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Effect of cerium ions on corrosion inhibition of PANI for iron in 0.5 M H_2SO_4

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Abstract

In recent years conducting polymers such as polyaniline are used as corrosion inhibitors for metals in acids. The performance of the inhibitor can be enhanced either by the addition of halide ions or metal cations. A study has been made on the effect of addition of ceric ions on the corrosion inhibition performance of polyaniline for iron in 0.5 M H_2SO_4. Techniques such as electrochemical impedance spectroscopy, potentiodynamic polarization and linear polarization resistance methods have been employed to study the corrosion inhibition. The polyaniline has been used in the concentration range of 10–100 ppm and the ceric ions concentration has been maintained at 1×10^{-3} M. The inhibition efficiency of polyaniline at 10 ppm has been increased from 53 to 88% and for 50 ppm from 71 to 90% in the presence of ceric ions. The enhanced inhibition of polyaniline in presence of ceric ions is due to the higher coverage of polyaniline–cerium complex.

Keywords: Corrosion inhibition; Iron; Sulphuric acid; Cerium ions; Polyaniline; EIS

1. Introduction

Industrial applications like acid pickling, acid cleaning of boilers, descaling and oil well acidizing utilize various of acidic solutions [1–3]. To prevent the base metal attack during these processes, corrosion inhibitors are widely employed. The selection of appropriate inhibitors mainly depends on the type of acid, its concentration, temperature, velocity, presence of dissolved solids and the type of metallic materials involved. An important criterion in characterizing the efficiency of inhibitors is their efficiency/concentration ratio. Schmitt [4] in his review, discussed extensively about the types of inhibitors recommended to protect metallic materials especially ferrous metals and alloys from corrosion in acid solutions during picking, acid cleaning, scale removing and oil and gas well acidizing. Nitrogen, sulphur and oxygen containing compounds are recognized as good inhibitors [5]. The most efficient inhibitors are organic compounds having π bonds in their structures [6]. The efficacy of an organic compound as a successful inhibitor is mainly dependent on its ability to get adsorbed on the metal surface. The inhibitive effect of aliphatic amines [7], low molecular weight straight chain amines [8], aniline and alkylamine [9], p-substituted anilines [10], o-substituted anilines [11] and N-substituted anilines [12] is attributed to the interaction of π-electron cloud of aromatic ring on iron and steel surface through vacant 'd' orbital of iron leading to the formation of co-ordination bond between Fe–N. Polymer amines have abundance of π electrons and unshared electron pairs on the nitrogen atoms which can interact with the empty d-orbitals of iron. Because of this reason, polymer amines are found to be efficient corrosion inhibitors for iron in acid solutions. Substituted [13,14] and unsubstitued polyanilines [15], poly(aminoquinone) [16] and poly(diphenylamine) [17] were reported for their corrosion inhibition properties. Addition of halide ions [18,19] and metal cations such as manganese ions [20] is found to enhance the corrosion inhibition properties of polymer amines due to their co-adsorption along with the polymer. Cerium ions are known for their own corrosion preventive applications mostly for non-ferrous alloys either by coatings [21] or as inhibitors [22]. Hence by combining polyaniline and cerium ions, better performance of corrosion inhibition can be expected at lower concentration of polyaniline.

In this paper, the influence of cerium ions addition on the corrosion inhibition property of polyaniline on iron in 0.5 M H_2SO_4 is reported.

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2. Experimental

2.1. Synthesis of water soluble polyaniline

Reagent grade aniline was purified by distillation in the presence of small amount of zinc dust. Sodium salt of dodecyl benzne sulphonic acid (0.1 M) was used as dopant and was neutralized with conc. HCl. To this solution, 0.1 M of freshly distilled aniline dissolved in 0.1 M HCl was added and precooled. To this reaction mixture, freshly prepared solution of 0.1 M ammonium persulphate kept at a temperature of 5–10 °C was slowly added with constant stirring for 2 h [23,24]. Finally, a dark green solution of polyaniline was obtained and the efficiency of polymerization was about 50%. The un-reacted aniline was recovered by distillation. The poly(aniline) was characterized by UV–vis (Hitachi—U 3400), FTIR (Perkin-Elmer—Paragon 500) spectroscopy and the results are reported elsewhere [15]. The average molecular weight (Mw) was determined by GPC method (Shimadzu, Japan) and found to be 16,260.

