

Polyaniline as Corrosion Inhibitor for Iron in Acid Solutions

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ABSTRACT: In recent years, polymer amines have been studied as an efficient corrosion inhibitor for iron in acid media. In this article, the performance of water soluble polyaniline as corrosion inhibitor for iron in 0.5M H₂SO₄ has been evaluated by potentiodynamic polarization, linear polarization, and electrochemical impedance spectroscopy and compared with the performance of the aniline monomer. It has been found that polyaniline is an efficient inhibitor, since the maximum efficiency of 84% has been observed at a concentration of 100 ppm, whereas the monomer has accel-

erated the corrosion. FTIR studies have shown that the polyaniline is strongly adsorbed on the iron surface and inhibits the corrosion effectively. However, aniline has been found to improve the passivation tendency of iron at higher concentrations. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2144–2153, 2006

Key words: corrosion inhibition; polymer amines; polyaniline; polarization; impedance

INTRODUCTION

The use of inhibitors is one of the most effective and often successful methods of protection of corrosion of metals in acidic media.^{1–3} The efficiency and life time of the equipments in chemical plants, power plants, steel mills, sugar plants, oil, and water pipelines are decreased to great extent because of the formation of scales either by process compounds or circulating water. It is a well-known fact that acids are used in many operations such as pickling, cleaning, descaling, etc. Because of their aggressiveness, inhibitors are used to reduce the rate of dissolution of metals.

Compounds containing nitrogen, sulfur, and oxygen are being reported for this purpose.^{4,5} The most effective and efficient inhibitors are organic compounds having π bonds in their structures. The efficacy of an organic compound as a successful inhibitor is mainly dependent on its ability to get adsorbed on the metal surface, which consists of the replacement of water molecule at a corroding interface.

The adsorption of these compounds is greatly influenced by the presence of functional groups such as =NH, —N=N—, —CHO, R—OH, R=R, etc., in the inhibitor molecule, and also by the steric factors, aromaticity, and electron density at the donor atoms.^{6–9} The role of molecular area¹⁰ and molecular weight¹¹ of the organic molecule on its inhibition efficiency was

also reported. Aliphatic amines and its derivatives^{12–15} were examined for their inhibition property in acidic environment. The electron donating character of N atom having unshared pair of electrons available in 4-acetylpyridine¹⁶ and aliphatic amines^{17,18} such as dimethylamine, ethylamine, diethylamine, butylamine, butyldiethylamine, butyloctylamine, and other derivatives of octylamine was found to inhibit the iron corrosion in acidic solutions to great extent. Hydroxylamine,¹⁹ aromatic amine,²⁰ and more recently polymer amines²¹ were evaluated for their inhibition properties on the corrosion of iron and steel in acid solutions. Ortho-substituted anilines²² and substituted polyanilines^{23,24} were also studied more recently. In this article, the inhibition effect of polyaniline on the corrosion of iron in 0.5M H₂SO₄ is discussed.

EXPERIMENTAL

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 benzene sulfonic acid (0.1M) was used as dopant and was neutralized with conc. HCl. To this solution, 0.1M of freshly distilled aniline dissolved in 0.1M HCl was added and precooled. To this reaction mixture, freshly prepared solution of 0.1M ammonium persulphate kept at a temperature of 5–10°C was slowly added with constant stirring for 2 h.^{25,26} Finally, a dark green solution of polyaniline was obtained and the efficiency of polymerization was about

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50%. The un-reacted aniline was recovered by distillation. The polyaniline was characterized by UV-visible (HITACHI-U 3400), FTIR (Perkin Elmer-PARAGON 500) spectroscopy. The average molecular weight (M_w) was determined by GPC method (Shimadzu, Japan) using THF as eluant and found to be 16,260. The surface morphology was studied by SEM (HITACHI S 3000H) under the magnification of 1000 for iron surface exposed to 0.5M H_2SO_4 solution with and without inhibitors.

The adsorption peak of polyaniline at 336 nm shows the $\pi-\pi^*$ transition in the benzenoid ring and at 578 nm shows the donor-acceptor interaction of quinonoid ring [Fig. 1(a)]. The well-known cation radicals and localized polaron peaks were observed at 449 and 775 nm. The major IR adsorption bands [Fig. 1(b)] at 1555 and 1453 cm^{-1} are the characteristics band because of nitrogen-quinonoid ring structure and peaks for polyaniline observed at 1632 cm^{-1} , for N-H bending, 1555 and 1494 cm^{-1} for nitrogen benzenoid-quinonoid ring structure, the other IR characteristics are observed at 1126 and 1036 cm^{-1} . The polyaniline is shown as follows (Scheme 1):

Electrochemical studies

Experiments were made using a conventional three electrode cell assembly. The working electrode was a

