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Inhibition of iron corrosion in 0.5 M sulphuric acid by metal cations

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Abstract

Corrosion inhibitors are widely used in acid solutions during pickling and descaling. Mostly organic compounds containing N, O, and S groups are employed as inhibitors. In this study, the inhibition performance of metal cations such as Zn^{2+}, Mn^{2+} and Ce^{4+} ions in the concentration range $1–10 \times 10^{-3}$ M has been found out. The corrosion behaviour of iron in 0.5 M H_2SO_4 in the presence of metal cations is studied using polarization and impedance methods. It is found that the addition of these metal cations inhibits the corrosion markedly. The inhibition effect is in the following order $Ce^{4+} \gg Mn^{2+} > Zn^{2+}$.

Keywords: Iron; Corrosion; Sulphuric acid; Metal cations; Polarization; Elecrochemical impedance spectroscopy

1. Introduction

Acid solutions are widely used in industries for pickling, acid cleaning of boilers, descaling and oil well acidizing. Corrosion inhibitors are widely used in order to control the corrosion of metallic materials by the cleaning acids. Inhibition of corrosion of metals is of high technological importance [1] and progress made in this field has been phenomenal in last few decades [2,3]. Mostly, sulphuric and hydrochloric acids are employed for such purposes. The efficacy of an inhibitor is mainly dependent on its ability to get adsorbed on the metal surface. Most of the earlier studies on the inhibition of corrosion of metals in acids have been related to the studies of organic compounds having π bonds and or containing N, O and S groups [4–8].

Only very limited number of studies have been carried out on the effect of metal cations on the corrosion behaviour of iron in acid media. Earlier studies [9] on the inhibiting effect of Al_2O_3 and Sb_2O_3 on corrosion of iron in acid have indicated the inhibition of iron dissolution has been attributed to the deposition of the metal ions on iron and raising the over voltage of hydrogen evolution reaction. Drazic and Vorkapic [10] have studied the inhibition effects of manganese, cadmium and zinc ions on hydrogen evolution reaction and corrosion of iron in 0.25 M sulphuric acid solution and explained the inhibition by metal cations due to under potential deposition of ad atoms of these metals on iron. However, the adsorption characterization of the metal cations is not studied so far. In the present study, the adsorption properties of metal cations such as Zn^{2+}, Mn^{2+} and Ce^{4+} ions on iron and the corrosion inhibition behaviour of iron in 0.5 M H_2SO_4 solution have been found out.

2. Experimental

Experiments were made using a conventional three-electrode cell assembly. The working electrode was a pure iron sample of one cm^2 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 working electrode was polished with 1/0, 2/0 and 3/0 emery papers, washed with water and degreased with trichloroethylene. The corrosion inhibition studies were carried out in deaerated 0.5 M H_2SO_4 solution containing $1–10 \times 10^{-3}$ M Zn^{2+}, Mn^{2+} and Ce^{4+} ions. The metal cations containing solutions were prepared by dissolving $ZnSO_4$, $MnSO_4$ and $Ce(SO_4)_2$ salts at required concentrations. Electrochemical analyzer (Solartron, Model 1280 B) interface with an IBM computer was used for electrochemical

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measurements. The polarization studies were made after the specimen attained a steady-state potential. The polarization was carried out using a Corrware software from a cathodic potential of −0.2 V to an anodic potential of +0.2 V with respect to the corrosion potential at a sweep rate of 0.5 mV/s. The linear Tafel segments of the anodic and cathodic curves in E versus log I curves were extrapolated to corrosion potential to obtain the corrosion current densities (i_{corr}). The corrosion inhibition efficiency was evaluated from the measured i_{corr} values using the relationship

$$\mathrm{IE\%} = \left\{ \frac{i_{\mathrm{corr}} - i'_{\mathrm{corr}}}{i_{\mathrm{corr}}} \right\} \times 100$$

where i_{corr} and i'_{corr} are the corrosion current densities without and with the addition of metal cations.

