

# Investigation of the inhibitive effect of poly(diphenylamine) on corrosion of iron in 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions

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## Abstract

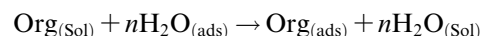
In recent years, polymer amines such as polyaniline has been reported as an efficient corrosion inhibitor for iron in acid media. In this paper, the performance of poly(diphenylamine) as corrosion inhibitor for iron in 0.5 M H<sub>2</sub>SO<sub>4</sub> has been evaluated by potentiodynamic polarization, linear polarization and electrochemical impedance spectroscopy and compared with the performance of the diphenylamine monomer. It has been found that poly(diphenylamine) is an efficient inhibitor since the maximum efficiency of 96% has been observed at very low concentration of 10 ppm where as the monomer has given an efficiency of 75% at 1000 ppm. Besides, poly(diphenylamine) has been found to improve the passivation characteristics of iron in 0.5 M H<sub>2</sub>SO<sub>4</sub>. FTIR studies have shown that the poly(diphenylamine) is strongly adsorbed on the iron surface and inhibits the corrosion effectively.

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**Keywords:** Corrosion inhibition; Polymer amines; Poly(diphenylamine); Polarization; Impedance

## 1. Introduction

The investigation of the inhibition of corrosion of iron is a matter of high theoretical as well as practical interest [1]. 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, sulphur and oxygen are being used as inhibitors [2]. The most efficient inhibitors are organic compounds having  $\pi$  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 as



The adsorption of these compounds is influenced by the electronic structure of the inhibiting molecules [3,4] and also by the steric factors, aromaticity, electron density at

the donor atoms and also by the presence of functional groups such as =NH, –N=N–, –CHO, R–OH, R=R, etc., in the inhibitor molecule [5,6]. The role of molecular area [7] and molecular weight [8] of the organic molecule on its inhibition efficiency was also reported. Aniline and alkylamine [9] *p*-substituted anilines [10] are reported for its inhibition which is mainly due to the  $\pi$  electron interaction and the formation of co-ordination bond between Fe–N substituted anilines. More recently polymer amines [11,12] were evaluated for their inhibition properties on the corrosion of iron and steel in acid solutions. Ortho-substituted anilines [13] and polyanilines [14,15] were also studied more recently. In this paper, the inhibition effect of poly(diphenylamine) (PDA) on the corrosion of iron in 0.5 M H<sub>2</sub>SO<sub>4</sub> is discussed.

## 2. Experimental

### 2.1. Synthesis of poly(diphenylamine) [16,17]

Reagent grade diphenylamine was purified by distillation in the presence of small amount of zinc dust. Sodium

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salt of dodecyl benzene sulphonic acid was used as dopant and was neutralized with conc. HCl. To this solution, 0.1 M of freshly distilled diphenylamine 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. The efficiency of polymerization was about 50% and was characterized by UV–visible, FTIR spectroscopy and molecular weight was determined by GLPC method (Shimadzu, Japan).

The electrochemical experiments were made using a conventional three electrode cell assembly at  $28 \pm 1$  °C. All the solutions were prepared using AR grade chemicals using triple distilled water and was deaerated by purging purified nitrogen for half an hour before the start of the experiments. The working electrode was a pure iron sample of 1 cm<sup>2</sup> area and the rest being covered with araldite epoxy. A large rectangular platinum foil was used as counter electrode and saturated calomel electrode as reference electrode. The working electrode was polished with different grades of emery papers, washed with water and degreased with trichloroethylene. The polarization and impedance studies were made after 30 min of immersion using Solartron Electrochemical Analyser (Model 1280 B). The polarization was carried out using a Corware software from a cathodic potential of –0.2 V to an anodic potential of +1.5 V with respect to the corrosion potential at a sweep rate of 0.5 mV/s. The data in the tafel region (–0.2 to +0.2 V vs. corrosion potential) have been processed for evaluation of corrosion kinetic parameters. The linear tafel segments of the anodic and cathodic curves were extrapolated to corrosion potential for obtaining the corrosion current values.

