The Inhibitive Effect of Poly(*p*-toluidine) on Corrosion of Iron in 1*M* HCl Solutions

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ABSTRACT: In recent years, polymer amines have been recognized as an excellent corrosion inhibitors for iron in acid solutions. In this work, the inhibitive effect of *p*-toluidine and poly(*p*-toluidine) on corrosion of iron in 1*M* HCl has been studied by the electrochemical methods such as impedance, linear polarization, Tafel polarization techniques. The effectiveness of poly(*p*-toluidine) was found to be high in comparison with that of monomer. The results showed that *p*-toluidine and poly(*p*-toluidine) suppressed both cathodic and anodic processes of iron dissolution in 1*M* HCl. The inhibition efficiency of both *p*-toluidine and poly(*p*-toluidine) were found to increase with the inhibitor concentrations. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 2595–2601, 2007

Key words: *p*-toluidine; poly(*p*-toluidine); iron; HCl; inhibition; corrosion

INTRODUCTION

Acid inhibitors are widely used in chemical industries, acidizing of oil wells, cleaning of boilers, etc. The organic amine compounds are found to be more effective and highly efficient inhibitors due to the presence of nitrogen oxygen, sulfur, and π bonds in their structure. Many investigators[1–4] have studied polyaniline, which was found to be an active inhibitor in hydrochloric acid solutions. It was found that a very small quantity of certain water soluble polymers was found to be effective in inhibiting the corrosion of iron.[5–9]

Grchev et al.[5] have found that poly(acrylic acid) and polyacrylamide were more effective on iron and gold in acid chloride solutions. Manivel and Venkatachari have studied the effect of poly(*p*-anisidine),[6] poly(*p*-aminophenol),[7] and poly(*p*-amino benzoic acid)[8] in acid solutions and found that they were effective in 1*M* hydrochloric acid solutions. Sathyanarayanan et al.[9,10] have studied the inhibitive properties of poly(*o*-methoxy aniline) and poly(*o*-ethoxy aniline) in acid solutions and found that they were effective in hydrochloric acid solutions. Kraljic et al.[11] investigated that the corrosion protection of stainless steel by electrochemically deposited polyaniline modified by addition of *o*-phenylene diamine found to be more effective.

Earlier studies[4–12] have shown that the inhibitive properties of polyaniline and their derivatives on corrosion of iron in acid chloride solutions are due to the presence of π electrons, quaternary nitrogen atom and the larger molecular size which ensures greater coverage of the metallic surface. So the adsorption of polymer molecules on the iron electrode surface is more, which leads to more inhibition efficiency. Since a very few studies have been made on water soluble polymer amines, in this work, the inhibitive behavior of poly(*p*-toluidine) on iron in 1*M* HCl solution has been studied in comparison with that of monomer.

EXPERIMENTAL

Preparation of polymer

Reagent grade *p*-toluidine was used for the preparation of water soluble poly(*p*-toluidine). A fresh solution of 0.1*M* *p*-toluene sulfonic acid was prepared using double distilled water. To this solution, 0.1*M* of *p*-toluidine dissolved in 0.1*M* HCl, was added and cooled to 0.5°C in a bath of ice and salt mixture. To this solution, freshly prepared solution of 0.1*M* Ammonium per sulfate was added slowly (to avoid warming) with constant stirring. The temperature was maintained below 5°C by the addition of crushed ice and stirring was continued for 2 h, to ensure the completion of reactions. The obtained polymer was characterized by FTIR and UV spectra,

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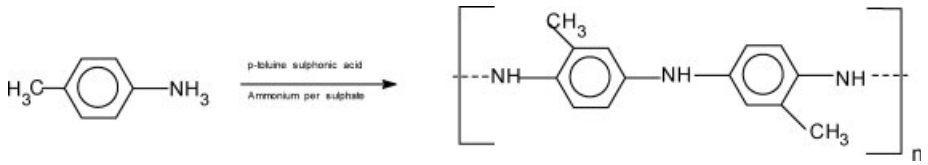
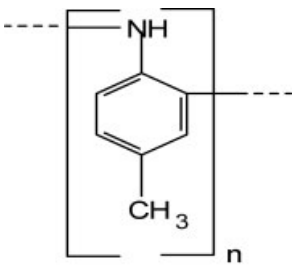
and the molecular weight determination was carried out by GPC. The average molecular weight of the above polymer was found to be 7773. The formation of poly(*p*-toluidine) is given as follows.