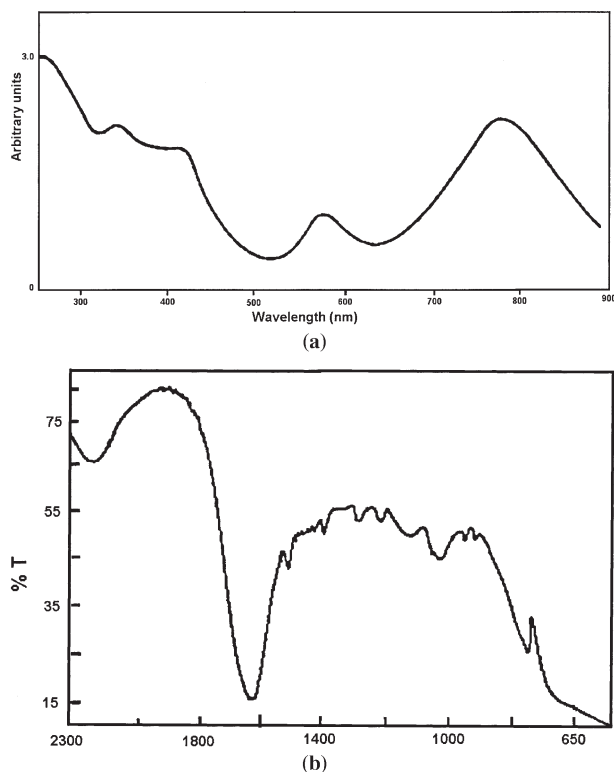
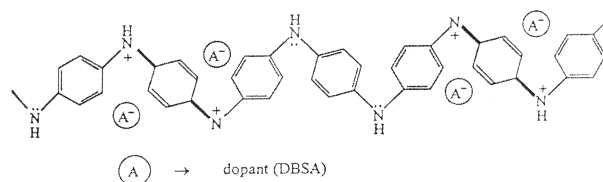


Figure 1 (a) UV-visible spectrum of polyaniline; (b) FTIR Spectrum of polyaniline.



Scheme 1

pure iron (Johnson Matthey 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. 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 $(28 \pm 1)^\circ C$. The polarization was carried out using a Corware software from a cathodic potential of -0.2 V to an anodic potential of $+1.2$ V with respect to the corrosion potential at a sweep rate of 0.5 $mV s^{-1}$ to see the effect of inhibitors on corrosion and passivation. The linear TAFEL segments of the anodic and cathodic curves (-0.2 to $+0.2$ V versus corrosion potential) were extrapolated to corrosion potential to obtain the corrosion current densities. 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. 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 analyzed with Z view software.

The corrosion inhibition efficiency was evaluated from the measured i_{corr} values obtained from Tafel polarization method using the relationship

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

where i_{corr} and i'_{corr} are the corrosion current densities without and with the addition of various concentrations of the inhibitor. The inhibition efficiencies were evaluated from the measured slope of the linear region, the polarization resistance, R_p values as

$$I.E. \% = \frac{R'_p - R_p}{R'_p} \times 100$$

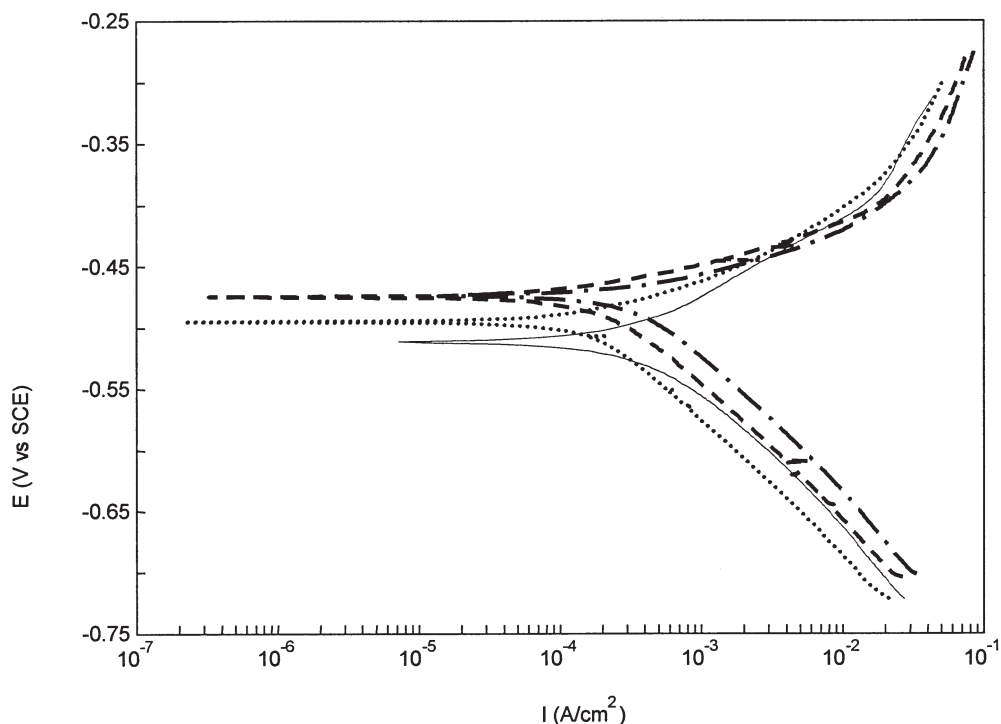


Figure 2 Potentiodynamic polarization behavior of iron in 0.5M H₂SO₄ with the addition of aniline. —, Blank;, 100 ppm; ---, 500 ppm; — · —, 1000 ppm.