The inhibition efficiency was evaluated from the measured  $i_{\text{corr}}$  values using the relationship

$$\text{IE}\% = \frac{i_{\text{corr}} - i'_{\text{corr}}}{i_{\text{corr}}} \times 100,$$

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

For LPR measurements, the potential of the electrode was scanned from –0.02 to +0.02 V vs. corrosion potential a scan rate of 0.5 mV/s and the polarization resistance ( $R_p$ ) was measured from the slope of  $\eta$  vs.  $i$  curve in the vicinity of corrosion potential. From the measured polarization resistance values, the inhibition efficiency has been calculated using the relationship

$$\text{IE}\% = \frac{R'_p - R_p}{R'_p} \times 100,$$

where  $R_p$  and  $R'_p$  are the polarization resistance values without and with the addition of inhibitors.

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 ( $R_{\text{ct}}$ ), values were obtained from the diameter of the semi circles of the Nyquist plots. The inhibition efficiency of the inhibitor has been found out from the charge transfer resistance values using the following equation:

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

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

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

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

and the surface coverage  $\theta$  by the inhibitor molecule is given by

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

(since  $C_{\text{dls}} \ll C_{\text{dl}}$ ), where  $C_{\text{dl}}$ ,  $C'_{\text{dl}}$  and  $C_{\text{dls}}$  are the double layer capacitance values in the absence, presence of diphenylamine inhibitors and saturated value in the presence of inhibitor, respectively [18–20].

### 3. Results and discussion

#### 3.1. Corrosion inhibition by diphenylamine

The potentiodynamic polarization behaviour of iron in 0.5 M H<sub>2</sub>SO<sub>4</sub> with the addition of various concentrations of diphenylamine in the tafel region is shown in Fig. 1. The corrosion kinetic parameters derived from these curves are given in Table 1. From the table, it is clear that the

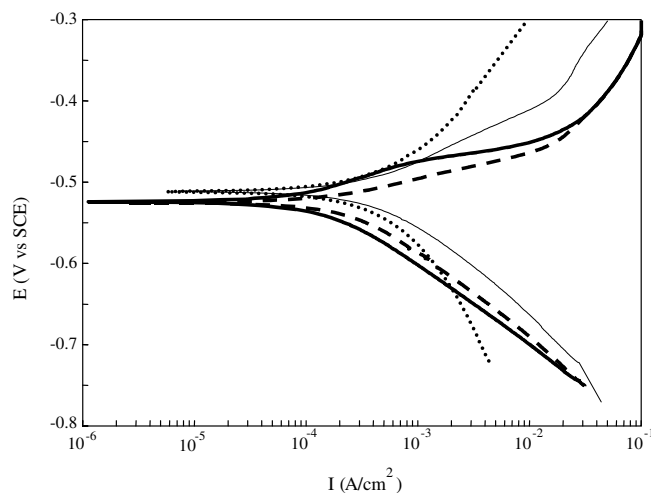


Fig. 1. Potentiodynamic polarization behaviour of iron in 0.5 M H<sub>2</sub>SO<sub>4</sub> with the addition of diphenylamine: — blank; ····· 100 ppm; --- 500 ppm; ——— 1000 ppm.

Table 1  
Corrosion kinetic parameters of pure iron in 0.5 M H<sub>2</sub>SO<sub>4</sub> with diphenylamine

Concentration of diphenylamine (ppm)	$E_{\text{corr}}$ (mV) vs. SCE	$b_a$ (mV/dec)	$b_c$ (mV/dec)	$i_{\text{corr}}$ ( $\mu\text{A cm}^{-2}$ )	Inhibition efficiency (%)
Blank	-508	76	109	410	–
100	-521	53	110	315	23
250	-517	76	102	240	41
500	-555	70	107	210	49
750	-554	62	105	180	56
1000	-516	61	100	144	65

addition of diphenylamine in the concentration range 100–1000 ppm decreases the dissolution rate of iron in 0.5 M H<sub>2</sub>SO<sub>4</sub>. The corrosion current value ( $i_{\text{corr}}$ ) is decreased from 410  $\mu\text{A cm}^{-2}$  for the inhibitor free solution to 144  $\mu\text{A cm}^{-2}$  at the highest concentration of diphenylamine studied.