Characterization of poly(*p*-toluidine)

The absorption peak at 260 nm shows the π-π* transition in the benzenoid ring. The cation radicals and localized polaran peaks were observed at 360 nm and at 420 nm (Fig. 1). The major IR absorption bands at 1558 cm^{-1} and 1516 $cm^{-1}$are the characteristics band due to nitrogen benzenoid ring structure (Fig. 2). The peak at 3236 cm^{-1} indicates *N*-H stretching and the IR absorption band 1635 cm^{-1} indicates the substitution for poly(*p*-toluidine) monomer unit at 1,4 positions. The other characteristics peaks for amino polymers observed at 1482 cm^{-1}, 1400 cm^{-1}, 1354 cm^{-1}, 1287 cm^{-1}, 1191 cm^{-1}, 1123 cm^{-1}, 1055 cm^{-1}, 1008 cm^{-1}, and 883 cm^{-1}. The structure of poly(*p*-toluidine) is as shown below.



Poly p-toluidine

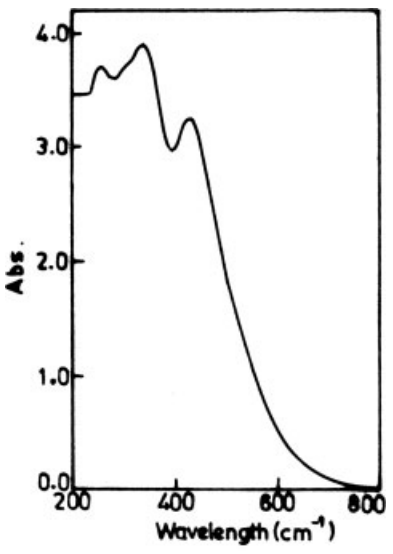


Figure 1 UV–visible spectrum for poly(*p*-toluidine).

Methodology

The electrochemical studies were carried out using a double walled glass cell having provisions for the working electrode, counter platinum electrode and luggin capillary as shown in Figure 3. The potential of the working electrode was measured with respect to saturated calomel electrode (SCE) through the luggin capillary. The working electrode was a pure iron (99.998%) and it was embedded in Araldite, so as to expose the surface area of 1 cm^2. The electrode was polished with different grades of emery papers, and then degreased with trichloroethylene. The experiments were carried out after the steady state attainment of corrosion potentials (20 m) at (30 ± 1)°C. All the solutions were prepared using AR grade chemicals in double distilled water.

The impedance and polarization experiments were carried out using Solartron Electrochemical Analyser (model 1280B) with a software package of Z plot 2 and Corr ware 2. The impedance measurements were carried out at corrosion potential with the A.C. amplitude of 20 mV for the frequency range of 10 kHz to 10 mHz. The real and imaginary parts of the impedance were plotted in Nyquist plots. From the Nyquist plots, the charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) values were calculated. The inhibitor efficiency

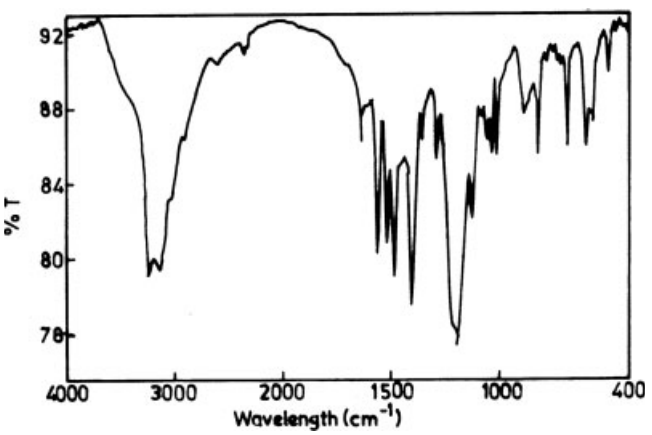


Figure 2 FTIR spectrum for poly(*p*-toluidine).