For linear polarization resistance (LPR) measurements, the potential of the electrode was scanned from −0.02 to +0.02 V versus corrosion potential at a scan rate of 0.5 mV/s and the polarization resistance (R_{p}) was measured from the slope of η versus i curve in the vicinity of corrosion potential. From the measured polarization resistance values, the inhibition efficiency has been calculated using the relationship

$$\mathrm{IE\%} = \frac{R'_{\mathrm{p}} - R_{\mathrm{p}}}{R'_{\mathrm{p}}} \times 100$$

where R_{p} and R'_{p} are the polarization resistance values without and with the addition of metal cations.

The impedance measurements were carried out using ac signals of 10 mV amplitude for the frequency spectrum from 100 KHz to 0.01 Hz. The Nyquist representations of the impedance data were analysed with Zview software. The charge-transfer resistance (R_{ct}), values were obtained from the diameter of the semicircles of the Nyquist plots. The inhibition efficiency of the inhibitor has been found out from the charge-transfer resistance (R_{ct}) values using the following equation.

$$\mathrm{IE\%} = \frac{R'_{\mathrm{ct}} - R_{\mathrm{ct}}}{R'_{\mathrm{ct}}} \times 100$$

where R_{ct} and R'_{ct} are the charge-transfer resistance values in the absence and presence of metal cations.

The interfacial double layer capacitance (C_{dl}) value has been estimated from the impedance value of the frequency having maximum imaginary component ($f_{\max}$) in the Nyquist plot by using the following equation.

$$C_{\mathrm{dl}} = \frac{1}{2\pi f_{\max} R_{\mathrm{ct}}}$$

and the surface coverage θ by the inhibitor molecule is given by

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

(since $C_{\mathrm{dls}} \ll C_{\mathrm{dl}}$) where C_{dl}, C'_{dl} and C_{dls} are the double layer capacitance values in the absence, presence of metal cations and saturated value in the presence of inhibitor, respectively [11–13].

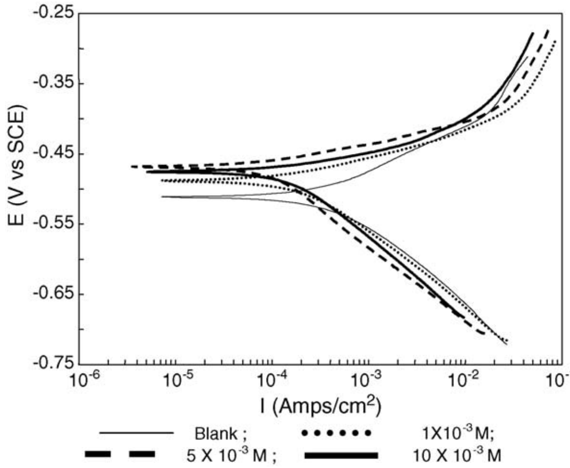


Fig. 1. Polarization curves for iron in 0.5 M H_2SO_4 with different concentrations of Zn^{2+} ions — Blank; ··· 1×10^{-3} M; ▬ ▬ ▬ 5×10^{-3} M; ▬▬▬ 10×10^{-3} M.

3. Results and discussion

3.1. Inhibition by Zn^{2+} ions

The potentiodynamic polarization behaviour of iron in 0.5 M H_2SO_4 without and with the addition of Zn^{2+} ions is shown in Fig. 1. The corrosion kinetic parameters derived from these curves are presented in Table 1. From the table it is clear that the addition of Zn^{2+} ions in the concentration range 10^{-3}–10^{-2} M reduces significantly the dissolution rate of iron in 0.5 M H_2SO_4. The corrosion current density, i_{corr}, is decreased from 410 μA cm^{-2} for the inhibitor free solution to 157 μA cm^{-2} with the inhibition efficiency of 62% at the highest studied concentration of Zn^{2+}. The steady-state corrosion potentials E_{corr} are in the range of −510 ± 10 mV. The anodic tafel slopes are in the range 68 ± 8 mV and the cathodic tafel slopes are in the range 105 ± 5 mV.

