

Corrosion Inhibition of Iron in 0.5 mol L⁻¹ H₂SO₄ by Halide Ions

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O efeito de inibição de íons haletos, tais como iodeto, brometo e cloreto, na corrosão de ferro em solução 0,5 mol L⁻¹ de H₂SO₄, e o comportamento da adsorção desses íons na superfície do eletrodo, foram estudados pelos métodos de polarização e de impedância. Foi observada uma inibição de aproximadamente 90% para íons iodeto a 2,5 × 10⁻³ mol L⁻¹ e para íons brometo a 10 × 10⁻³ mol L⁻¹, e de 80% para íons cloreto a 2,5 × 10⁻³ mol L⁻¹. O efeito da inibição aumenta com o aumento da concentração dos íons haletos I⁻ e Br⁻, mas decresce no caso do Cl⁻, para concentrações maiores que 5 × 10⁻³ mol L⁻¹. Os valores de capacitância de dupla camada diminuíram consideravelmente na presença dos íons haletos, o que indicou que esses ânions são adsorvidos no ferro no potencial de corrosão.

The inhibition effect of halide ions such as iodide, bromide and chloride ions on the corrosion of iron in 0.5 mol L⁻¹ H₂SO₄ and the adsorption behaviour of these ions on the electrode surface have been studied by polarization and impedance methods. It has been found that the inhibition of nearly 90% has been observed for iodide ions at 2.5 × 10⁻³ mol L⁻¹, for bromide ions at 10 × 10⁻³ mol L⁻¹ and 80% for chloride ions at 2.5 × 10⁻³ mol L⁻¹. The inhibition effect is increased with increase of halide ions concentration in the case of I⁻ and Br⁻ ions, whereas it has decreased in the case of Cl⁻ ion at concentrations higher than 5 × 10⁻³ mol L⁻¹. The double layer capacitance values have decreased considerably in the presence of halide ions which indicate that these anions are adsorbed on iron at the corrosion potential.

Keywords: corrosion inhibition, iron, sulphuric acid, halide ions

Introduction

Adsorption of anions over metal surfaces leading to the inhibitive or stimulation effects on metallic corrosion have been reported by earlier researchers.¹⁻⁶ It is well known that the dissolution of iron in H₂SO₄ solutions occurs in four different states viz. active, passive, transpassive and brightening states as determined by the nature and kinetics of reaction involved, which depend on the potential and electrolyte composition. Combined adsorption of anions and cations together on the surface have also been studied. Electrostatic interaction is the main reason for the specific adsorption of anions on metal surface.^{7,8} Possibility of chemisorption of the anions on metal by the formation of a covalent type bond is also suggested by Grahame.⁹ Quantum chemical calculations have been used to describe the chemisorption of the halide ions on the metal electrode surface by the formation of partial charge transfer bonds.¹⁰ Pearson suggested that the stability of the anion adsorption bond over metal

surface should resemble to hard and soft acids and bases principle if the adsorption occurs by forming a donor – acceptor type bond.^{11,12} The specific adsorption behaviour of some of the anions on metal electrode surface and their effects on corrosion have been qualitatively related to this HSAB principle.^{13,14}

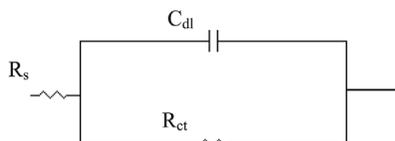
The breakdown of the iron passivity and initiation of pitting corrosion induced by the adsorption of halide ions are of technological interest.¹⁵⁻²⁰ Due to the complex physico – chemical reaction involved, the mechanism and kinetics of passivity and pitting initiation are not fully understood. Current – potential oscillations as well as other anodic reactions associated with the physico – chemical process leading to pitting corrosion have attracted significant attention.²¹⁻³⁰ It is reported that, the aggressive anions like Cl⁻, Br⁻ and I⁻ are found to catalyze the iron dissolution reaction in higher concentrations.³¹ But some studies³²⁻³⁶ have shown that halide ions in lower concentrations inhibit the corrosion of iron in sulphuric acid. However the adsorption characteristics of halide ions on iron surface has not been well established. Hence a study has been made to find the adsorption characteristics

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of halide ions on the iron surface in 0.5 mol L⁻¹ H₂SO₄ and the effect of adsorbed halide ions on corrosion.