where R_p and R_p' are the polarization resistances without and with the addition of inhibitors. In the case of impedance measurements, the inhibition efficiency was evaluated from the measured charge transfer resistance R_{ct} values as

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

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

RESULTS AND DISCUSSION

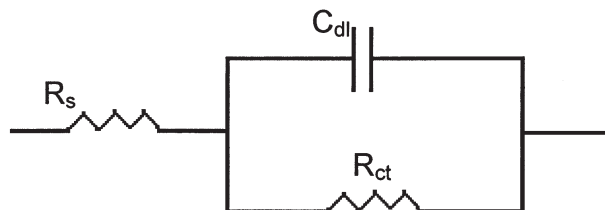
Inhibition by aniline

The potentiodynamic polarization behavior of iron in 0.5M H₂SO₄ in the Tafel region with the addition of various concentrations of aniline is shown in Figure 2. The corrosion kinetic parameters derived from these curves are presented in Table I. From the Table, it is clear that the addition of low concentrations of aniline makes a small decrease in the corrosion current (i_{corr}) values of iron in 0.5M H₂SO₄. At high concentrations, i_{corr} values increase sharply (from 410 $\mu\text{A cm}^{-2}$ for the inhibitor free solution to 569 $\mu\text{A cm}^{-2}$ at the highest concentration of aniline), indicating the acceleration of corrosion.

From the $\eta - I$ plots near the vicinity of steady-state corrosion potential, the polarization resistance R_p val-

ues were obtained, which showed a decrease in R_p values from 34 to 20 $\Omega \text{ cm}^2$ with the addition of aniline, which is in accordance with the results of Tafel extrapolation method.

The Nyquist representation of the impedance values of the iron in 0.5M H₂SO₄ with and without the addition of various concentrations of aniline is shown in Figure 3. The existence of a single semi circle depicts the presence of single charge transfer process during dissolution, which is unaffected by the presence of added aniline. The slightly depressed nature of the semicircle, which has the center below the x -axis, indicates the generation of micro roughness at the surface during the corrosion process.²⁷⁻²⁹ The impedance data were analyzed using the following equivalent circuit:



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

The diameter of the semi circle, the charge transfer resistance R_{ct} , and the interfacial double layer capaci-

TABLE I
Corrosion Kinetic Parameters of Pure Iron in 0.5M H₂SO₄ with Aniline

Concentration of aniline (ppm)	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	—
100	-525	45	115	391	7
250	-520	60	109	315	23
500	-512	58	109	431	—
750	-517	50	110	467	—
1000	-521	53	118	569	—

tance C_{dl} derived from these curves are given in Table II. R_{ct} decreases from the value of 33 to 17 $\Omega \text{ cm}^2$ and C_{dl} increases from 2244 to 2615 $\mu\text{F cm}^{-2}$ with the addition of 1000 ppm aniline inhibitor. The surface coverage θ was estimated from the measured double layer capacitance C_{dl} values using the relationship^{22,30}

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

where C_{dl} and C'_{dl} are the double layer capacitances in the absence and presence of aniline inhibitors, indicating no appreciable coverage of the iron surface by the aniline molecules.

Amines in aqueous acidic solutions may exist as either neutral molecules or in the form of cations³¹ depending upon the concentration of H⁺ ions in the

solutions. In acidic solutions, they predominantly exist as cations and adsorb through electrostatic interaction between the positively charged anilinium cation and negatively charged metal surface.³² Moreover, in aromatic amines, the interaction between π -electrons of benzene ring and the positively charged metal surface also plays a role.³³ Murakawa and Hackerman³⁴ suggested that the stronger adsorption of organic molecules is not always a direct combination of organic molecules with the metal surface, but in some cases, it occurs through already adsorbed sulfate ions, which will interfere with the adsorption of organic molecules.

From the results, it is found that aniline is not an effective inhibitor at all concentrations studied for iron in 0.5M H₂SO₄. This is mainly due to the delocalization of lone pair electron density of nitrogen atom by