The steady-state corrosion potentials are found to be shifted by 10–40 mV in the cathodic direction in the presence of inhibitor. Besides, the anodic and cathodic tafel slopes are in the range of  $65 \pm 5$  and  $105 \pm 5$  mV, respectively. Since there is no remarkable change in the corrosion potential and tafel slopes in the presence of inhibitor, it can be inferred that diphenylamine is a mixed inhibitor.

The polarization resistance ( $R_p$ ) values showed an increase in values from 34 to 150  $\Omega \text{cm}^2$  with the addition of diphenylamine inhibitor. The Nyquist representation of the impedance behaviour of iron in 0.5 M H<sub>2</sub>SO<sub>4</sub> with and without the addition of various concentrations of diphenylamine is shown in Fig. 2. The existence of a single semicircle shows the presence of single charge transfer process during dissolution which is unaffected by the presence of inhibitor molecules. The slightly depressed nature of the semicircle which has the center below the  $x$ -axis is the characteristic for solid electrodes and such frequency dispersion has been attributed to micro roughness and other inhomogeneities of the solid electrode [21,22]. The charge transfer resistance ( $R_{\text{ct}}$ ) and the interfacial double layer capacitance ( $C_{\text{dl}}$ ) values derived from these curves are given in Table 2. The  $R_{\text{ct}}$  is increased from the value of 33–145  $\Omega \text{cm}^2$  and  $C_{\text{dl}}$  is decreased from 2244 to 245  $\mu\text{F cm}^{-2}$  with the addition of diphenylamine inhibitor. The values of double layer capacitance  $C_{\text{dl}}$  for iron in 0.5 M H<sub>2</sub>SO<sub>4</sub> has been reported as 1775  $\mu\text{F cm}^{-2}$  [23], 750  $\mu\text{F cm}^{-2}$  [24], and 42.3  $\mu\text{F cm}^{-2}$

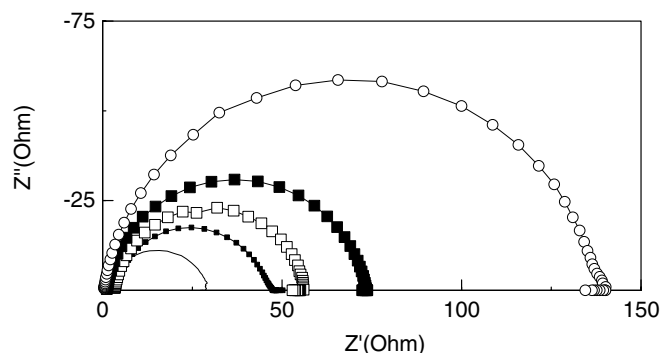


Fig. 2. Impedance behaviour of iron in 0.5 M H<sub>2</sub>SO<sub>4</sub> with the addition of diphenylamine: — blank; ■ 100 ppm; □ 500 ppm; ● 750 ppm; ○ 1000 ppm.

[13]. These variations may be due to the variation in the purity of iron used.

Amines in aqueous acidic solutions may exist as either neutral molecules or in the form of cations [25] depending upon the concentration of H<sup>+</sup> ions in the solutions. The PZC of iron in sulphuric acid solutions is about -650 mV vs. SCE [9]. In this condition, the aromatic amines interact through the  $\pi$ -electrons of benzene ring with the positively charged metal surface [26] where as in acidic chloride solutions the amines adsorb through electrostatic interaction between the positively charged anilinium cation and negatively charged metal surface due to specific adsorption of chloride on the metal [27]. The adsorption of the inhibitor molecules can be visualized as predominantly as RNH<sub>3</sub><sup>+</sup> ions lying flat on the electrode surface, with the principal adsorption forces arising from a  $\pi$ -bond orbital as reported by Blomgren and Bockris [28].