Experimental

Experiments were made using a conventional three electrode cell assembly at 28 ± 1 °C. The working electrode was a pure iron sample (99.99% purity, Johnsons Matthey Ltd., UK) of one cm² area with the rest being covered with araldite epoxy and a large rectangular platinum foil was used as counter electrode and saturated calomel electrode as reference electrode. The reference electrode was connected to the main cell through a luggin capillary in order to avoid the contamination of 0.5 mol L⁻¹ H₂SO₄ with chloride ions. The working electrode was polished with 1/0 to 4/0 grades of emery papers, washed with water and degreased with trichloroethylene. All solutions were prepared using AR grade chemicals using triple distilled water and deaerated by purging purified nitrogen for half an hour before the start of the experiment under stationary condition. Solartron Electrochemical analyzer (Model 1280 B) interface with an IBM computer and Corrware and Z plot corrosion software were used for data acquisition and analysis. The polarization and impedance studies were made after 30 minutes of immersion since the specimen attained a steady state potential (± 0.005 V). The polarization was carried out using a Corrware software from a cathodic potential of -0.2V to an anodic potential of +0.2 V with respect to the corrosion potential at a sweep rate of 0.5 mV s⁻¹. E vs log I curves were plotted. The linear tafel segments of the anodic and cathodic curves were extrapolated to corrosion potential to obtain the corrosion current densities. For linear polarization resistance measurements, polarization was done from -0.020 V to + 0.020 V with respect to corrosion potential at a sweep rate of 0.5 mV s⁻¹ and the slope of the linear segment at corrosion potential was obtained as polarization resistance R_p. AC signals of 10 mV amplitude and a frequency spectrum from 10 KHz to 0.01 Hz was impressed and the Nyquist representations of the impedance data were analysed with Zview software using the following equivalent circuit due to the presence of single semi circle in the impedance diagram.



where R_s is the solution resistance, R_{ct} is the charge transfer resistance and C_{dl} is the double layer capacitance.

The diameter of the semicircle was measured as the charge transfer resistance R_{ct} . For Tafel polarization method, the corrosion inhibition efficiency was evaluated from the measured i_{corr} values using the relationship

$$I.E.\% = \left\{ \frac{i_{corr} - i_{corr}'}{i_{corr}} \right\} \times 100$$

where i_{corr} and i_{corr}' are the corrosion current densities without and with the addition of halide ions. The inhibition efficiencies were evaluated from the measured R_p values in linear polarization resistance method as

$$I.E.\% = \left\{ \frac{R_p' - R_p}{R_p} \right\} \times 100$$

Where R_p and R_p' are the polarization resistance values without and with the addition of halide ions. In the impedance method, the inhibition efficiency was evaluated from the measured charge transfer resistance R_{ct} values as

$$I.E.\% = \left\{ \frac{R_{ct}' - R_{ct}}{R_{ct}} \right\} \times 100$$

where R_{ct} and R_{ct}' are the charge transfer resistance values in the absence and presence of halide ions.