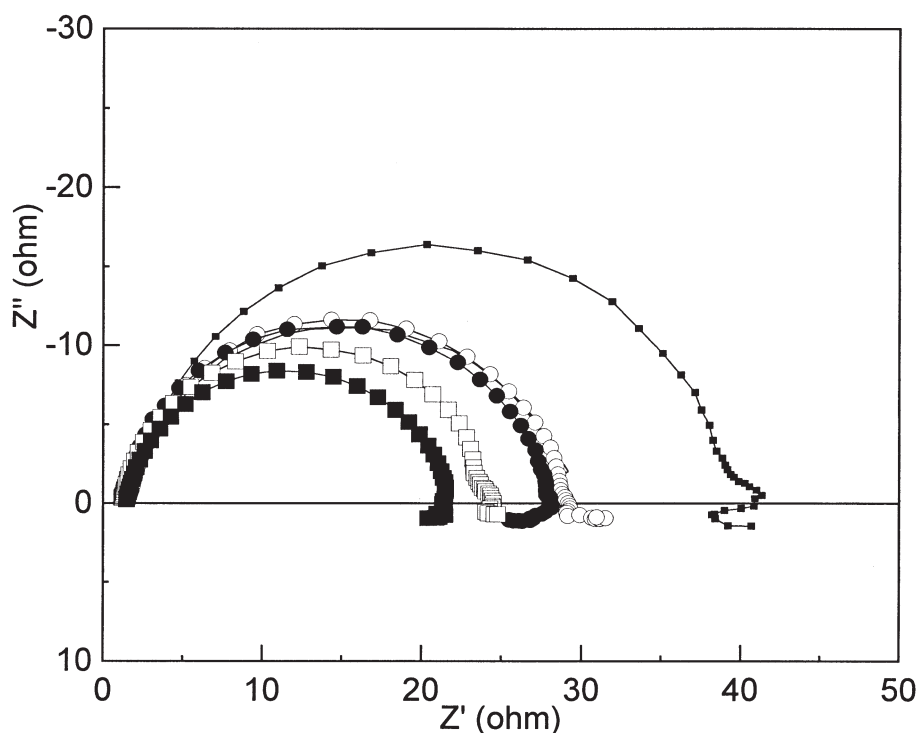


Figure 3 Impedance behavior of iron in 0.5M H₂SO₄ with the addition of aniline. —, Blank; ■, 100 ppm; ○, 250 ppm; ●, 500 ppm; □, 750 ppm; ■, 1000 ppm.

TABLE II
Electrochemical Impedance and Linear Polarization Parameters for Pure Iron in 0.5M H₂SO₄ with Aniline

Concentration of aniline (ppm)	Impedance method			LPR method		
	R_{ct} (Ω cm ²)	C_{dl} (μ F cm ⁻²)	Inhibition efficiency (%)	Surface coverage (θ)	R_p (Ω cm ²)	Inhibition efficiency (%)
Blank	33	2244	—	—	34	—
100	38	2346	13	—	23	—
250	30	2051	—	0.0838	26	—
500	28	1947	—	0.1324	23	—
750	25	1655	—	0.2625	20	—
1000	17	2615	—	—	20	—

inductive effect of phenyl group and the possibility of electron donation to the metal via nitrogen is very less. Further, it has been reported that aniline has got low bonding energy with iron.³⁵ However, if the hydrogen atom of aniline is substituted by methyl or amino group, it showed higher inhibition efficiency than aniline because of strong binding of inhibitor molecule to the metal surface.³⁶ A comparison of inhibition efficiency for anisidines with those for aniline and amino phenol, which is reported elsewhere,³⁷ clearly brings out the fact that anisidines are more inhibitive than the other two, because of the presence of electron releasing —OCH₃ group with increased molecular area.³⁸ The inhibitive effect of p-substituted aniline for iron in HCl was reported to be less effective.^{39,16}

Inhibition by polyaniline

It is well known that the molecular weight and its bulky structure may cover more area on the active electrode surface. If such a bulky molecule can have a chemisorptive property, it is naturally expected to offer better inhibition.

Figure 4 shows the tafel polarization curves for iron in 0.5M H₂SO₄ with the addition of various concentrations of polyaniline. The important corrosion parameters obtained from these curves are presented in Table III. It is evident from the table that the corrosion current values (i_{corr}) decrease from 410 μ A cm⁻² of that of blank to 67 μ A cm⁻² with the addition of highest concentration of polyaniline (75 ppm). This