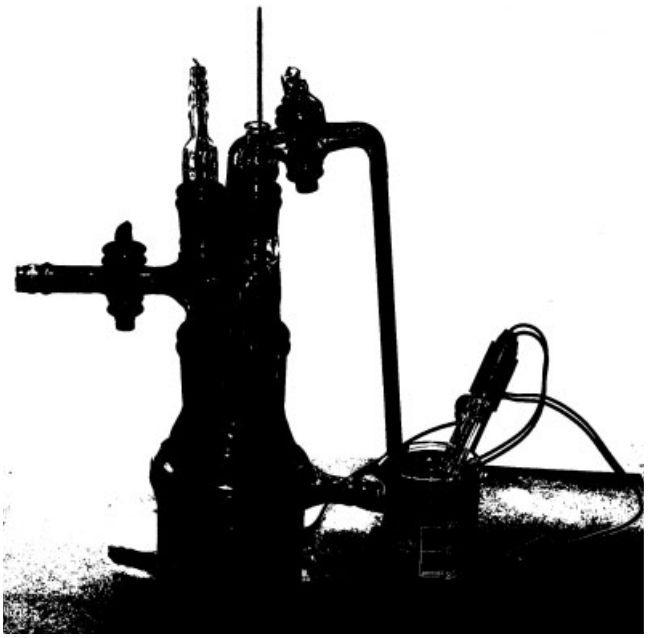


Figure 3 Polarization cell.

(I.E.) was calculated from R_{ct} values using the following equation:

$$\text{I.E. } (\%) = \frac{R_{ct(i)} - R_{ct}}{R_{ct(i)}} \quad (1)$$

where R_{ct} and $R_{ct(i)}$ are charge transfer resistance values in the absence and presence of inhibitor. The surface coverage (θ) values were calculated from the C_{dl} values using the following equation:

$$\theta = \frac{C_{dl} - C_{dl(i)}}{C_{dl}} \quad (2)$$

TABLE I
Electrochemical Parameters of Iron in 1*M* HCl without and with Different Concentrations of *p*-Toluidine

Concentration (molar)	R_{ct} (Ω cm^2)	$C_{dl.}$ (μF/cm^2)	%I.E.	Surface coverage (θ)
Nil	15.6	330.1	–	–
1×10^{-3}	32.2	148.3	51.6	0.55
5×10^{-3}	39.6	148.3	60.7	0.55
7.5×10^{-3}	45.4	127.1	65.7	0.61
1×10^{-2}	47.6	107.7	67.3	0.67
2.5×10^{-2}	49.9	107.6	68.8	0.67
5.0×10^{-2}	54.1	108.6	71.3	0.67

where, C_{dl} and $C_{dl(i)}$ were the capacitance values in the absence and presence of inhibitors.

For linear polarization resistance studies, the measurements were carried out within the potential range of −15 mV to +15 mV with respect to open circuit potential and the current response was measured at a scan rate of 1 mV/s. The *E* and **i** data were plotted in a linear scale to get LPR plots and the slope of the plots gave the polarization resistance (R_p). The inhibitor efficiency (I.E.) was calculated R_p values using the following equation:

$$\text{I.E. } (\%) = \frac{R_{p(i)} - R_p}{R_{p(i)}} 100 \quad (3)$$

where R_p and $R_{p(i)}$ are the polarization resistance values in the absence and presence of inhibitor.