The LPR studies showed an increase in polarization resistance R_{p} values from 34 to 68 Ω cm^2 in the presence of 10×10^{-3} M Zn^{2+} ions (Table 2).

The Nyquist representation of the impedance values of the iron in 0.5 M H_2SO_4 with the addition of Zn^{2+} cations is shown in Fig. 2. The existence of a single semicircle depicts the presence of single charge-transfer process during dissolution which is unaffected by the presence of metal cations. The slightly depressed nature of the semicircle which has the center below the real axis is due to the generation of

Table 1
Corrosion kinetic parameters of pure iron in 0.5 M H_2SO_4 with Zn^{2+} ions

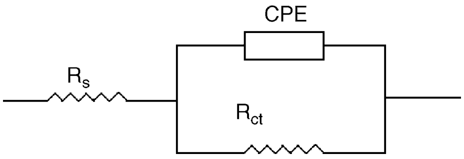
Concentration of Zn^{2+} ions × 10^{-3} M	E_{corr} (mV) vs. SCE	b_{a} (mV/dec)	b_{c} (mV/dec)	i_{corr} (μA/cm^2)	IE (%)
Blank	−508	76	109	410	–
1.0	−518	60	100	303	26
2.5	−516	68	99	190	54
5	−513	61	105	124	69
7.5	−500	68	110	120	71
10	−503	61	109	157	62

Table 2
Electrochemical impedance and linear polarization parameters for pure iron in 0.5 M H_2SO_4 with Zn^{2+} ions

Concentration of Zn^{2+} ions × 10^{-3} M	Impedance method						LPR method	
	R_{ct} (Ω cm^2)	Y_0 (μ Ω^{-1} s^n)	n	C_{dl} (μF cm^{-2})	IE (%)	Surface coverage (θ)	R_p (Ω cm^2)	IE (%)
Blank	33.0	362	0.83	186	–	–	34	–
1.0	34.5	216	0.90	123	4.3	0.34	40	15
2.5	45.1	174	0.89	117	26.8	0.37	49	30
5.0	52.5	212	0.88	105	37.1	0.44	65	48
7.5	61.5	164	0.90	101	46.3	0.46	75	55
10.0	56.7	131	0.90	75	41.8	0.59	68	50

micro roughness at the surface during the corrosion process [14,15].

The impedance data were analysed using the equivalent circuit



where R_s is the solution resistance, R_{ct} the charge-transfer resistance and CPE is the constant phase element of the double layer capacitance (C_{dl}).

Assumption of a simple $R_{ct} - C_{dl}$ is usually a poor approximation especially for systems showing depressed semicircle behaviour. For the description of a frequency independent phase shift between an applied AC potential and its current response, a constant phase element (CPE) is used which is defined in impedance representation as

$$Z(\mathrm{CPE}) = Y_0^{-1}(j\omega)^{-n}$$

where Y_0 is the CPE constant, ω is the angular frequency (in rad s^{-1}), $j^2 = -1$ is the imaginary number and n is the CPE exponent. Depending on n, CPE can represent resistance ($Z(\mathrm{CPE}) = R$, $n = 0$), capacitance ($Z(\mathrm{CPE}) = C$, $n = 1$), inductance ($Z(\mathrm{CPE}) = L$, $n = -1$) or Warburg impedance for ($n = 0.5$) [16]. The correct equation to convert Y_0 into C_{dl} is [17]

$$C_{dl} = Y_0(\omega''_m)^{n-1}$$

where C_{dl} is the double layer capacitance and ω''_m is the angular frequency at which Z'' is maximum. The diameter of the semicircle, the charge-transfer resistance (R_{ct}) and the interfacial double layer capacitance (C_{dl}) values derived from impedance plots are given in Table 2. The R_{ct} values are found to increase from 33 Ω cm^2 for inhibitor free solution to 56.7 Ω cm^2 to the highest studied concentration of Zn^{2+} ions. The C_{dl} values are decreased with the increase of concentration of zinc ions due to coverage of the iron surface by adsorption.