2.2. Electrochemical studies

Experiments were made using a conventional three electrode cell assembly. The working electrode was a pure iron (Johnson Mattey Ltd., UK) sample of 1 cm^2 area with the rest being covered with araldite epoxy and a rectangular platinum foil of 6 cm^2 was used as counter electrode and saturated calomel electrode as reference electrode. The working electrode was polished with 1/0, 2/0, 3/0 and 4/0 grade emery papers, washed with distilled water and degreased with trichloroethylene. The solutions were deaerated by purging purified nitrogen gas for 30 min before the start of the experiment. Studies have been made with polyaniline in the concentration range of 10–100 ppm and cerium ions in the concentration range of 1.0×10^{-3} to 10.0×10^{-3} M separately to find their individual inhibition characteristics. The combined effect of polyaniline and cerium ions has been studied for the cerium ion concentration of 1.0×10^{-3} M for all the concentrations of polyaniline. The low concentration of cerium ion has been chosen since its own inhibition efficiency is higher at high concentrations. Solatron Electrochemical analyzer (Model 1280 B) interfaced with an IBM computer was used for measurements. The polarization studies were made at the end of 30 min of immersion at 28 ± 1 °C. 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^{-1} in order to see the effect of inhibitors on corrosion. The linear TAFEL segments of the anodic and cathodic curves were extrapolated to corrosion potential to obtain the corrosion current densities. The inhibition efficiency was evaluated from the measured i_{corr} values using the relationship,

$$\mathrm{I.E.\%} = \frac{i_{\mathrm{corr}} - i'_{\mathrm{corr}}}{i_{\mathrm{corr}}} \times 100$$

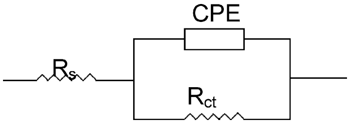
where i_{corr} and i'_{corr} are the corrosion current values without and with the addition of various concentrations of inhibitor.

For linear polarization measurements, a sweep from −0.02 to +0.02 V versus open circuit potential at a sweep rate of 0.5 mV s^{-1} was used 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,

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

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

Z plot software was used for data acquisition and analysis of interfacial impedance. AC signals of 10 mV amplitude and a frequency spectrum from 100 kHz to 0.01 Hz was impressed and the Nyquist representations of the impedance data were analysed with Zview software. The impedance data were analysed using the equivalent circuit, since most of the curves in Nyquist plots show one depressed semicircle.



In the above equivalent circuit, R_{s} is the solution resistance, R_{ct} the charge transfer resistance and CPE is the constant phase element.

Assumption of a simple R_{ct}–C_{dl} is usually a poor approximation especially for systems showing depressed semicircle behaviour due to non-ideal capacitive behaviour of solid electrodes [25]. 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

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

where Y_0 is the CPE constant, ω the angular frequency (in rad s^{-1}), $\mathrm{j}^2 = -1$ 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 ($n = 0.5$) [26]. The correct equation to convert Y_0 into C_{dl} is [27],

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

where C_{dl} is the double layer capacitance and ω''_{m} is the angular frequency at which Z'' is maximum. The surface coverage θ was estimated from the measured double layer capacitance C_{dl} values using the relationship [28,29],

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

where C_{dl} and C'_{dl} are the double layer capacitance values in the absence and presence of inhibitors.

The charge transfer resistance (R_{ct}) is obtained from the diameter of the semicircle in Nyquist representation. The

Table 1
Electrochemical impedance and linear polarization parameters for pure iron in 0.5 M H_2SO_4 with poly(aniline)

Conc. PANI (ppm)	Impedance method						LPR Method	
	R_{ct} (Ω cm^2)	Y_0 ($\mu\ \Omega^{-1}$ s^n cm^{-2})	n	C_{dl} (μF cm^{-2})	I.E. (%)	Surface coverage (θ)	R_p (Ω cm^2)	Inhibition efficiency (%)
Blank	33	362	0.83	186	–	–	34	–
10	55	214	0.88	130	40	0.30	57	40
25	57	260	0.89	112	42	0.40	68	50
50	74	124	0.88	73	55	0.61	80	58
75	111	123	0.89	69	70	0.63	125	73
100	110	128	0.89	69	70	0.63	122	72

inhibition efficiency of the inhibitor has been found out from the relationship,

$$\text{I.E.\%} = \frac{R'_{ct} - R_{ct}}{R'_{ct}} \times 100$$

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

The experimental values are reproducible within ±3%.