From the measured double layer capacitance C_{dl} , the surface coverage θ of inhibitor is given by

$$\theta = \frac{C_{dl} - C_{dl}'}{C_{dl} - C_{dls}} = \frac{C_{dl} - C_{dl}'}{C_{dl}}$$

since $C_{dls} \ll C_{dl}$ where C_{dl} , C_{dl}' and C_{dls} are the double layer capacitance values in the absence, presence and saturation value in the presence of halide ions respectively.³⁷⁻³⁹

Results and Discussion

Iodide ions

The potentiodynamic polarisation behaviour of iron in 0.5 mol L⁻¹ H₂SO₄ without and with the addition of iodide ions is shown in Figure 1. The corrosion kinetic parameters derived from these curves are presented in Table 1. From the table it is clear that the addition of iodide ions in the concentration range 0.5 × 10⁻³ to 5 × 10⁻³ mol L⁻¹ markedly reduces the dissolution rate of iron in 0.5 mol L⁻¹ H₂SO₄. The corrosion current density, i_{corr} , decreases from 410 μA cm⁻² for the inhibitor free solution to 46 μA cm⁻². Beyond 5 × 10⁻³ mol L⁻¹ concentration, the increase of iodide ion concentration leads to a slight increase in corrosion current density. The steady state corrosion

potential E_{corr} shifts to the more anodic value. This shows that iodide ions act as anodic inhibitor.

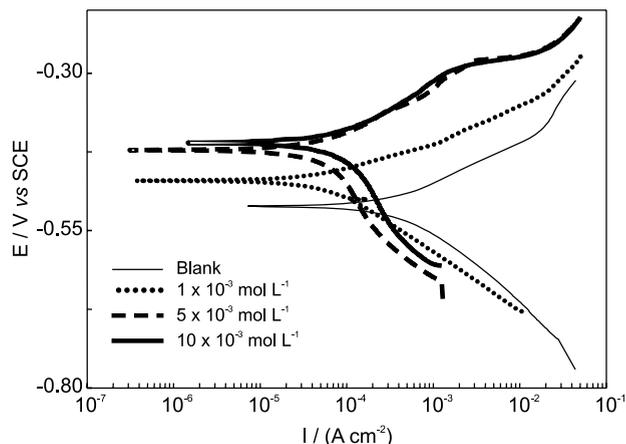


Figure 1. Potentiodynamic polarisation behaviour of iron in 0.5 mol L⁻¹ H₂SO₄ without and with the addition of iodide ions.

Table 1. Corrosion kinetic parameters of pure iron in 0.5 mol L⁻¹ H₂SO₄ with I⁻ ions

Concentration of I ⁻ ions (10 ⁻³ mol L ⁻¹)	E_{corr} (mV vs SCE)	b_a (mV dec ⁻¹)	b_c (mV dec ⁻¹)	i_{corr} ($\mu\text{A cm}^{-2}$)	Inhibition Efficiency (%)
Blank	-508	76	109	410	—
0.5	-503	53	95	89	78
1.0	-480	63	90	78	81
2.5	-452	86	107	46	89
5.0	-429	76	118	53	87
7.5	-445	61	111	54	87
10.0	-405	68	122	62	85

The Nyquist representation of the impedance values of the iron in 0.5 mol L⁻¹ H₂SO₄ with and without the addition of iodide ions is shown in Figure 2. The existence of a single semi circle depicts the presence of single charge transfer process during dissolution which is unaffected by the presence of halide ions. The slightly depressed nature of the semi circle which has the center below the real axis indicates the generation of micro roughness surface heterogeneities at the surface during the corrosion process.^{40,41} The charge transfer resistance R_{ct} and the interfacial double layer capacitance C_{dl} derived from these curves are given in Table 2.

It is observed that the R_{ct} values increase from 33 $\Omega \text{ cm}^2$ to 288 $\Omega \text{ cm}^2$ at $2.5 \times 10^{-3} \text{ mol L}^{-1}$ KI where the highest inhibition efficiency of 89% is observed. The C_{dl} values are also decreased from 2244 $\mu\text{F cm}^{-2}$ in the presence of iodide ions. The higher surface capacitance values for iron is due to the micro roughness of the surface during corrosion process. Similar higher values of 1775 $\mu\text{F cm}^{-2}$,⁴² 750 $\mu\text{F cm}^{-2}$ ⁴³ and 1504 $\mu\text{F cm}^{-2}$ ⁴⁴ have been reported for iron in 0.5 mol L⁻¹ H₂SO₄ solutions. Typical linear polarization curves for iron in 0.5 mol L⁻¹ H₂SO₄ with and without the addition of various concentrations of iodide ions is shown in Figure 3. The slope