For potentio dynamic polarization studies, the experiments were carried out over a potential range of −200 mV to +200 mV with respect to open circuit potential at a scan rate of 1 mV/s. The various

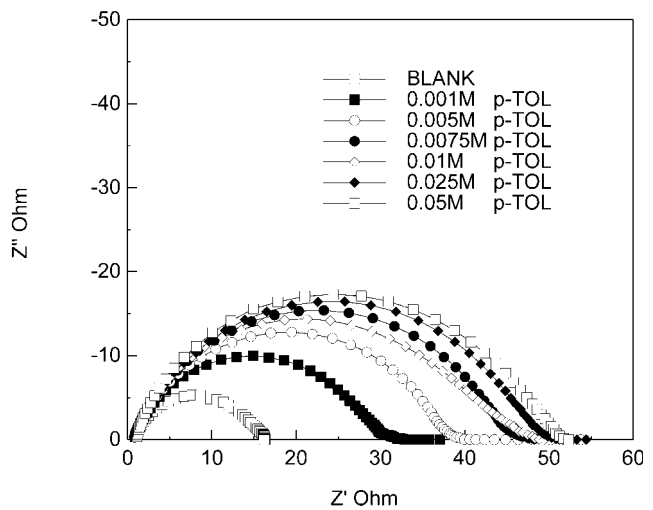


Figure 4 Nyquist plots of iron in 1*M* HCl with different concentrations of *p*-toluidine.

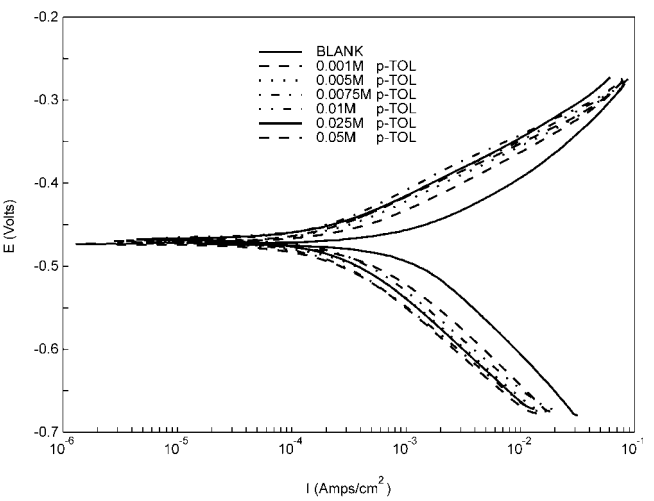


Figure 5 Polarization curves of iron in 1*M* HCl with different concentrations of *p*-toluidine.

TABLE II
Electrochemical Parameters of Iron in 1*M* HCl without and with Different Concentrations of *p*-Toluidine

Concentration (molar)	E_{corr} (mV)	R_p (Ω cm^2)	%I.E.	b_a (mV)	b_c (mV)	$I_{corr.}$ (μA/cm^2)	%I.E.
Nil	−488.4	17.4	–	99.7	133.1	1425.5	–
1×10^{-3}	−475.5	49.2	64.7	74.2	120.1	472.3	66.9
5×10^{-3}	−474.5	68.0	74.5	67.4	118.7	374.4	73.7
7.5×10^{-3}	−474.5	85.8	79.7	64.5	116.5	269.9	81.1
1×10^{-2}	−474.8	92.5	81.2	65.9	111.1	256.9	82.0
2.5×10^{-2}	−472.3	69.0	74.8	67.3	117.9	236.2	83.4
5.0×10^{-2}	−472.1	79.9	78.2	72.1	120.7	227.9	84.0

kinetic parameters such as i_{corr}, b_a and b_c have been obtained from the polarization curves. The inhibitor efficiency (I.E.) was calculated from the $\mathbf{i}_{corr}$ values using the following equations,

$$\text{I.E. } \% = \frac{i_{corr} - i_{corr(i)}}{i_{corr}} 100 \quad (4)$$

where $\mathbf{i}_{corr}$ and $\mathbf{i}_{corr(i)}$ are the corrosion current in the absence and presence of inhibitor.