On comparing the inhibition efficiency values at 10×10^{-3} M Zn^{2+} ion, the value is 5–10% less with 7.5×10^{-3} M Zn^{2+} ion. The reason for the small decrease in inhibition efficiency at higher concentration is not clear.

3.2. Inhibition by Mn^{2+} ions

Fig. 3 shows the potentiodynamic polarization behaviour of iron in 0.5 M H_2SO_4 with the addition of Mn^{2+} cations. The corrosion kinetic parameters derived from these plots are presented in Table 3. It is observed from Table 3 that the manganese ions show a better performance than zinc ions. The

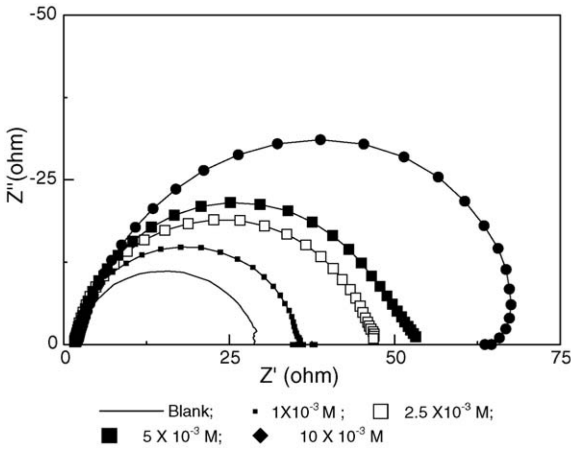


Fig. 2. Nyquist plots of iron in 0.5 M H_2SO_4 with different concentrations of Zn^{2+} ions — Blank; ■ 1×10^{-3} M; □ 2.5×10^{-3} M; ■ 5×10^{-3} M; ◆ 10×10^{-3} M.

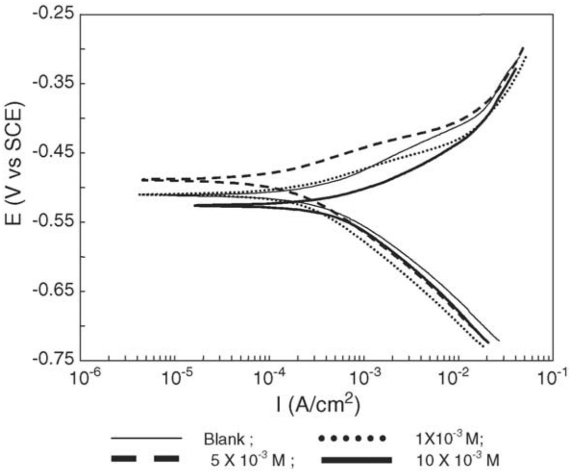


Fig. 3. Polarization curves for iron in 0.5 M H_2SO_4 with different concentrations of Mn^{2+} ions — Blank; ··· 1×10^{-3} M; ▬ ▬ ▬ 5×10^{-3} M; ▬▬ 10×10^{-3} M.

Table 3
Corrosion kinetic parameters of pure iron in 0.5 M H_2SO_4 with Mn^{2+} ions

Concentration of Mn^{2+} ions × 10^{-3} M	E_{corr} (mV) vs. SCE	b_a (mV/dec)	b_c (mV/dec)	i_{corr} (μA/cm^2)	IE (%)
Blank	−508	76	109	410	–
1.0	−513	60	106	280	31
2.5	−511	60	99	235	42
5	−498	66	100	188	54
7.5	−491	65	113	150	63
10	−497	67	111	109	73

corrosion current value is decreased from 410 to 109 μA cm^{-2} for 10 × 10^{-3} M Mn^{2+} ions. The maximum inhibition efficiency of 73% is observed at 10 × 10^{-3} M for Mn^{2+} ions. The E_{cor} values (−500 ± 10 mV), the anodic tafel slope values (68 ± 8 mV) and the cathodic tafel slope values (105 ± 8 mV) are not significantly affected by the addition of Mn^{2+} ions. The polarization resistance R_p obtained from linear polarization resistance method (Table 4) showed an increase with an increase of Mn^{2+} ions concentration and the inhibition efficiency is increased upto 70%.