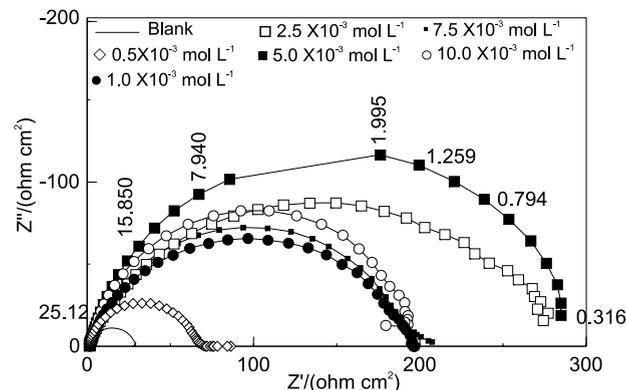


Figure 2. Nyquist plots of iron in 0.5 mol L⁻¹ H₂SO₄ with and without the addition of iodide ions.

of these curves, the polarization resistance R_p showed an increase values from 34 $\Omega \text{ cm}^2$ to 327 $\Omega \text{ cm}^2$ and then decreases with the further addition of iodide ions (Table 2). As observed in the case of potentiodynamic method, linear polarization method and impedance method have showed that further increase of iodide ion concentrations leads to gradual decrease in inhibition efficiency. Surface coverage " θ " values suggest that uniform adsorption of iodide ions on iron surface at lower concentrations and a small amount of desorption of the same at higher concentrations.

Bromide ions

Figure 4 shows the potentiodynamic polarization behaviour of iron in 0.5 mol L⁻¹ H₂SO₄ with the addition of bromide ions. The corrosion kinetic parameters derived from these plots are presented in the Table 3. It is seen from the Table 3 that the bromide ions are not as effective as iodide ions even though the inhibition efficiency is increased with the increase in the concentration of the bromide ions. The corrosion current values decrease from 410 $\mu\text{A cm}^{-2}$ to 52 $\mu\text{A cm}^{-2}$ with the maximum concentration of bromide ions (i.e.

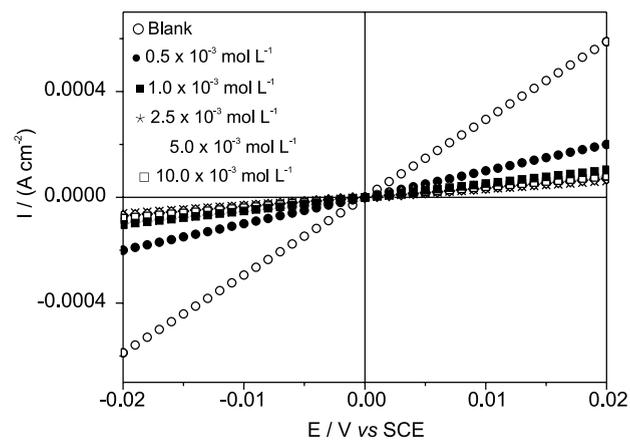
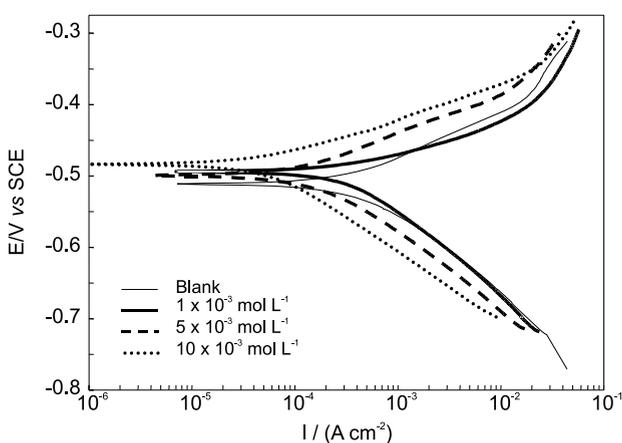


Figure 3. Linear polarization curves for iron in 0.5 mol L⁻¹ H₂SO₄ with and without the addition of iodide ions.