RESULTS AND DISCUSSION

Inhibition by *p*-toluidine

The impedance measurements for iron in 1*M* HCl and 1*M* HCl with different concentrations of *p*-toluidine in the concentration range $1 \times 10^{-3}M$ to $5 \times 10^{-2}M$. Figure 4 shows the Nyquist plots for iron in 1*M* HCl containing *p*-toluidine. The charge transfer resistance(R_{ct}) values, the double layer capacitance(C_{dl}) values, and surface coverage (θ) values calculated from the impedance diagrams are given in Table I. It is observed that the charge transfer resistance values are increased from 32.2 Ω cm^2 to 54.1 Ω cm^2 with increase of *p*-toluidine concentration from $1 \times 10^{-3}M$ to $5 \times 10^{-2}M$. The decrease of C_{dl} values from 148.3 to 108.6 μF/cm^2 indicates the good surface adsorption of inhibitor. The maximum inhibition efficiency obtained for this inhibitor is 71.3% at 0.05*M* concentration.

The polarization behavior of iron in 1*M* HCl and 1*M* HCl containing *p*-toluidine is shown in Figure 5. The electrochemical parameters obtained from these plots are shown given in Table II. In linear polarization study, the polarization resistance (R_p) is increased from 49.2 Ω cm^2 to 79.85 Ω cm^2 with increase in efficiency from 64.7% to 78.2%, with increase in concentration of inhibitor. It is found that there is no significant variation in the E_{corr} values in the presence of inhibitors suggesting that this polymer behaves as mixed type of inhibitor. Further, it is observed that the $\mathbf{i}_{corr}$ values are decreased from 472.3 to 227.85 μA/cm^2 with increase in concentration of *p*-toluidine. The I.E. value is also found to increase from 66.9% to 84.0%. It is observed that there is a steady increase of inhibitor efficiencies with concentration as observed in the impedance results.

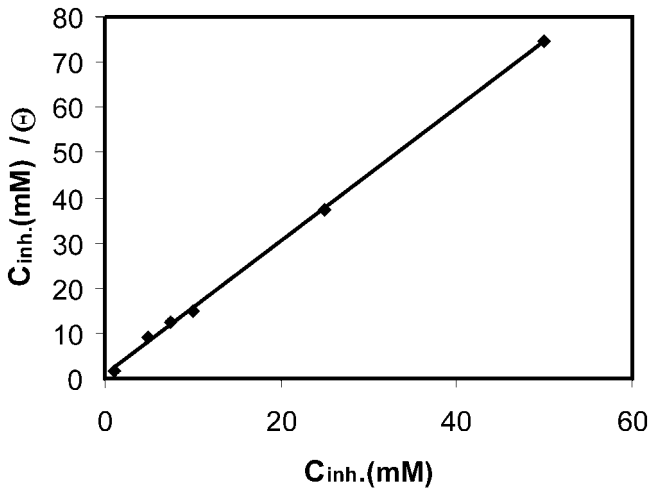


Figure 6 Langmuir isotherm plot for *p*-toluidine.