3. Results and discussion

3.1. Inhibition by polyaniline

The impedance behaviour of iron in 0.5 M H_2SO_4 with the addition of various concentrations of polyaniline is shown in Fig. 1. These curves show a single semicircle indicating the occurrence of a single charge transfer reaction. These curves are depressed in nature with its center below the x-axis. This observation is due to the origin of micro roughness and other inhomogeneties of the solid electrode/solution interface formed during corrosion [30–32].

The impedance parameters such as R_{ct}, C_{dl} and θ obtained from the curves in Fig. 1 are given in Table 1. The charge transfer resistance is increased from 33 Ω cm^2 for polyaniline free solution to 110 Ω cm^2 with the addition of 100 ppm of polyaniline resulting in 70% inhibition efficiency. The double layer capacitance is decreased from 186 to 69 μF cm^{-2} for 100 ppm of polyaniline. Decrease in the C_{dl} is due to a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer. This indicates that the inhibitor adsorbs at the metal–solution interface [33]. The surface coverage also reaches a maximum of 0.70 for the highest concentration of polyaniline added.

It has been found from the LPR studies that the polarization resistance (R_p) values (Table 1) are increased from 34 Ω cm^2 of that of blank to 122 Ω cm^2 for the highest concentration of inhibitor studied indicating the good inhibition character of the added polyaniline.

The potentiodynamic tafel polarization curves without and with the addition of various concentrations of polyaniline is shown in Fig. 2. The important corrosion kinetic parameters viz. corrosion potential E_{corr}, the corrosion current density I_{corr}, anodic tafel slopes (b_a) and cathodic tafel slopes (b_c) obtained from these curves are given in Table 2. It is evident from the table that the corrosion current values (i_{corr}) are decreased from 410 μA cm^{-2} of that of blank to 67 μA cm^{-2} with the addition of 100 ppm of polyaniline. The addition of polyaniline does not alter the values of E_{corr} indicating the mixed type inhibiting behaviour of polyaniline. The anodic tafel slopes are in the range of 49 ± 1 mV in the presence of polyaniline. The lower values of anodic tafel slopes may be due to the increase of interfacial pH of the inhibited solution in comparison with blank solution as has been reported by Bala [34] in the study of corrosion of iron in sulphuric acid. The cathodic tafel slopes are not affected significantly.

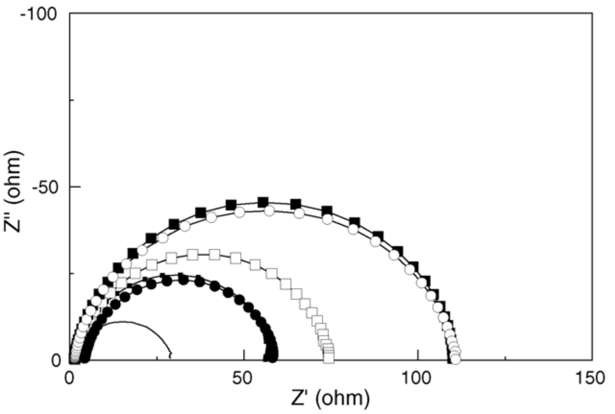


Fig. 1. Nyquist plots of iron in 0.5 M H_2SO_4 with different concentrations of poly(aniline). (—) Blank; (●) 10 ppm; (■) 25 ppm; (□) 50 ppm; (○) 75 ppm; (■) 100 ppm.

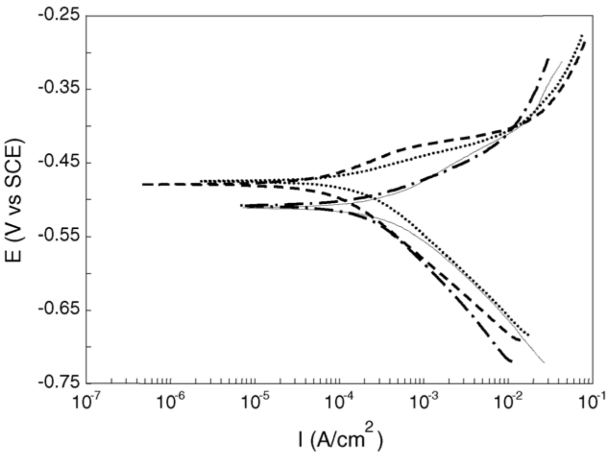


Fig. 2. Polarization curves of iron in 0.5 M H_2SO_4 with different concentrations of poly(aniline). (—) Blank; (· · ·) 10 ppm; (- - -) 50 ppm; (– · –) 100 ppm.