Table 2. Electrochemical impedance and linear polarization parameters for pure iron in 0.5 mol L⁻¹ H₂SO₄ with I⁻ ions

Concentration of I ⁻ ions (10 ⁻³ mol L ⁻¹)	Impedance Method				LPR Method	
	R _{ct} (Ω cm ²)	C _{dl} (μF cm ²)	Inhibition Efficiency (%)	Surface Coverage (θ)	R _p (Ω cm ²)	Inhibition Efficiency (%)
Blank	33	2244	—	—	34	—
0.5	67	731	50	0.61	100	66
1.0	199	802	83	0.64	225	85
2.5	288	685	89	0.69	327	90
5.0	290	682	89	0.70	286	88
7.5	193	812	83	0.64	255	87
10.0	194	839	83	0.63	194	83

10.0 × 10⁻³ mol L⁻¹) where the inhibition efficiency is 87%. The corrosion potential E_{corr} remains unaffected by the added bromide ions which indicates the mixed mode of action.

**Figure 4.** Potentiodynamic polarisation behaviour of iron in 0.5 mol L⁻¹ H₂SO₄ without and with the addition of bromide ions.

The charge transfer resistance (R_{ct}) values derived from the Nyquist plots (Figure 5) are given in Table 4 along with the polarization resistance values obtained from the linear polarization resistance method. The R_{ct} values are increased from 33 Ω cm² to 201 Ω cm² with a corresponding increase of inhibition efficiency to 84%. The interfacial double layer capacitance C_{dl} values are decreased from 2244 μF cm² to 131 μF cm² while the surface coverage θ values are increased from 0.47 to 0.94 indicating the uniform adsorption of Br⁻ ions on the iron electrode.

Chloride ions

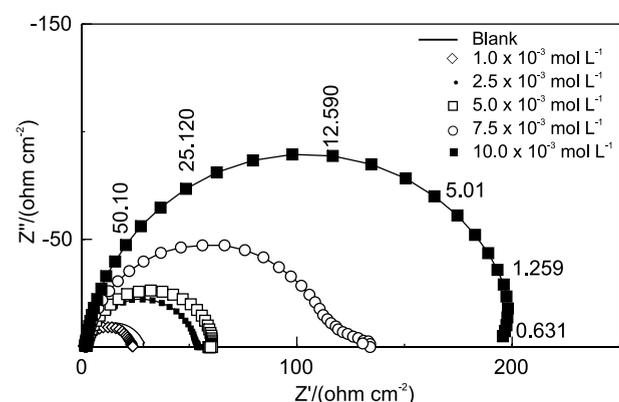
Table 4 shows the corrosion kinetic parameters derived from the polarization curves (Figure 6) after the addition of various concentrations of chloride ions. It is observed that the i_{corr} values are decreased to 90 μA cm⁻² for 5.0 × 10⁻³ mol L⁻¹ of KCl corresponding to an inhibition efficiency of 78% and after that a sharp rise

Table 3. Corrosion kinetic parameters of pure iron in 0.5 mol L⁻¹ H₂SO₄ with Br⁻ ions

Concentration of Br ⁻ ions (10 ⁻³ mol L ⁻¹)	E _{corr} (mV vs SCE)	b _a (mV dec ⁻¹)	b _c (mV dec ⁻¹)	i _{corr} (μA cm ⁻²)	Inhibition Efficiency (%)
Blank	-508	76	109	410	—
1.0	-488	49	100	296	28
2.5	-506	61	103	195	52
5	-496	45	97	140	65
7.5	-510	72	91	54	86
10	-480	50	96	52	87