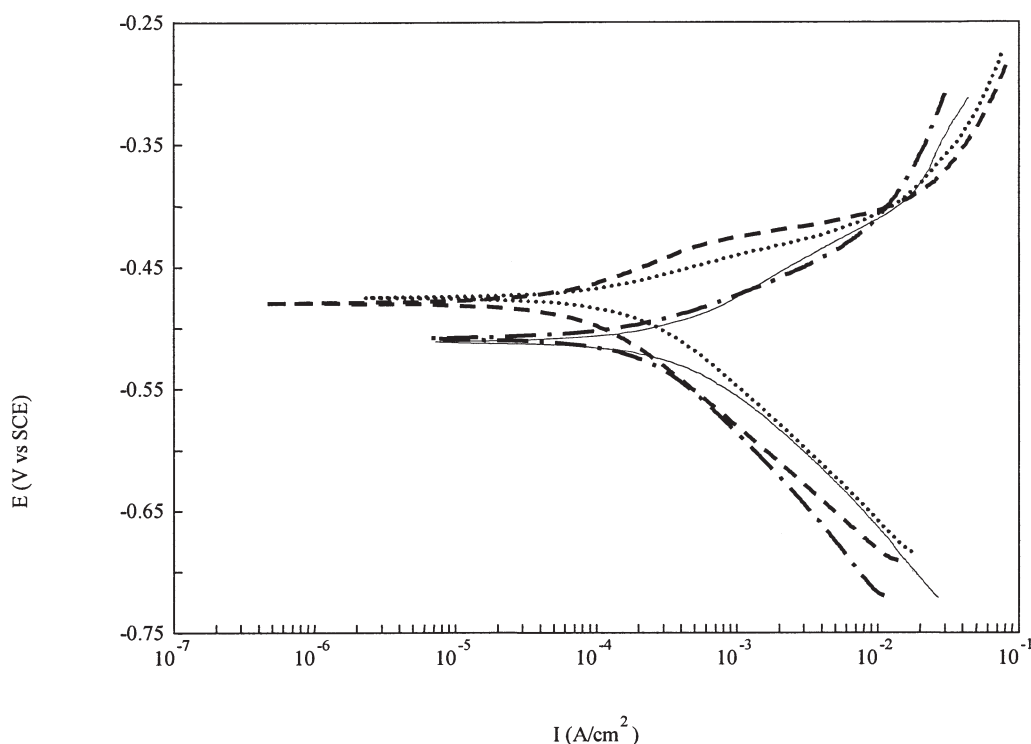


Figure 4 Potentiodynamic polarization behavior of iron in 0.5M H₂SO₄ with the addition of polyaniline. —, Blank;, 10 ppm; ---, 50 ppm; — · —, 100 ppm.

TABLE III
Corrosion Kinetic Parameters of Pure Iron in 0.5M H₂SO₄ with Polyaniline

Concentration of polyaniline (ppm)	E_{corr} (mV vs. SCE)	b_a (mV dec ⁻¹)	b_c (mV dec ⁻¹)	i_{corr} (μ A 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

can be compared with the increased value of 569 μ A cm⁻² obtained by the addition of 1000 ppm of aniline monomer. The addition of polyaniline does not alter the values of E_{corr} , b_a , and b_c , significantly indicating the mixed type inhibiting behavior of the added inhibitor.

From the LPR studies too, it has been found that the polarization resistance (R_p) values increase from 34 Ω cm² of that of blank to 125 Ω cm² with the highest concentration of inhibitor added, indicating the good inhibition character of the added polyaniline.

As in the case of the aniline monomer, the Nyquist representation of the complex impedance of iron in 0.5M H₂SO₄ (Fig. 5) shows the presence of depressed semicircles, indicating the activation controlled nature of the reaction process with micro roughness at the interface. The charge transfer resistance R_{ct} interfacial

double layer capacitance C_{dl} , and hence the surface coverage θ derived from these figures as explained previously are given in Table IV. The R_{ct} values increase from 34 to 125 Ω cm² with a corresponding decrease in C_{dl} values from 2244 to 267 μ F cm⁻² for the added polyaniline concentrations. 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, suggests that the inhibitors adsorb at the metal-solution interface.⁴⁰ In contrast to the θ values of aniline monomer, the θ values increase to 0.9020 with 75 ppm of polyaniline.

Polyaniline is one of the most promising and most widely studied conducting polymers because of its stability and lower cost. It has got wide applications in electronic devices.⁴¹ Earlier studies showed the inhibitive properties of substituted polyaniline for mild

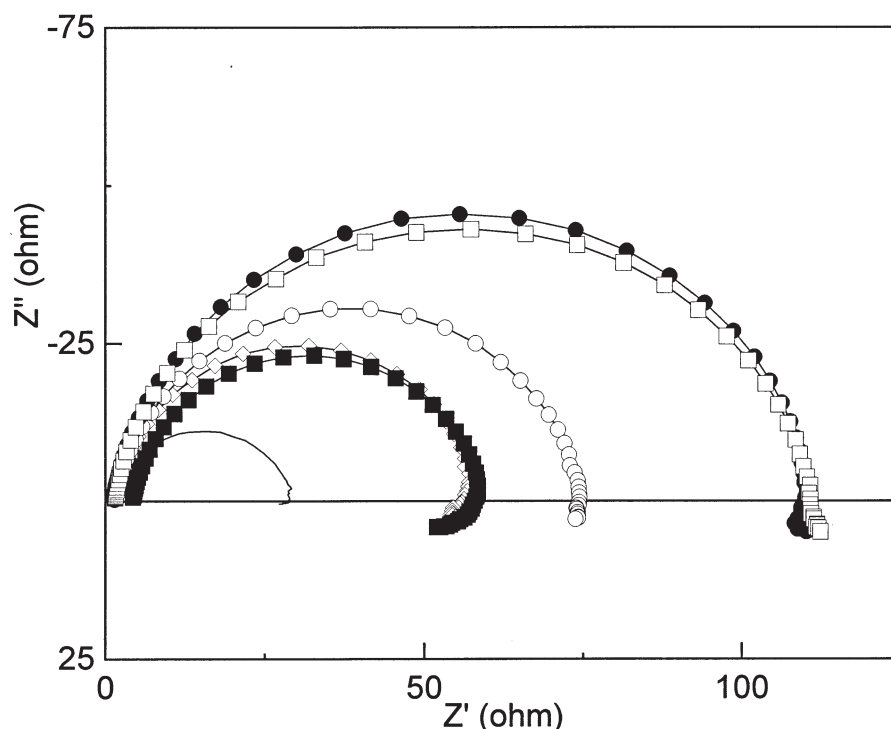


Figure 5 Impedance behavior of iron in 0.5M H₂SO₄ with the addition of polyaniline. —, Blank; \diamond , 10 ppm; \blacksquare , 25 ppm; \circ , 50 ppm; \blacklozenge , 75 ppm; \square , 100 ppm.