Table 2
Corrosion kinetic parameters of pure iron in 0.5 M H_2SO_4 with poly(aniline)

Concentration of polyaniline (ppm)	E_{corr} (mV vs. SCE)	b_a (mV/dec)	b_c (mV/dec)	i_{corr} (μA cm^{-2})	Inhibition efficiency (%)
Blank	−508	76	109	410	–
10	−521	50	113	191	53
25	−487	48	100	158	61
50	−491	48	96	120	71
75	−493	50	93	70	83
100	−488	50	95	67	84

Table 3
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 ($\times 10^{-3}$ M)	Impedance method						LPR method	
	R_{ct} (Ω cm^2)	Y_0 (Ω^{-1} s^n)	n	C_{dl} (μF cm^{-2})	I.E. (%)	Surface coverage (θ)	R_p (Ω cm^2)	Inhibition efficiency (%)
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	317	89
10.0	319	43	0.87	23	89.6	0.88	353	90

Poly(aniline) is one of the most promising and most widely studied conducting polymers for protection of corrosion due to its stability and lower cost [35–38]. Earlier studies have shown that the substituted poly(aniline) compounds are effective corrosion inhibitors for mild steel in acid chloride solutions [13,14]. The inhibitive property of poly(aniline) can mainly be attributed to the presence of plenty of π-electron clouds coexisting with quaternary nitrogen atom. The larger molecular size ensures the greater adsorption on the iron surface and decreases the effective area for corrosion reaction by blocking the reaction sites [39].

3.2. Inhibition by Ce^{4+} ions

Fig. 3 shows the Nyquist plots of iron in 0.5 M H_2SO_4 without and with the addition of Ce^{4+} cations in the concentration range 1.0×10^{-3} to 10.0×10^{-3} M. Table 3 shows the impedance parameters derived from these curves. It is found that the charge transfer resistance is increased to 319 Ω cm^2 from the blank value of 33 Ω cm^2 at the highest concentration of the Ce^{4+} ions studied corresponding to an inhibition efficiency of 90%. The double layer capacitance is also decreased to a lowest value of 23 μF cm^{-2}.

The polarization resistance R_p obtained from LPR studies showed an increase in the value from 34 to 353 Ω cm^2 corresponding to the maximum efficiency of 90%.

The corrosion kinetic parameters derived from the polarization curves (Fig. 4) without and with the addition of the various concentrations of cerium ions are given in Table 4. The corrosion current density value is decreased to 30 μA cm^{-2} from the blank value of 410 μA cm^{-2}. The corrosion potential E_{corr} has shifted to more positive value of −470 mV versus SCE from −508 mV versus SCE of blank acid. Both anodic and cathodic tafel slope values are not altered

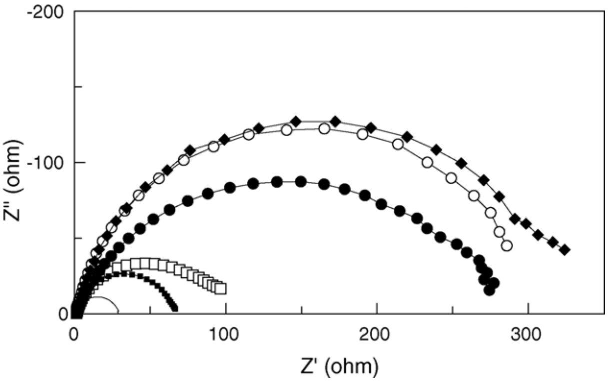


Fig. 3. Nyquist plots of iron in 0.5 M H_2SO_4 with different concentrations of Ce^{4+} ions. (—) Blank; (■) 1×10^{-3} M ; (□) 2.5×10^{-3} M; (●) 5×10^{-3} M; (○) 7.5×10^{-3} M; (◆) 10×10^{-3} M.