Table 4. Electrochemical impedance and linear polarization parameters for pure iron in 0.5 mol L⁻¹ H₂SO₄ with Br⁻ ions

Concentration of I ⁻ ions (10 ⁻³ mol L ⁻¹)	Impedance Method				LPR Method	
	R _{ct} (Ω cm ²)	C _{dl} (μF cm ²)	Inhibition Efficiency (%)	Surface Coverage (θ)	R _p (Ω cm ²)	Inhibition Efficiency (%)
Blank	33	2244	—	—	34	—
1.0	23	1178	—	0.48	27	—
2.5	51	487	35	0.78	62	45
5	60	381	45	0.83	59	42
7.5	118	375	72	0.83	148	77
10	201	131	84	0.94	179	81

**Figure 5.** Nyquist plots of iron in 0.5 mol L⁻¹ H₂SO₄ with and without the addition of bromide ions.

in corrosion current density is observed with further increase in concentration of chloride ions. As in the case of bromide ions, here also, the E_{corr} values are not changed significantly with the addition of chloride ions.

The charge transfer resistance R_{ct} values derived from the electrochemical impedance spectroscopy (Figure 7) and the polarization resistance R_p values obtained from LPR studies are given in Table 6. It is found that increase in inhibition efficiency up to a specific concentration of chloride ions which is very much agreeing with that of polarization measurements. Chloride ions inhibit the iron dissolution at lower concentrations more effectively than at higher concentrations.

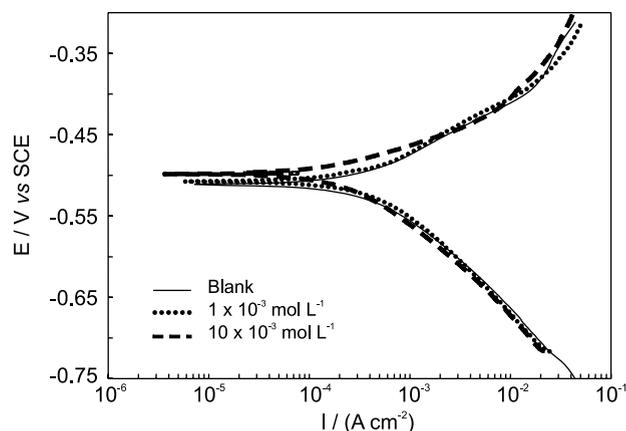


Figure 6. Potentiodynamic polarisation behaviour of iron in 0.5 mol L⁻¹ H₂SO₄ without and with the addition of chloride ions.

Table 5. Corrosion kinetic parameters of pure iron in 0.5 mol L⁻¹ H₂SO₄ with Cl⁻ ions

Concentration of Cl ⁻ ions (10 ⁻³ mol L ⁻¹)	E _{corr} (mV vs SCE)	b _a (mV dec ⁻¹)	b _c (mV dec ⁻¹)	i _{corr} (μA cm ⁻²)	Inhibition Efficiency %
Blank	-508	76	109	410	—
1.0	-504	68	109	347	15
2.5	-521	115	137	251	38
5	-508	84	140	90	78
7.5	-519	50	100	238	42
10	-501	77	106	245	40

The role of halide ions in the iron dissolution is still a matter of dispute. According to the present study, all halide ions influence the kinetics of metal dissolution to some extent depending on their nature and concentration. At lower concentrations and near the corrosion potential, the halide ions are chemisorbed more strongly on the iron electrode surface thereby reducing the free surface area of the metal for metal dissolution reaction to a larger extent than for hydrogen evolution.⁴⁵ The specific adsorption of halide ions on the iron surface gives rise to the inhibition of iron dissolution³²⁻³⁶ and the inhibitory action of these halide ions on the active dissolution of iron in H₂SO₄ has been reported by Walpert.⁴⁶ The inhibition of iron corrosion by halide ions has been reported to be caused by the adsorption on the electrode surface and by the formation of surface compounds which are insoluble in the corrosive media.⁴⁷⁻⁴⁸