TABLE IV
Electrochemical Impedance and Linear Polarization Parameters for Pure Iron in 0.5M H₂SO₄ with Polyaniline

Concentration of polyaniline (ppm)	Impedance method				LPR method	
	R_{ct} (Ω cm ²)	C_{dl} (μ F cm ⁻²)	Inhibition efficiency (%)	Surface coverage (θ)	R_p (Ω cm ²)	Inhibition efficiency (%)
Blank	33	2244	—	—	34	—
10	55	600	40	0.8217	57	40
25	57	365	42	0.8373	68	50
50	74	305	55	0.8640	80	58
75	111	267	70	0.9020	125	73
100	110	267	70	0.9020	122	72

steel in acid chloride solutions.^{23,24} The inhibitive property of polyaniline 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 coverage of the metallic surface and lesser adsorption of SO₄²⁻ ions on the metal surface, leaving more and more space for the organic molecules to get adsorbed.⁴²

Spectroscopic studies

Figure 6 shows the FTIR spectrum of iron surface exposed to 0.5M H₂SO₄ containing 50 ppm of polyaniline. The shift of characteristic band of benzenoid-quinonoid ring from 1560–1490 cm⁻¹ to 1560–1460 cm⁻¹ confirms the strongly adsorbed state of polyaniline on iron surface.

The UV reflectance spectra of iron in 0.5M H₂SO₄ with 500 ppm aniline and 50 ppm of polyaniline are shown in Figure 7. It can be seen that, the percentage reflectance is high for polished iron specimen and is very much reduced for iron exposed with 0.5M H₂SO₄. In the case of aniline, very low reflectance of iron surface, similar to that in 0.5M H₂SO₄, is observed. This shows the poor inhibition of aniline. But the reflectance of iron exposed to acid containing polyaniline is high, which confirms the better inhibition efficiency.

Adsorption isotherm

The adsorption isotherm gives the relationship between the coverage of the interface and the concentration of the specific species. The free energy of adsorp-

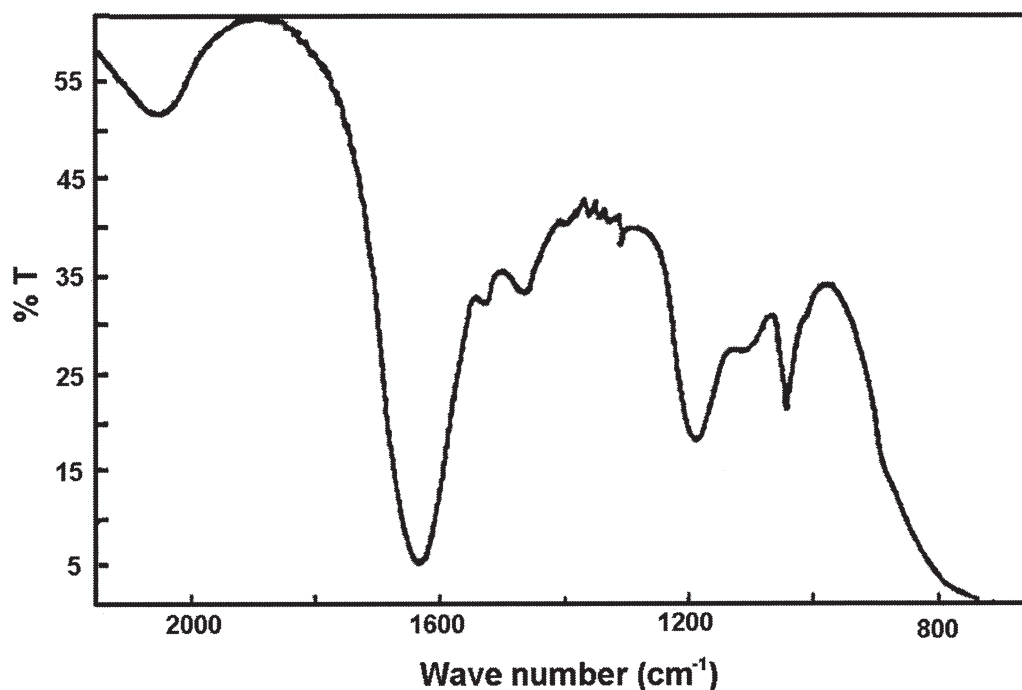


Figure 6 FTIR spectrum of adsorbed polyaniline film on iron surface.