The charge-transfer resistance R_{ct} derived from the Nyquist plots (Fig. 4) is presented in Table 4. These results also showed an increase in value from 33 to 95.7 Ω cm^2 with a corresponding increase of inhibition efficiency up to 65.5% for 10 × 10^{-3} M Mn^{2+} ions. The surface coverage of the Mn^{2+} ions is found to increase with the increase in concentration.

3.3. Inhibition by Ce^{4+} ions

Table 5 shows the corrosion kinetic parameters derived from the polarization curves (Fig. 5) after the addition of various concentrations of Ce^{4+} cations. It is observed that the maximum efficiency obtained is 93% in the presence of 10 × 10^{-3} M Ce^{4+} ions which is much better than the other two cations studied. The E_{corr} values have been found to be shifted to noble values by the addition of Ce^{4+} ions. This shows that the Ce^{r+} ions inhibits the anodic reaction predominantly. However, there are no marked changes in the anodic tafel slopes (68 ± 8 mV) and cathodic tafel slopes (108 ± 9 mV).

The polarization resistance R_p obtained from LPR studies showed an increase in the value from 34 to 453 Ω cm^2 corresponding to the maximum efficiency of 93% for the highest studied concentration.

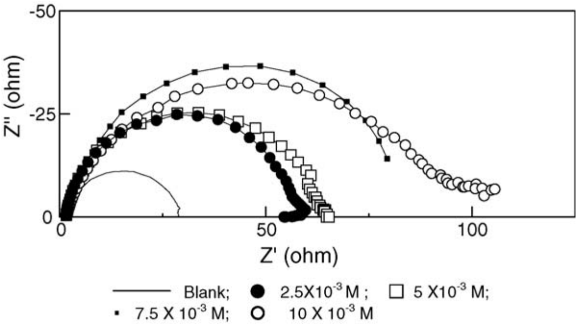


Fig. 4. Nyquist plots of iron in 0.5 M H_2SO_4 with different concentrations of Mn^{2+} ions — Blank; ● 2.5 × 10^{-3} M; □ 5 × 10^{-3} M; ■ 7.5 × 10^{-3} M; ○ 10 × 10^{-3} M.

Table 5
Corrosion kinetic parameters of pure iron in 0.5 M H_2SO_4 with Ce^{4+} ions

Concentration of Ce^{4+} ions × 10^{-3} M	E_{corr} (mV) vs. SCE	b_a (mV/dec)	b_c (mV/dec)	i_{corr} (μA/cm^2)	IE (%)
Blank	−508	76	109	410	–
1.0	−508	55	107	195	52
2.5	−499	64	107	164	60
5	−492	66	100	105	74
7.5	−464	60	108	42	89
10	−419	70	117	30	93

The charge-transfer resistance R_{ct} derived from the electrochemical impedance spectroscopy (Fig. 6) also showed (Table 6) an increase in inhibition efficiency which is very much agreeing with that of LPR measurements. The maximum value of θ is observed in the case of Ce^{4+} in comparison with that of Mn^{2+} and Zn^{2+} for the same concentration also confirms the better performance of cerium ions.

3.4. Adsorption isotherm of metal cations

The values of surface coverage (θ) have been obtained from the C_{dl} values for different concentrations of metal cations since adsorption of the metal cation is directly related to double layer capacitance. Tables 2, 4 and 6 give the surface coverage values for various concentrations of Zn^{2+}, Mn^{2+} and Ce^{4+} ions, respectively. The θ values are found to fit Langmuir adsorption isotherm and the corresponding plot is shown in Fig. 7.