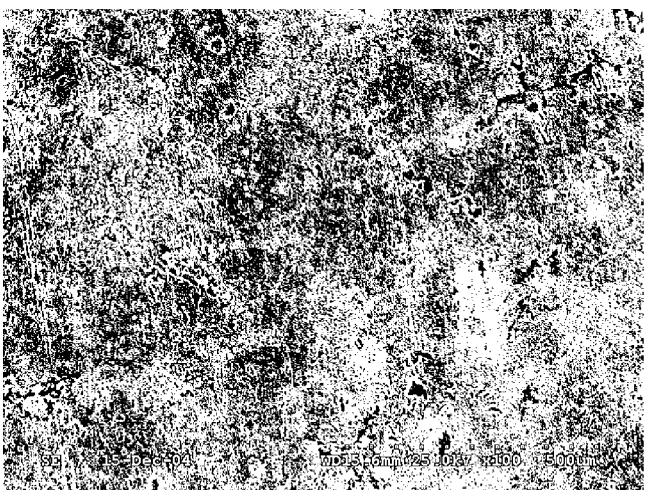


Figure 7 SEM photograph with (×100) magnification for iron in 1*M* HCl.

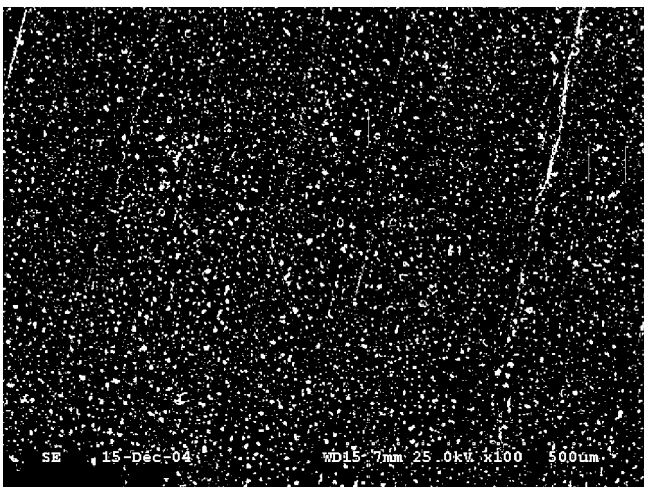


Figure 8 SEM photograph with (×100) magnification for iron in 1*M* HCl containing 0.05*M* *p*-toluidine.

Figure 6 shows the Langmuir adsorption isotherm plot of C_{inh} versus C_{inh}/θ, for *p*-toluidine. From this plot, it is observed that it obeys Langmuir adsorption isotherm through surface coverage of inhibitor adsorption on iron surface. The adsorption of the *p*-toluidine molecules with the metal surface is usually through the already adsorbed chloride ions. In acidic solutions, amines exist as cations and adsorb through electrostatic interaction between the positively charged anilinium cations and adsorbed chloride ions.[12]

The SEM photograph with (100×) magnification for iron in 1*M* HCl with and without presence of *p*-toluidine are given in Figures 7 and 8. It is observed from the photographs that the attack in presence of *p*-toluidine in 1*M* HCl is very less in comparison with the attack in absence of inhibitor in 1*M* HCl solution.

TABLE III
Electrochemical Parameters of Iron in 1*M* HCl without and with Different Concentrations of Poly(*p*-toluidine)

Concentration (ppm)	R_{ct} (Ω cm^2)	C_{dl} (μF/cm^2)	%I.E.	Surface coverage (θ)
Nil	15.6	330.1	–	–
50	72.6	192.0	78.5	0.42
100	84.9	173.1	81.6	0.48
250	98.8	161.2	84.2	0.51
500	112.1	144.1	86.1	0.56

Inhibition by poly(*p*-toluidine)

The impedance studies for iron in 1*M* HCl containing poly(*p*-toluidine) in the concentration range 50 to 500 ppm are conducted. Figure 9 shows the Nyquist plots for iron in 1*M* HCl containing poly(*p*-toluidine). The charge transfer resistance (R_{ct}) values, the double layer capacitance (C_{dl}) values, and surface coverage (θ) values calculated from the impedance diagrams are given in Table III. It is found that the R_{ct} values are increased steadily from 72.6 to 112.1 Ω cm^2 with increase of inhibitor concentrations from 50 to 500 ppm. Also, it is observed that C_{dl} values are decreased from 192.0 to 144.1 μF/cm^2 with increase in concentration of inhibitor, which shows the inhibition is absorbed due to surface adsorption.