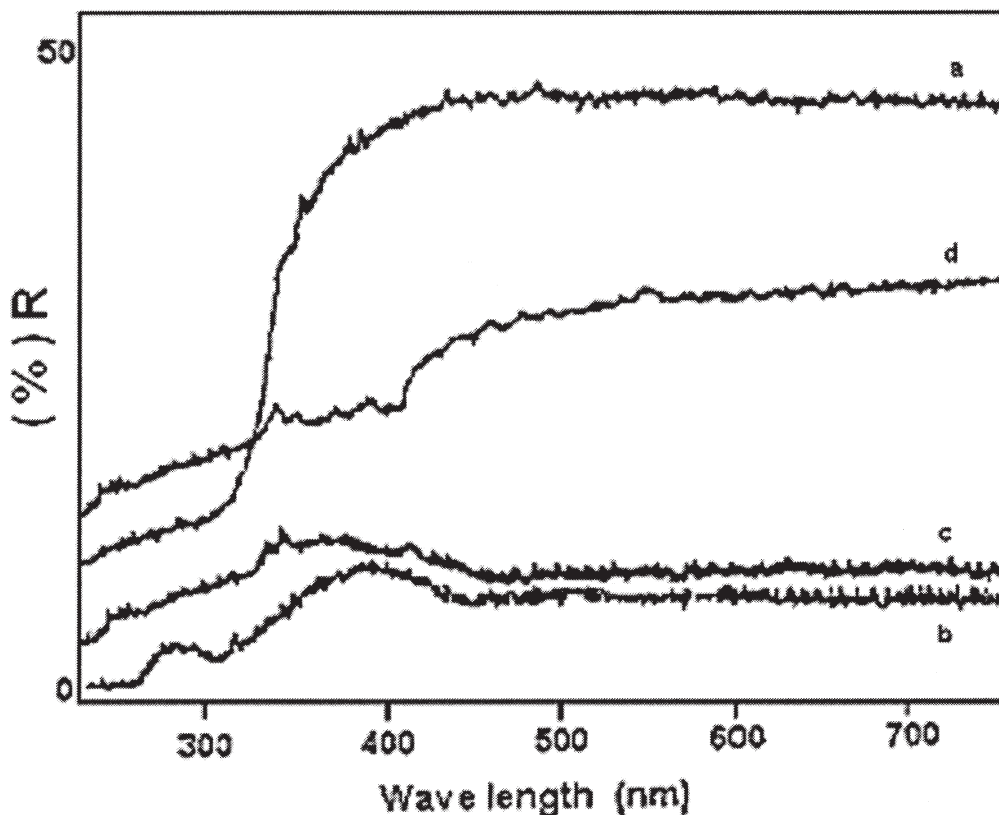


Figure 7 UV reflectance curves for iron under different conditions. (a) Polished; (b) iron treated with 0.5M H₂SO₄; (c) iron treated with 0.5M H₂SO₄ in the presence of 500 ppm aniline. (d) iron treated with 0.5M H₂SO₄ in the presence of 50 ppm poly(aniline).

tion is obtained by fitting the data in the adsorption isotherm.⁴³ Figure 8 shows the plot of logarithmic concentration of the polyaniline with surface cover-

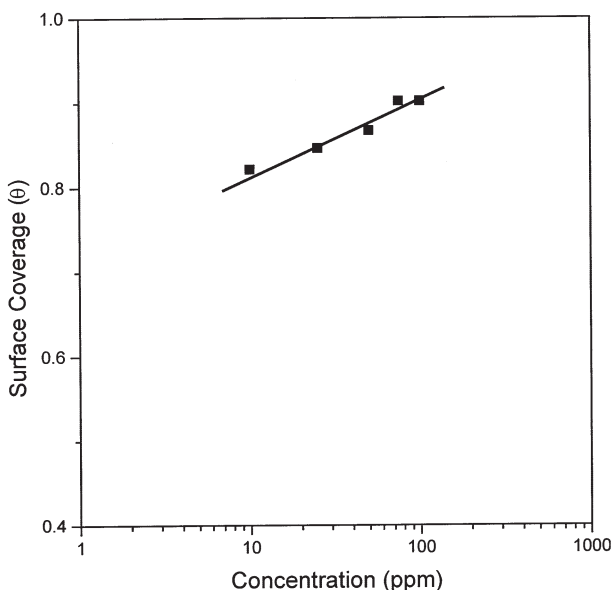


Figure 8 Temkin adsorption plot for iron in 0.5M H₂SO₄ containing polyaniline.

age. The linear relationship shown in the figure indicates that the adsorption of polyaniline over iron surface obeys Temkin adsorption isotherm. The free energy of adsorption of polyaniline on iron in 0.5M H₂SO₄ has been found to be -13.5 kJ mol⁻¹. This value indicates that the mechanism of adsorption is physical adsorption, which is due to the electrostatic interaction between the charged molecules and the charged metal.^{44,45}

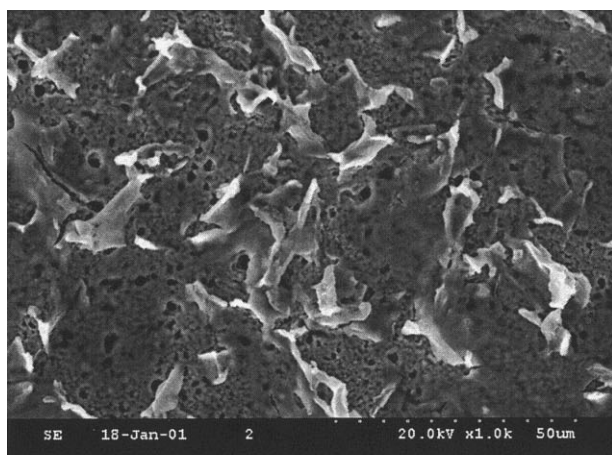
SEM studies

The morphologies of iron surface after corrosion in the presence and absence of inhibitors in 0.5M H₂SO₄ are shown in Figure 9(a-9c). It can be seen that the uniform attack is observed in the case of iron exposed to 0.5M H₂SO₄ and 0.5M H₂SO₄ containing 1000 ppm of aniline and for the iron surface exposed to 0.5M H₂SO₄ containing 100 ppm of polyaniline, the formation of thin layer of adsorbed polyaniline is observed.