Table 2  
Electrochemical impedance and linear polarization parameters for pure iron in 0.5 M H<sub>2</sub>SO<sub>4</sub> with diphenylamine

Concentration of diphenylamine (ppm)	Impedance method				LPR method	
	$R_{\text{ct}}$ ( $\Omega \text{cm}^2$ )	$C_{\text{dl}}$ ( $\mu\text{F cm}^{-2}$ )	Inhibition efficiency (%)	Surface coverage ( $\theta$ )	$R_p$ ( $\Omega \text{cm}^2$ )	Inhibition efficiency (%)
Blank	33	2244	–	–	34	–
100	47	718	28	0.6800	53	35
250	56	638	37	0.7157	73	53
500	66	557	50	0.7518	76	55
750	80	397	58	0.8230	106	68
1000	145	245	77	0.8908	150	77

### 3.2. Corrosion inhibition by poly(diphenylamine)

It is a well-known fact that compounds with high molecular weight and bulky structure may cover more area on the active electrode surface [7]. If such a bulky molecule can have a chemisorptive property, it is naturally expected to inhibit corrosion more effectively.

In the UV–Vis spectra of poly(diphenylamine), an absorption peak at 316 nm shows the  $\pi$ – $\pi^*$  transition in the benzenoid ring and the 627 nm peak show the donor–acceptor interaction of the quinonoid ring. The well-known cation radical peak was observed at 407 nm. The major IR (Fig. 3, curve a) absorption bands at 1600 and 1400  $\text{cm}^{-1}$  are the characteristic bands due to quinonoid–benzenoid rings, the peak at 1300  $\text{cm}^{-1}$  is for N–H bond. The other IR characteristics are absorption peaks at 1126, 1036 and 920  $\text{cm}^{-1}$ . The molecular weight has been found to be 57,458 by GPLC and the structure of poly(diphenylamine) is shown in Fig. 4.

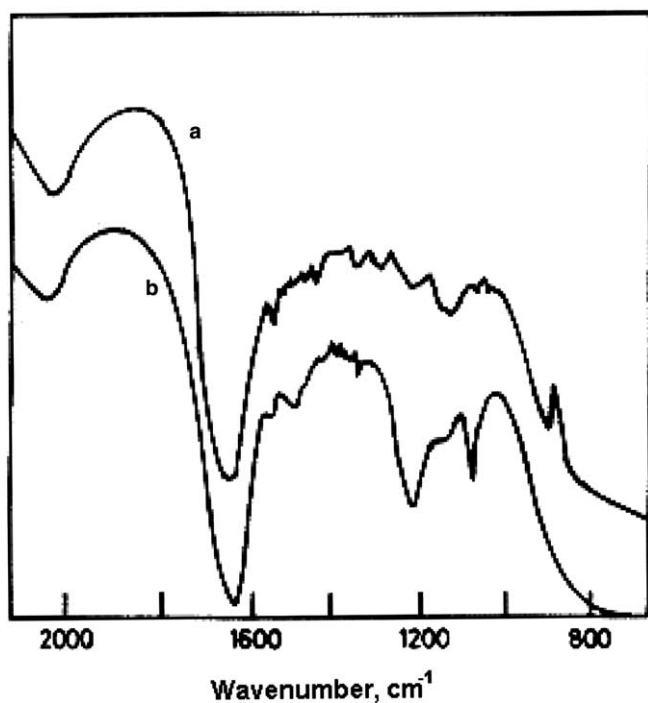


Fig. 3. FTIR spectra of (a) poly(diphenylamine); (b) poly(diphenylamine) adsorbed on iron surface.

