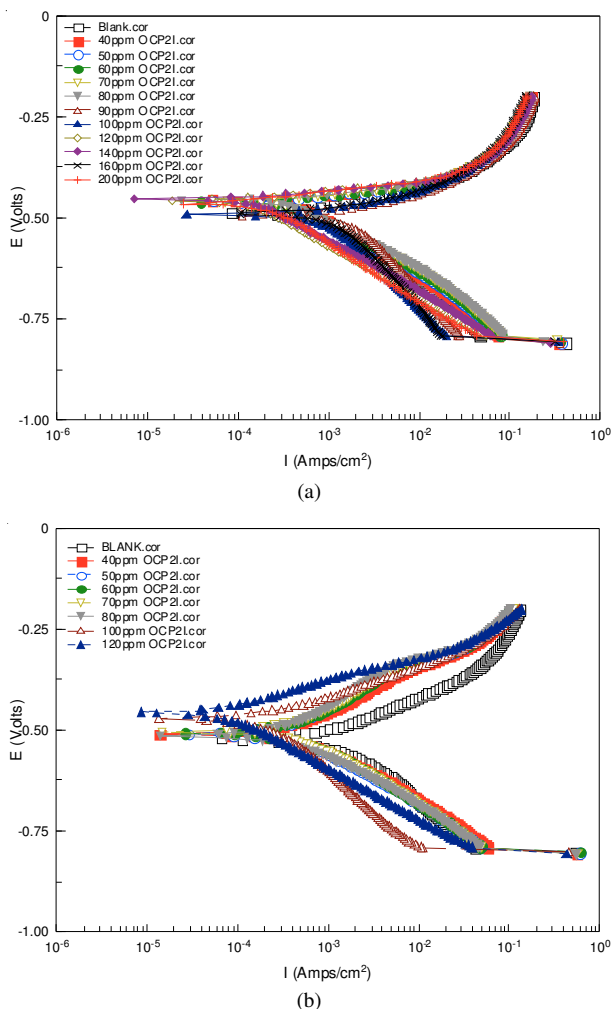

(a)

(b)

Fig. 4. Polarization studies for mild steel in the presence of *o*-chlorophenyl-2-imidazoline in 0.5 M H_2SO_4 (a) and 1 M HCl (b)

It is observed that presence of the inhibitor lowers I_{corr} values with increasing concentration of the inhibitor. The lower concentration current density I_{corr} values in the presence of *o*-chlorophenyl-2-imidazoline without causing significant changes in corrosion potential E_{corr} suggest that the compound is mixed type inhibitor[26]. The addition of *o*-chlorophenyl-2-imidazoline hinders the attack on the mild steel. The values of Tafel slopes b_a and b_c are found to change with inhibitor concentration which clearly indicated that the inhibitor controlled both reactions[27]. Maximum inhibition efficiency was found to be 90.8 % (200 ppm concentration) in H_2SO_4 and 93.3 % (120 ppm concentration) in HCl. Values of R_p increases with increase in concentration of *o*-chlorophenyl-2-imidazoline in both examined media infer that inhibition process takes place by adsorption of *o*-chlorophenyl-2-imidazoline on mild steel surface.

Adsorption of *o*-chlorophenyl-2-imidazoline may be explained by the presence of nitrogen atom, π electrons of aromatic rings and electron donating groups. The hetero atoms such as nitrogen are the major adsorption centre in organic compounds for its interaction with the metal surface. The adsorption can also occur through electrostatic interaction between a negatively charged surface which is provided by a specifically adsorbed anion (Cl^-) on iron and the positive charge of inhibitor[28,29].

Electrochemical impedance spectroscopy (EIS): Nyquist plots for mild steel in 0.5 M H_2SO_4 and 1 M HCl in the absence and presence of the inhibitors at various concentration of *o*-chlorophenyl-2-imidazoline were shown in Fig. 5 and the impedance parameters such as charge transfer resistance (R_{ct}), double layer capacitance (C_{dl}) are given in Table-3.

The Nyquist plot shows that the diameter of the capacitive loop and consequently the value of the charge transfer resistance R_{ct} increased with the concentration of the *o*-chlorophenyl-2-imidazoline, which is an indication of the inhibitor action. The semicircle corresponds to a capacitive loop. The semicircle radii depend on the inhibitor concentration. The

TABLE-3
CORROSION KINETIC PARAMETERS OF MILD STEEL IN THE PRESENCE OF
o-CHLOROPHENYL-2-IMIDAZOLINE IN H_2SO_4 AND HCl

	Conc. (ppm)	R_p (ohm/cm^2)	IE (%)	R_{ct} (ohm/cm^2)	IE (%)	$C_{dl} \times 10^{-4}$ (µF/cm^2)	θ
H_2SO_4	Blank	19.54		5.62		4.14	
	40	20.08	2.680	12.27	54.31	3.90	0.0570
	50	21.13	7.520	13.06	56.96	3.68	0.1110
	60	22.68	13.84	14.74	61.87	3.03	0.2680
	70	22.74	14.07	14.77	61.94	2.59	0.3740
	80	23.76	17.76	15.64	64.06	2.18	0.4730
	100	39.55	50.59	19.70	71.47	1.63	0.6060
	120	45.96	57.48	20.26	72.26	1.51	0.6340
	140	48.64	59.82	20.64	72.77	1.27	0.6930
	160	57.22	65.85	30.06	81.30	1.11	0.7310
	200	68.81	71.60	34.44	83.68	1.06	0.7420
HCl	Blank	23.95		19.22		4.06	0.0512
	40	55.16	56.57	30.91	37.81	3.85	0.1500
	50	56.34	57.57	37.30	48.47	4.26	0.1700
	60	58.64	59.24	39.43	50.02	4.61	0.2200
	70	58.92	59.43	47.95	58.90	4.81	0.2300
	80	67.45	64.56	50.32	60.84	3.85	0.4000
	100	109.67	78.20	102.48	80.77	1.40	1.2700
	120	223.61	89.31	213.48	90.76	1.01	3.6600