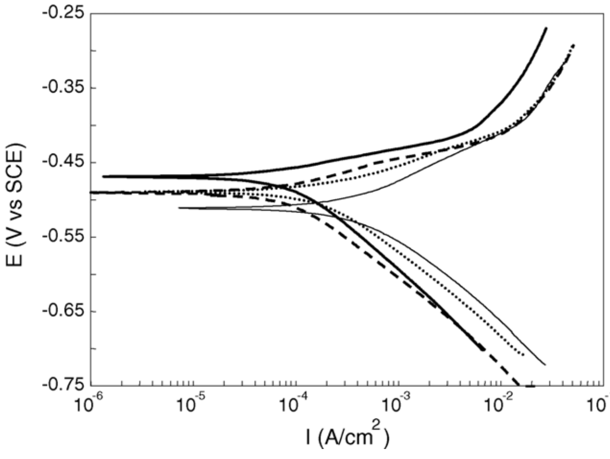


Fig. 4. Polarization curves of ion in 0.5 M H_2SO_4 with different concentrations of Ce^{4+} ions. (—) Blank; (· · ·) 1×10^{-3} M; (– – –) 5×10^{-3} M; (▬) 10×10^{-3} M.

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

Concentration of Ce^{4+} ions ($\times 10^{-3}$ M)	E_{corr} (mV vs. SCE)	b_a (mV/dec)	b_c (mV/dec)	i_{corr} (μA cm^{-2})	Inhibition efficiency (%)
Blank	−508	76	109	410	–
1.0	−490	65	107	195	52
2.5	−499	64	107	164	60
5	−492	66	100	105	74
7.5	−464	60	108	42	89
10	−470	80	117	30	93

Table 5
Electrochemical impedance and linear polarization parameters for pure iron in 0.5 M H_2SO_4 with polyaniline in presence of 1.0×10^{-3} M Ce^{4+} ions

Concentration of PANI (ppm)	Impedance method						LPR method	
	R_{ct} (Ω cm^2)	Y_0 (Ω^{-1} s^n)	n	C_{dl} (μF cm^{-2})	I.E. (%)	Surface coverage (θ)	R_p (Ω cm^2)	Inhibition efficiency (%)
Blank	33	362	0.83	186	–	–	34	–
10	195	88	0.88	46	83	0.75	207	84
25	186	80	0.81	44	82	0.76	208	84
50	219	56	0.77	37	85	0.80	230	85
75	248	51	0.88	34	87	0.82	252	87
100	310	39	0.87	23	89	0.88	329	90

significantly. It can be noted that the inhibition efficiency at 10×10^{-3} M concentration is more or less same as that obtained for 100 ppm of polyaniline. Hence, for studying the effect of ceric ions on the corrosion inhibition of polyaniline, lower concentration of 1.0×10^{-3} M has been chosen in order to find out the synergistic effect.

It has been reported [40] that the inhibition effect of the metal cations such as Mn^{2+}, Zn^{2+} and Cd^{2+} on iron corrosion in H_2SO_4 is in general due to the blocking of the free iron surface for the cathodic complementary hydrogen evolution reaction and decreasing the over all corrosion rate. These metal cations have more electronegative potentials than that of hydrogen evolution reaction (h.e.r.) and corrosion of iron in acid solution. The range of potential for hydrogen evolution reaction is more positive than the equilibrium potential for the deposition of these metal cations on the iron surface. Hence the inhibiting effect is explained by the under potential deposition (UPD) of these metals. However, 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 potentials to more noble direction with the addition of Ce^{4+} ions.

3.3. Synergistic effect of polyaniline with Ce^{4+} ions

Fig. 5 shows the Nyquist representation of the complex impedance of iron in 0.5 M H_2SO_4 with various concentrations of polyaniline along with 1.0×10^{-3} M Ce^{4+} ions. As in individual inhibited solutions, these curves also represent a single semicircle without much of depression. The R_{ct}, C_{dl} and θ values obtained from these curves are given in Table 5. The charge transfer resistance values are increased steadily with the increase in concentration of polyaniline and attained a maximum value of 310 Ω cm^2 yielding 89% of inhibition efficiency. This high value can be compared with 110 Ω cm^2 which is obtained for 100 ppm of polyaniline alone with 70% inhibition efficiency. The double layer capacitance C_{dl} value is decreased to 23 μF cm^{-2} which is very well lesser than 69 μF cm^{-2} of cerium ions free solutions.