The inhibition effect of the studied metal cations viz Zn^{2+} and Mn^{2+} ions is mainly due to adsorption on iron surface and

Table 4
Electrochemical impedance and linear polarization parameters for pure iron in 0.5 M H_2SO_4 with Mn^{2+} ions

Concentration of Mn^{2+} ions × 10^{-3} M	Impedance method						LPR method	
	R_{ct} (Ω cm^2)	Y_0 (μΩ^{-1} s^n)	n	C_{dl} (μF cm^{-2})	IE (%)	Surface coverage (θ)	R_p (Ω cm^2)	IE (%)
Blank	33.0	362	0.83	186	–	–	34	–
1.0	46.0	298	0.89	140	28.3	0.25	46	26
2.5	50.1	276	0.89	128	34.1	0.32	55	38
5.0	62.0	172	0.92	98	46.8	0.47	67	49
7.5	74.9	151	0.92	101	55.9	0.46	73	53
10.0	95.7	155	0.79	49	65.5	0.73	112	70

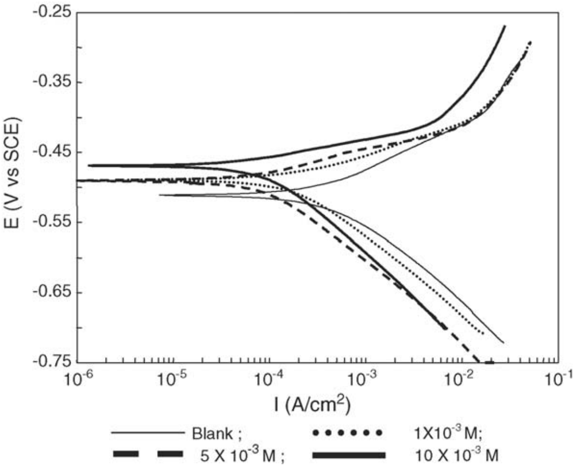


Fig. 5. Polarization curves for iron in 0.5 M H_2SO_4 with different concentrations of Ce^{4+} ions — Blank; ··· 1 × 10^{-3} M; ▬ ▬ ▪ 5 × 10^{-3} M; ▬▬ 10 × 10^{-3} M.

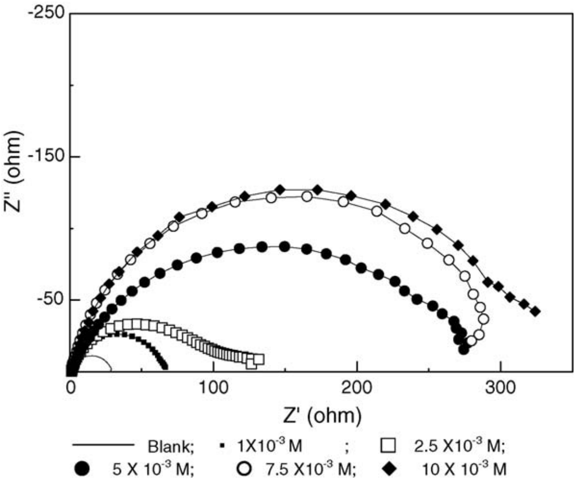


Fig. 6. Nyquist plots of iron in 0.5 M H_2SO_4 with different concentrations of Ce^{4+} ions — Blank; ■ 1 × 10^{-3} M; □ 2.5 × 10^{-3} M; ● 5 × 10^{-3} M; ○ 7.5 × 10^{-3} M; ◆ 10 × 10^{-3} M.