The inhibition behaviour of I⁻ ions at lower concentrations is mainly due to the strong adsorption of these ions on the electrode surface at E_{corr}.⁴⁹ The adsorption ability of halide ions on the iron surface has been estimated in the order^{2, 50-52}

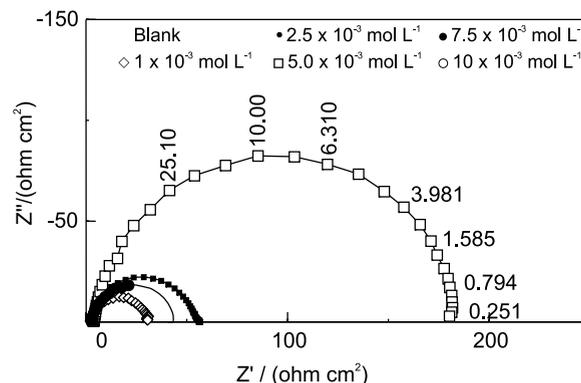


Figure 7. Nyquist plots of iron in 0.5 mol L⁻¹ H₂SO₄ with and without the addition of chloride ions.

Generally the adsorbability of anions is related to the degree of hydration; the less hydrated ion is preferentially adsorbed on the electrode surface.^{53,54} The ease of adsorption in the case of iodide ions may be due to its less degree of hydration. The inhibitive effect of halide ions is found to be in the same order as that of adsorption ability. The anodic tafel slope values in the presence of halide ions are 70 ± 10 mV and cathodic tafel slope values are 100 ± 10 mV. The anodic tafel slopes have been reported as 30 mV⁵⁵ and 40 mV⁵⁶ for iron in acid solutions. The higher anodic tafel slopes are attributed to the measurements made in shorter immersion time.³

Table 6. Electrochemical impedance and linear polarization parameters for pure iron in 0.5 mol L⁻¹ H₂SO₄ with Cl⁻ ions

Concentration of Cl ⁻ ions (10 ⁻³ mol L ⁻¹)	Impedance Method				LPR Method	
	R _{ct} (Ω cm ²)	C _{dl} (μF cm ⁻²)	Inhibition Efficiency (%)	Surface Coverage (θ)	R _p (Ω cm ²)	Inhibition Efficiency (%)
Blank	33	2244	—	—	34	—
1.0	29	1066	—	0.53	33	—
2.5	54	453	37	0.80	61	44
5	180	290	81	0.87	203	83
7.5	41	802	20	0.64	46	26
10	37	903	12	0.60	45	26

The corrosion potential E_{corr} values are found to be shifted in noble direction in the case of iodide ions whereas, the values remain unaffected in the case of bromide and chloride ions. This shows that iodide ions affect the anodic reaction significantly whereas bromide and chloride ions affect both the reactions.

There is a marked decrease in C_{dl} values in the presence of halide ions. This decrease in the C_{dl}, which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, signifying

that the halide ions act by adsorption at the solution/ interface.⁵⁷ Further, it is reported that these adsorbed halide ions do not participate in iron dissolution reaction since negative reaction orders have been observed in sulphate solutions.^{32,58,59} Cathodic polarization studies on the effect of addition of chloride and iodide ions on iron dissolution in H₂SO₄ solutions have revealed that the adsorbed halide ions inhibits the hydrogen evolution reaction predominantly.^{49,60} Hence the mechanism of inhibition of iron dissolution in sulphuric acid solution by halide ions is mainly due to blocking of surface by adsorption.

Conclusions

The halide ions are found to inhibit the corrosion of iron in 0.5 mol L⁻¹ H₂SO₄ to the extent of 80 to 90% at concentrations less than 5 x 10⁻³ mol L⁻¹. The order of inhibition is I⁻ > Br⁻ > Cl⁻. The inhibition of halide ions is mainly due to adsorption on iron surface at the corrosion potential.

Acknowledgments

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