The polarization behavior of iron in 1*M* HCl containing poly(*p*-toluidine) is shown in Figure 10. The electrochemical parameters obtained from these dia-

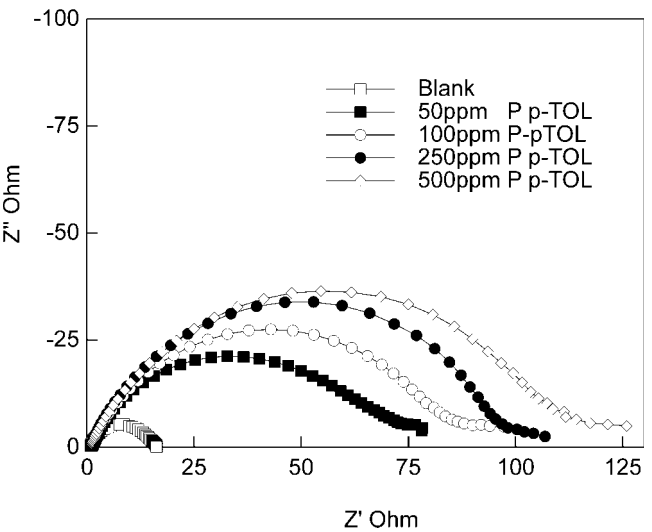


Figure 9 Nyquist plots of iron in 1*M* HCl with different concentrations of poly(*p*-toluidine).

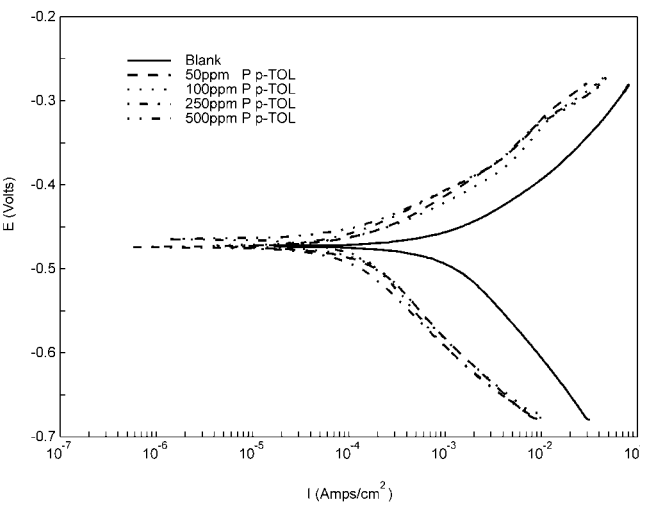


Figure 10 Polarization curves of iron in 1*M* HCl with different concentrations of poly(*p*-toluidine).

TABLE IV
Electrochemical Parameters of Iron in 1*M* HCl without and with Different Concentrations of Poly (*p*-toluidine)

Concentration (ppm)	E_{corr} (mV)	R_p (Ω cm^2)	%I.E.	b_a (mV)	b_c (mV)	$I_{corr.}$ (μA/cm^2)	%I.E.
Nil	−488.4	17.4	–	99.7	133.1	1425.5	–
50	−479.7	100.5	82.7	70.6	128.1	137.1	90.3
100	−479.0	111.1	84.3	58.1	32.7	130.6	90.8
250	−473.1	138.1	87.4	57.5	116.6	83.9	94.1
500	−472.5	130.6	86.7	53.3	111.5	76.6	94.6