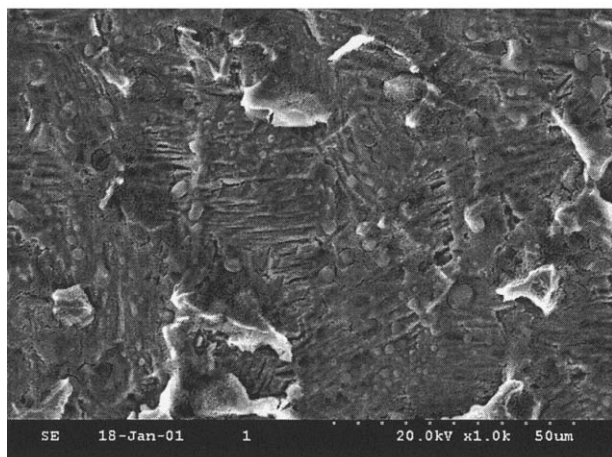
Passivation effect of aniline and polyaniline

Figure 10 shows the passivation behavior of iron in 0.5M H₂SO₄ in the presence of aniline and polyaniline.

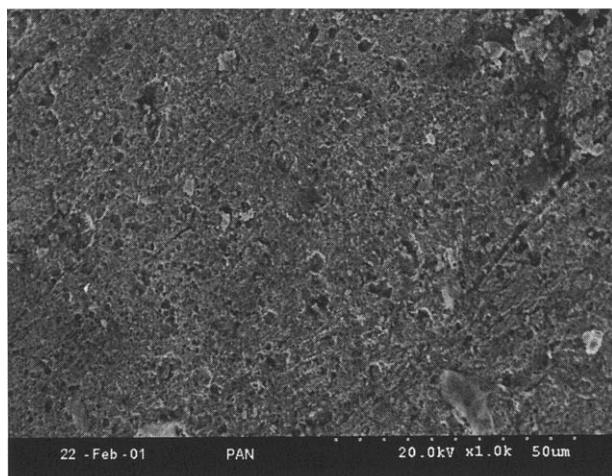
At more anodic potentials, aniline was found to stabilize the passive film on iron surface up to +900 mV. This may be due to the formation of electropolymerized film of aniline to polyaniline at this potential^{46,47} and after +950 mV, a gradual increase of current has



(a)



(b)



(c)

Figure 9 Scanning electron micrographs of iron in (a) 0.5M H_2SO_4 , (b) 0.5M H_2SO_4 containing 500 ppm of aniline, (c) 0.5M H_2SO_4 containing 50 ppm of polyaniline.

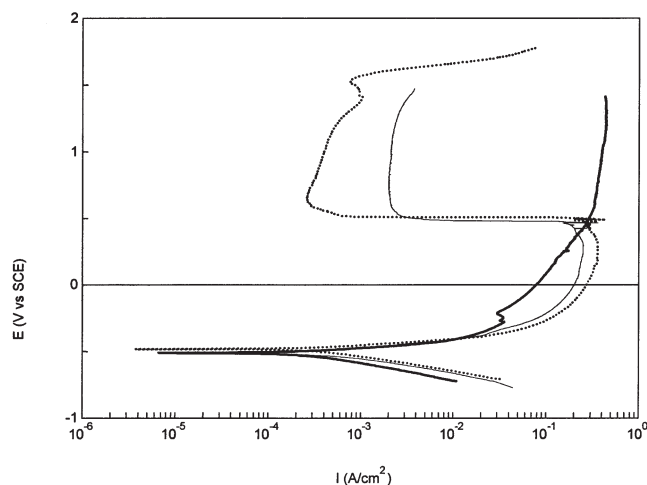


Figure 10 Anodic polarization behavior of iron in 0.5M H_2SO_4 in the presence of inhibitors. —, Blank; ·····, 1000 ppm of aniline; — · —, 100 ppm of polyaniline.

been observed because of the degradation of polyaniline film.^{48,49} However, at more anodic potentials, the adsorbed polyaniline prevents the passive film formation.

CONCLUSIONS

Aniline is found to accelerate the corrosion of iron in 0.5M H_2SO_4 . But, polyaniline is found to inhibit the corrosion of iron in 0.5M H_2SO_4 because of its strong adsorption. Besides, polyaniline is found to obey Temkin adsorption isotherm. However, aniline is found to improve the passivation ability of iron in 0.5M H_2SO_4 at high concentrations because of the formation of polyaniline film on the surface and polyaniline prevents the formation of passive film on iron.

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