The polarization resistance obtained from the linear polarization studies showed an increase in value of R_p (Table 5) and reached maximum of 329 Ω cm^2 in presence of 100 ppm of polyaniline with 1.0×10^{-3} M Ce^{4+} ions. For the same concentration of polyaniline without the cerium ions, the value is 122 Ω cm^2.

The potentiodynamic polarization curves for iron in 0.5 M H_2SO_4 with various concentrations of polyaniline along with cerium ions are shown in Fig. 6. The kinetic parameters obtained from these curves are presented in Table 6. The corrosion current density is decreased significantly (48 μA cm^{-2}) even at 10 ppm of polyaniline with cerium ions and is reached to a low value of 31 μA cm^{-2} for 100 ppm. The corrosion potential remains unaffected by the added inhibitors where as the anodic tafel slope

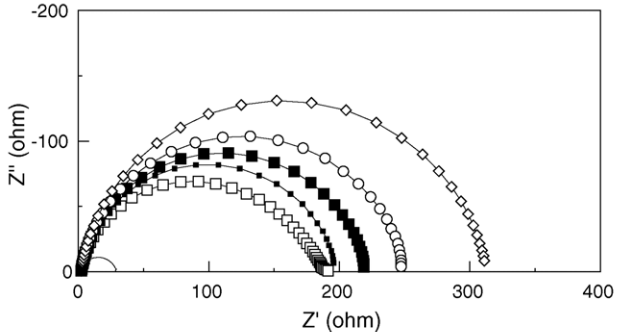


Fig. 5. Nyquist plots of iron in 0.5 M H_2SO_4 with different concentrations of polyaniline in presence of 1.0×10^{-3} M Ce^{4+} ions. (—) Blank; (■) 10 ppm; (□) 25 ppm; (■) 50 ppm; (○) 75 ppm; (◇) 100 ppm.

Table 6
Corrosion kinetic parameters of pure iron in 0.5 M H_2SO_4 with polyaniline in presence of 1.0×10^{-3} M Ce^{4+} ions

Concentration polyaniline (ppm)	E_{corr} (mV vs. SCE)	b_a (mV/dec)	b_c (mV/dec)	i_{corr} (μA cm^{-2})	Inhibition efficiency (%)	Synergism parameter (S)
Blank	−508	76	109	410	–	–
10	−506	56	98	48	88	1.90
25	−505	41	104	42	89	1.70
50	−507	51	91	38	90	1.40
75	−506	49	88	35	91	0.96
100	−511	47	104	31	92	0.96

values show a significant decrease in value as observed in the presence of polyaniline alone.

3.4. Adsorption isotherm

Fig. 7 shows the adsorption isotherm plots of polyaniline in the absence and presence of cerium ions. The linear relationship of θ versus log c shows that inhibitors obey Temkin adsorption isotherm.

All the experimental results have suggested that the addition of Ce^{4+} ions to the inhibited solution increases the inhibition efficiency and the degree of surface coverage (θ). This behaviour is attributed to the synergistic effect between added cerium ions and polyaniline.

The extent of synergism between cerium ions and polyaniline has been analysed by estimating the synergism parameter obtained from the inhibition efficiency (from tafel polarization method) according to Aramaki and Hackerman [41] as

$$S_I = \frac{1 - I_{1+2}}{1 - I'_{1+2}}$$

where $I_{1+2} = (I_1 + I_2) - (I_1 I_2)$, I_1 is the inhibition efficiency in the presence of synergistic cerium ions, I_2 the inhibition efficiency of polyaniline and I'_{1+2} is the measured inhibition efficiency of synergistic ions in combination with polyaniline.