The tafel polarization curves for iron in 0.5 M  $\text{H}_2\text{SO}_4$  with the addition of various concentrations of poly(diphenylamine) are shown in Fig. 5. The corrosion parameters obtained from these curves are given in Table 3. It is evident from the table that the corrosion current value ( $i_{\text{corr}}$ ) is decreased from 410  $\mu\text{A cm}^{-2}$  of that of blank to 67  $\mu\text{A cm}^{-2}$  with the addition of 1.0 ppm of poly(diphenylamine) and it gets further reduced gradually with increasing concentration of the inhibitor. The trend in variation of  $E_{\text{corr}}$  on the addition of PDA is not regular. The shift of  $E_{\text{corr}}$  is  $\pm 50$  mV with respect to the value of the blank. Besides, the variations of  $b_a$  and  $b_c$  in the presence of PDA is not marked, these suggest that the mechanism of inhibition of PDA is by adsorption and the inhibitor acts as a mixed inhibitor.

From the LPR studies too, it has been found that the polarization resistance ( $R_p$ ) values increase from 34  $\Omega \text{cm}^2$  of that of blank to 276  $\Omega \text{cm}^2$  with the highest concentration of inhibitor added (Table 3).

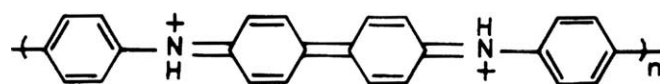


Fig. 4. Structure of poly(diphenylamine).

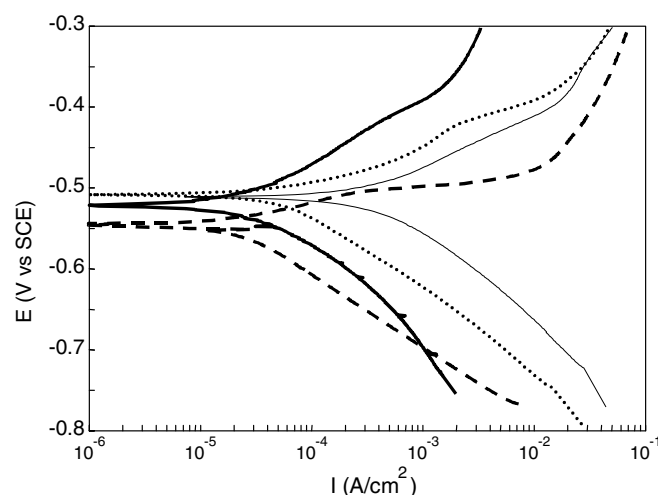


Fig. 5. Potentiodynamic polarization behaviour of iron in 0.5 M  $\text{H}_2\text{SO}_4$  with the addition of poly(diphenylamine): — blank; ..... 1 ppm; ——— 5 ppm; - - - 10 ppm.

Table 3

Corrosion kinetic parameters of pure iron in 0.5 M  $\text{H}_2\text{SO}_4$  with poly(diphenylamine)

Concentration of poly(diphenylamine) (ppm)	$E_{\text{corr}}$ (mV) vs. SCE	$b_a$ (mV/dec)	$b_c$ (mV/dec)	$i_{\text{corr}}$ ( $\mu\text{A cm}^{-2}$ )	Inhibition efficiency (%)
Blank	–508	76	109	410	–
1.0	–504	60	94	67	83
2.5	–519	50	93	37	91
5.0	–527	50	90	27	93
7.5	–519	60	91	24	91
10.0	–521	60	110	15	96