decreasing the over all corrosion rate. The earlier studies [9] on the inhibiting effect of Sb_2O_3 and As_2O_3 have been attributed to the deposition of the metal on iron and raising the hydrogen over voltage and thereby reducing the corrosion. It has been reported that the deposition of Pb, Cd and Bi on noble metals Pt, Pd, In [18–20] at potentials more positive than their reversible potential and in an amount which can even produce a monolayer of the deposited ad atoms. Earlier studies by Drazic and Vorkapic [10] on the effect of Mn^{2+}, Zn^{2+} and Cd^{2+} ions on the hydrogen evolution reaction and the corrosion of iron in H_2SO_4 have shown the inhibition nature of metal cations. Since the range of potential over which the hydrogen evolution reaction was inhibited lies more positive than the equilibrium potential for the deposition of these metals on the iron surface, the inhibiting effects have been explained by the under potential deposition (UPD) of these metals. The importance of the study is that cations of the metals which are more negative than the corrosion potential if present in the electrolyte, cannot be considered only as ''neutral salt'' until it is experimentally proven that there is no UPD of these metals with corresponding effect. The slightly higher inhibition efficiency value for Mn^{2+} ion in comparison with Zn^{2+} ion may be due to higher reversible potential ($E_{r,Zn} = -0.760$; $E_{r,Mn} = -1.180$ V) of manganese ions which facilitate more inhibition of hydrogen evolution reaction

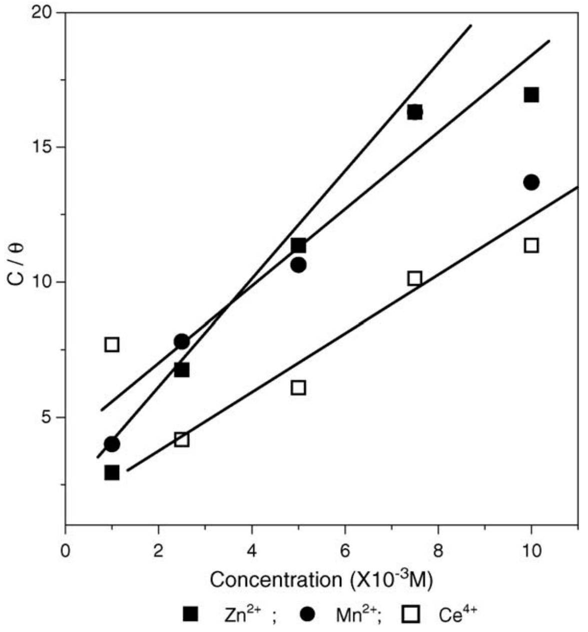


Fig. 7. Langmuir adsorption isotherm for metal cations ■ Zn^{2+}; ● Mn^{2+}; □ Ce^{4+}.

Table 6
Electrochemical impedance and linear polarization parameters for pure iron in 0.5 M H_2SO_4 with Ce^{4+} ions

Concentration of Ce^{4+} ions × 10^{-3} M	Impedance method						LPR method	
	R_{ct} (Ω cm^2)	Y_0 (μΩ^{-1} s^n)	n	C_{dl} (μF cm^{-2})	IE (%)	Surface coverage (θ)	R_p (Ω cm^2)	IE (%)
Blank	33.0	362	0.83	186	–	–	34	–
1.0	64.8	282	0.88	161	49.1	0.13	70	51
2.5	108.1	192	0.81	75	69.4	0.60	103	67
5.0	269	43	0.77	33	87.7	0.82	265	83
7.5	297	77	0.88	48	88.8	0.74	347	90
10.0	319	43	0.87	23	89.6	0.88	453	93

due to increased adsorption. In the case of Ce^{4+} ions, the inhibition effect may be due to the decrease in the anodic reaction rate which has been evidenced from the shift of corrosion potential to more noble direction with the addition of Ce^{4+} ions. The future research program is aimed to study the nature of adsorption of metal cations on iron surface by spectroscopic techniques.

4. Conclusions

The addition of metal cations such as Zn^{2+}, Mn^{2+} and Ce^{4+} ions in 0.5 M sulphuric acid solution inhibits the dissolution of iron to a considerable extent. This inhibition effect of Zn^{2+} and Mn^{2+} ions is attributed to their blocking nature of these metal cations to the iron dissolution reaction. In the case of Ce^{4+} ions, the inhibition is due to the decrease in the anodic metal dissolution reaction. The order of the inhibitive effect has been found to be $Ce^{4+} \gg Mn^{2+} > Zn^{2+}$.

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