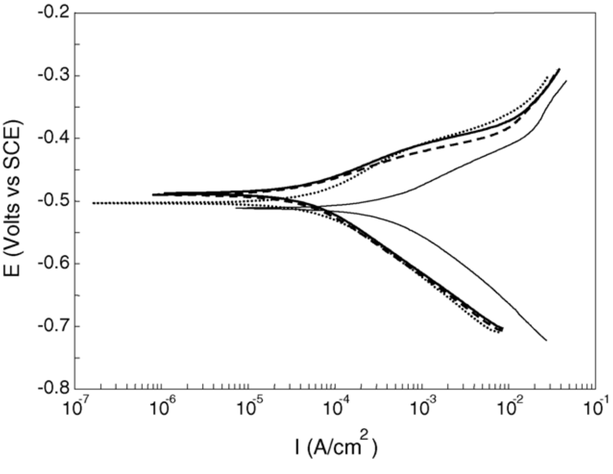


Fig. 6. Polarization curves of iron in 0.5 M H_2SO_4 with different concentrations of polyaniline in presence of 1.0×10^{-3} M Ce^{4+} ions. (—) Blank; (· · ·) 10 ppm; (– – –) 50 ppm; (━━) 100 ppm.

Table 6 gives the computed S_I values and the values are found to be more than unity in most of the cases suggesting the synergistic action of cerium ions with the polyaniline.

Earlier studies [42] on the effect of Cu^{2+}, As^{3+}, Sb^{3+} and Sn^{2+} on the corrosion of iron in HCl in the presence of hexamine have shown that the higher efficiency of hexamine in the presence of cation is due to the absorption of anionic complexes of metal–amines. In a similar way, the adsorption of cerium–polyaniline complex can enhance the inhibition efficiency of polyaniline.

Mechanisms of chemical interactions of PANI and transition metals were extensively discussed by Hirao et al. [43–46]. Depending on the metal ions used, different morphologies have been revealed in the complex PANI [47]. This may be either grain forming type or large aggregates type. In the grain morphology type, the PANI chains fold around the inorganic metal ions which serve as centers of polymer chain co-ordination leading to growth of chain. In the other type of interaction, instead of grains, larger aggregates are revealed to constitute the complex structure.

When the grain forming type is allowed to interact on a substrate, it has reported that the material form a network-like structure spanned onto the substrate [48]. The electronic spectra

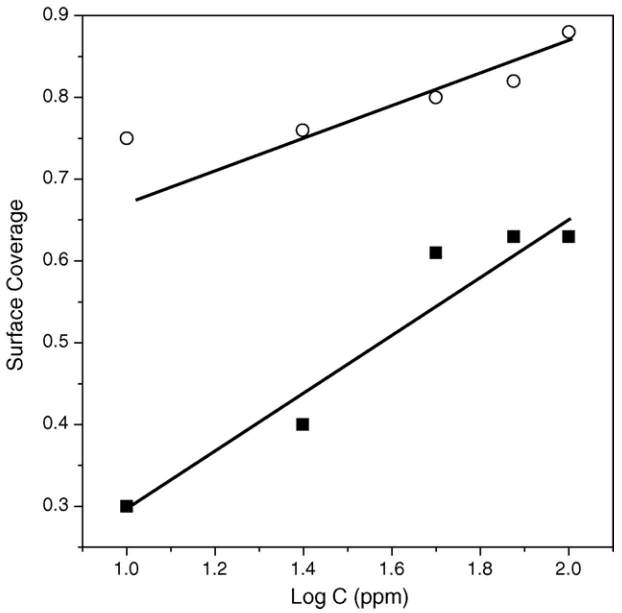


Fig. 7. Temkin adsorption plot for iron in 0.5 M H_2SO_4 containing polyaniline. (■) Without cerium and (○) with cerium.

of those complex doped by the metal ions showed the presence of benzenoid-to-quinoid transition which is located in the range of 600–640 nm for the undoped PANI.

In the present study, the cerium ions addition to the polyaniline containing acid solution may result in folded polyaniline chain with the cerium ion forming a network-like structure spread over the substrate. The availability of more quinoid structures helps to increase the number of anchoring points facilitating stronger adsorption on iron surface. This will result more coverage of the surface and enhance the corrosion inhibition efficiency.

4. Conclusions

Polyaniline inhibits corrosion of iron in 0.5 M H_2SO_4 by adsorption on the metal surface. Ceric ions act as anodic inhibitor and inhibit the corrosion of iron in 0.5 M H_2SO_4 markedly. The inhibitive performance of polyaniline in increased significantly in the presence of ceric ions. Since polyaniline has been reported to form complexes with transition metal ions and thereby change the morphology and structure, the enhanced performance of polyaniline in the presence of cerium ions may due to the formation of metal–amine complex with more quinoid moiety which facilitate strong adsorption and higher coverage on iron surface.

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