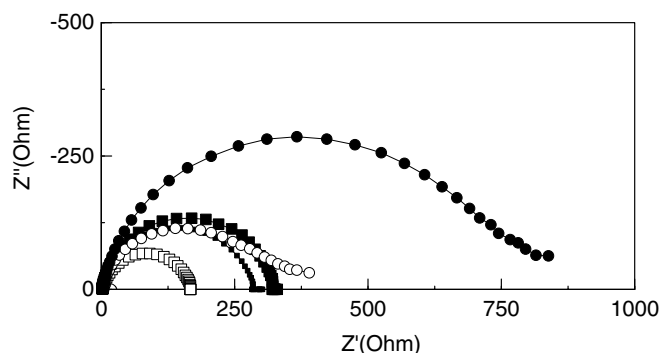


Fig. 6. Impedance behaviour of iron in 0.5 M  $\text{H}_2\text{SO}_4$  with the addition of poly (diphenylamine): — blank;  $\square$  1 ppm;  $\blacksquare$  2.5 ppm;  $\circ$  7.5 ppm;  $\bullet$  10 ppm.

As in the case of the diphenylamine monomer, the Nyquist representation of the complex impedance of iron in 0.5 M  $\text{H}_2\text{SO}_4$  (Fig. 6) shows the presence of depressed semicircles indicating the activation controlled nature of the corrosion process with micro roughness of the electrode [21,22]. The charge transfer resistance ( $R_{ct}$ ), interfacial double layer capacitance ( $C_{dl}$ ) values and the surface coverage ( $\theta$ ) values derived from these figures are given in Table 4. The  $R_{ct}$  values are increased from 33 to 766  $\Omega \text{ cm}^2$  with a corresponding decrease in  $C_{dl}$  values from 2244 to 157  $\mu\text{F cm}^{-2}$  for the added poly(diphenylamine). The  $\theta$  value is increased to 0.85 by the addition of 1 ppm of poly(diphenylamine) which can be compared to the value of 0.89 obtained by the addition of addition of 1000 ppm of the monomer.

Fig. 3 curve b shows the FTIR spectra of iron surface exposed to 0.5 M  $\text{H}_2\text{SO}_4$  containing 5 ppm of poly(diphenylamine). The spectra is similar to that observed for poly(diphenylamine). However, there is a slight shift of characteristic bands of benzenoid and quinonoid rings which confirms the strongly adsorbed state of poly(diphenylamine) on iron surface.

The UV reflectance spectra of iron in 0.5 M  $\text{H}_2\text{SO}_4$  with 5 ppm poly(diphenylamine) is shown in Fig. 7. It can be seen that, the percentage reflectance is high for polished iron specimen and is very much reduced for iron treated with 0.5 M  $\text{H}_2\text{SO}_4$ . The reflectance in the case of iron treated with 0.5 M  $\text{H}_2\text{SO}_4$  in presence of poly(diphenylamine) is high confirming the better inhibition efficiency of the polymer.

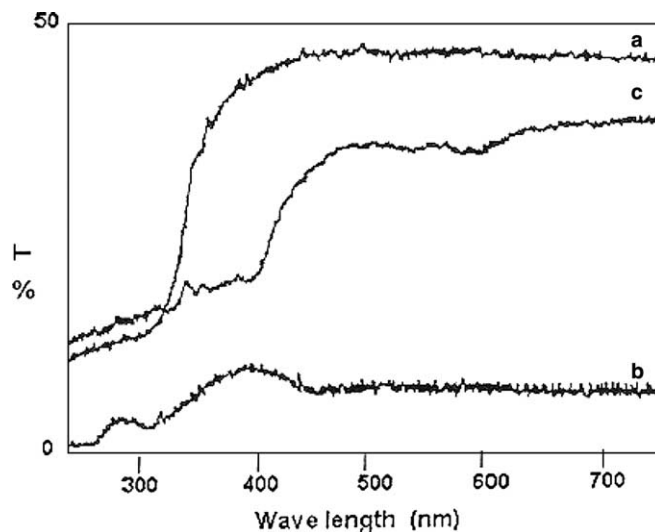


Fig. 7. UV-reflectance curves for iron under different conditions: a – polished; b – iron treated with 0.5 M  $\text{H}_2\text{SO}_4$ ; c – iron treated with 0.5 M  $\text{H}_2\text{SO}_4$  in the presence of poly(diphenylamine).