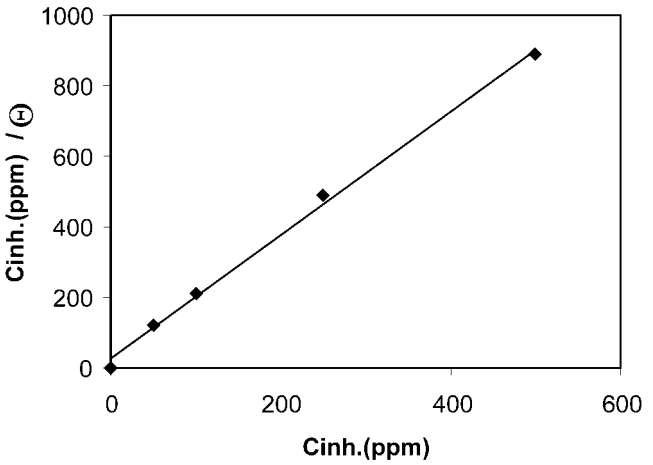


Figure 11 Langmuir isotherm plot for poly(*p*-toluidine).

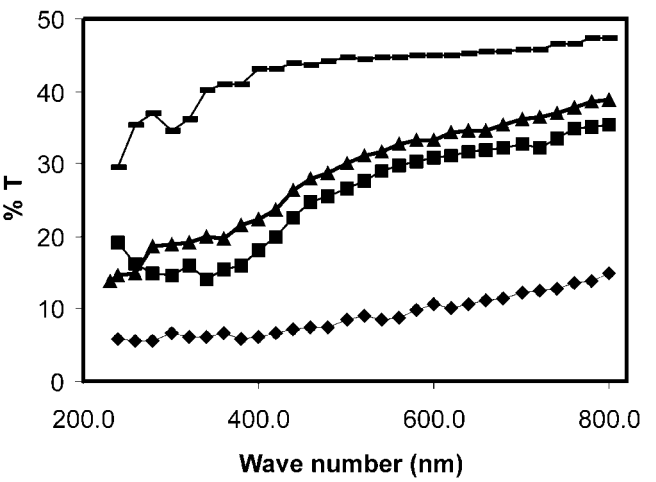


Figure 12 UV reflectance plot for poly(*p*-toluidine).

grams are shown given in Table IV. It is found that there is no significant variation in the E_{corr} values in the presence of inhibitors suggesting that this polymer behaves as mixed type of inhibitor. The inhibitor efficiency values calculated from linear polarization resistance (R_p) values are found to increase with increase in concentrations.

The Tafel slopes remained unaffected in the presence of inhibitor poly(*p*-toluidine). The i_{corr} values are found to decrease from 137.1 to 76.6 μA/cm^2 and it shows that there is a steady increase of inhibitor efficiencies with concentration. Figure 11 shows the adsorption isotherm [plot of C_{inh} versus C_{inh}/θ] for poly(*p*-toluidine). It is found that poly

Figure 13 SEM photograph with (×100) magnification for iron in 1*M* HCl containing 500 ppm poly(*p*-toluidine).

(*p*-toluidine) obeys Languimer isotherm. The higher inhibitive property of poly(*p*-toluidine) is also due to the presence of π electrons, quaternary nitrogen atom and the larger molecular size which ensures greater coverage of the metallic surface.[6–16] Similarly the reflectance study (Fig. 12) indicates the more protective nature of poly(*p*-toluidine) than that of monomer.

The SEM photograph with (100×) magnification for iron in 1*M* HCl containing 500 ppm poly(*p*-toluidine) is given in Figure 13. It is seen from the photograph that the attack in presence of 500 ppm poly(*p*-toluidine) in 1*M* HCl is very less in comparison with that of monomer in 1*M* HCl solution.

CONCLUSIONS

1. The inhibition efficiency for both monomer and polymer of *p*-toluidine increases with increase in concentrations.
2. Poly(*p*-toluidine) has shown a better performance of inhibition efficiency for iron in 1*M* HCl solutions when compared with its monomer.
3. Both *p*-toluidine and poly(*p*-toluidine) were found to be mixed type of inhibitor.
4. The adsorption of both monomer and polymer of *p*-toluidine on iron surface in 1*M* HCl obey Langmuir adsorption isotherm.

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