diameter of the capacitive loop increased with increasing inhibitor concentration and the values of C_{dl} decreases with increase in the concentration of *o*-chlorophenyl-2-imidazoline. The decrease in C_{dl} values indicate that the inhibitor molecules are being adsorbed on mild steel surface and thus reduce corrosion process. The same trend was observed for H_2SO_4 medium also. The change in R_{ct} and C_{dl} values was caused by the gradual replacement of water molecules by the anions of the acid and adsorption of the organic molecules on the metal surface, reducing the extent of dissolution[30].
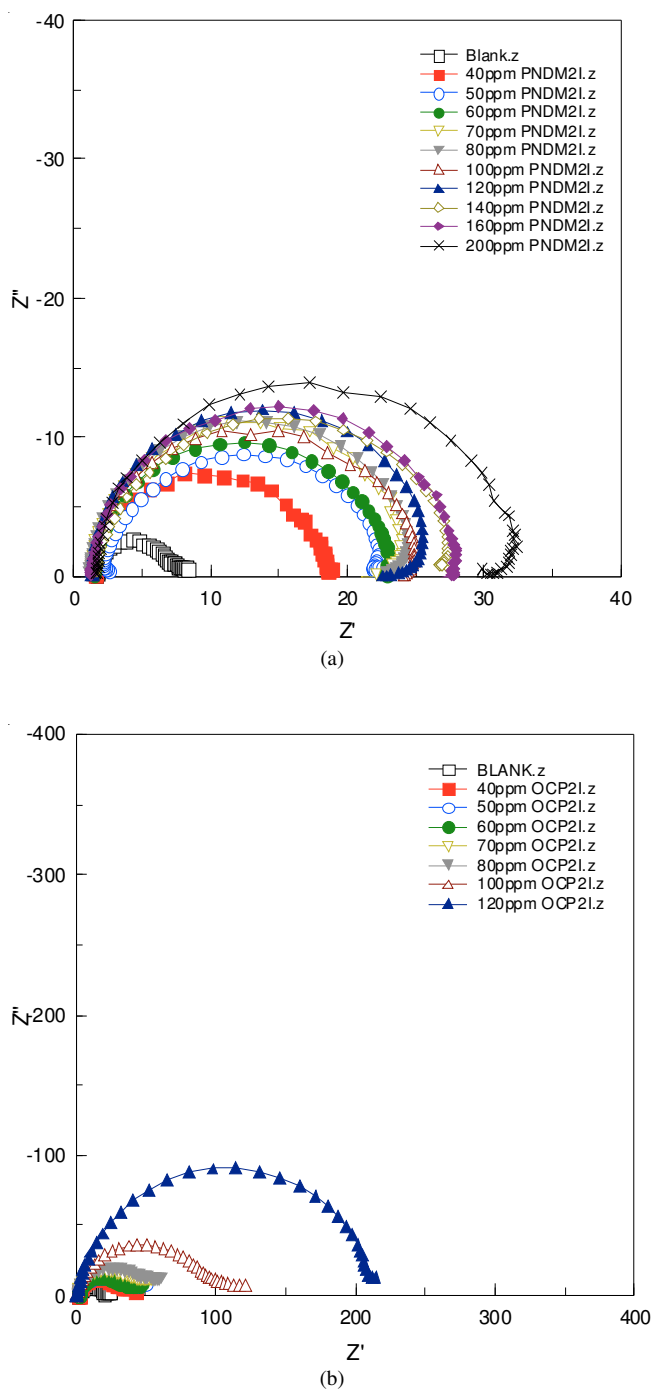

(a)

(b)

Fig. 5. Impedance diagram of mold steel in the presence of o-chlorophenyl-2-imidazoline in 0.5 H H_2SO_4 (a) and 1 M HCl (b)

Conclusion

The inhibitor shows a maximum effciencyof 84.55 % at 200 ppm concentration in sulphuric acid medium and 91.42 % at 120 ppm concentration in hydrochloric acid. The inhibitor obeys Langmiur and Temkin adsorption isotherms. Kinetic and thermodynamic parameters infer the strong adsorption of inhibitor molecule on mild steel surface. The lower current density I_{corr} values in the presence of *o*-chlorophenyl-2-imidazoline and no change in corrosion potential suggest that the compound is mixed type inhibitor. The change in R_{ct} and C_{dl} values was caused by the gradual replacement of water molecules by the anions of the acid and adsorption of the organic molecules on the metal surface, reducing the extent of dissolution. Results obtained by weight loss and electrochemical measurements are quite comparable. Thus *o*-chlorophenyl-2-imidazoline proved to be an effective inhibitor in sulphuric acid as well as in hydrochloric acid medium.

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