The higher inhibitive property of poly(diphenylamine) is mainly attributed to the presence of extensive delocalized of  $\pi$ -electron clouds coexisting with quaternary nitrogen atom. Besides the larger molecular size ensures the greater coverage of the metallic surface. This is evident from the high  $\theta$  values of poly(diphenylamine) at low concentrations.

### 3.3. Passivation of iron by DPA and PDA

Fig. 8 shows the effect of addition of DPA and PDA on the passivation behaviour of iron in 0.5 M  $\text{H}_2\text{SO}_4$ . There is no significant improvement in the passivation characteristics of iron with the addition of diphenylamine where as the PDA has been found to improve the passivation. It has been explained by Li et al. [29] that the inhibitor which can form hydrogen bond with the oxide can stabilize the passive film. In the case of PDA, there is a possibility of forming hydrogen bonding through the presence of large number of N–H groups in the inhibitor molecule which can form hydrogen bond with the oxide film very easily. Besides, the PDA can act as a redox electrode and enhance the passivity as it has been observed in the case of polyaniline [30].

Table 4  
Electrochemical impedance and linear polarization parameters for pure iron in 0.5 M  $\text{H}_2\text{SO}_4$  with poly(diphenylamine)

Concentration of poly(diphenylamine) (ppm)	Impedance method				LPR method	
	$R_{ct}$ ( $\Omega \text{ cm}^2$ )	$C_{dl}$ ( $\mu\text{F cm}^{-2}$ )	Inhibition efficiency (%)	Surface coverage ( $\theta$ )	$R_p$ ( $\Omega \text{ cm}^2$ )	Inhibition efficiency (%)
Blank	33	2244	–	–	34	–
1.0	165	347	80	0.8454	81	61
2.5	252	288	87	0.8717	91	63
5.0	323	258	80	0.8859	116	71
7.5	375	238	91	0.8939	241	86
10.0	766	157	96	0.9300	276	89

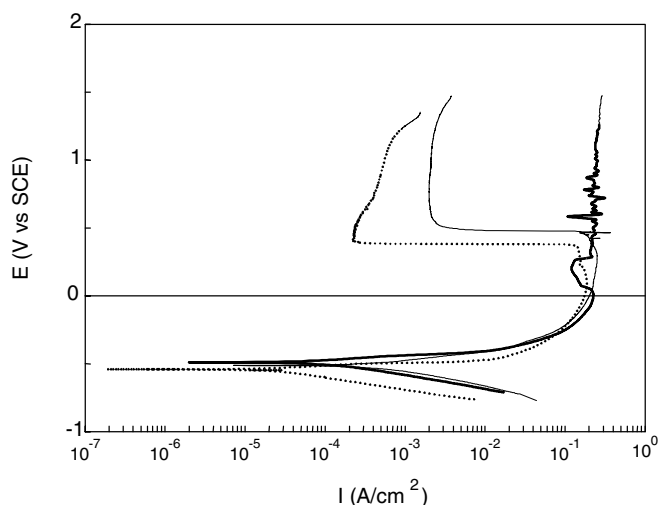


Fig. 8. Anodic polarization behaviour of iron in 0.5 M  $\text{H}_2\text{SO}_4$  in presence of inhibitors: — blank; — 500 ppm of DPA; ····· 5 ppm of PDA.

#### 4. Conclusions

Poly(diphenylamine) has been synthesized by chemical oxidative method and evaluated for its inhibitive characteristics for iron in 0.5 N  $\text{H}_2\text{SO}_4$  by electrochemical methods. Even at the very low concentration of 1 ppm, the inhibition effect is more than 80% where as the inhibition effect of monomer is 77% for 1000 ppm. FTIR studies of the iron surface after exposure to inhibited acid have shown that polydiphenylamine is strongly adsorbed on the iron surface. The PDA has been found to improve the passivation characteristics of iron in 0.5 M  $\text{H}_2\text{SO}_4$ .

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