● *Research Articles*

The Inhibitive Effect of para-Amino Benzoic Acid and Its Polymer on Corrosion of Iron in 1 mol/L HCl Solution

P.Manivel[1)†] *and G.Venkatachari*[2)]

1) A.C. College of Engineering & Technology, Karaikudi-630 004, India
2) Central Electrochemical Research Institute, Karaikudi-630 003, India

Poly p-aminobenzoic acid has been synthesized by chemical oxidation method. The inhibitive effect of poly p-aminobenzoic acid on iron in 1 mol/L HCl solution was investigated by polarization and electrochemical impedance spectroscopy and compared with that of monomer p-aminobenzoic acid. The effectiveness of poly p-aminobenzoic acid is very high in comparison with that of monomer. The results show that both cathodic and anodic processes were suppressed by p-aminobenzoic acid and poly p-aminobenzoic acid of iron dissolution in 1 mol/L HCl by their adsorption on the iron surface. The inhibition efficiency of both p-aminobenzoic acid and poly p-aminobenzoic acid were found to increase with the inhibitor concentrations. Ultraviolet (UV) reflectance studies of the iron surface after exposure to inhibitor acid show that poly p-aminobenzoic acid is strongly adsorbed on iron surface.

KEY WORDS: p-aminobenzoic acid; Poly p-aminobenzoic acid; HCl; Inhibition; Corrosion

1. Introduction

Hydrochloric acid solutions are widely used for pickling, cleaning, descaling, *etc.*, for iron in chemical and electrochemical industries. High protection at low concentration of inhibitors is required not only for economic consideration but also for maintaining appropriate concentrations and avoiding insufficient inhibition. The polymer amines and their derivatives are found to show distinct corrosion inhibition effect in acidic media[1~3]. The polymers of aromatic amines are highly useful in chemical industries as effective inhibitors for iron in acid solutions.

The inhibitive properties of aniline derivatives[3], poly aniline[1~3], poly methyleneimine[4], poly ethoxy aniline[5], poly methoxy aniline[6], poly p-anisidine[7], poly p-aminophenol[8] have been studied for their inhibitive effectiveness for iron in acid chloride solutions. However, no report is available on the acid substituted aniline and its polymer on the inhibitive effect of iron dissolution in acid solution. In this work, the inhibitive behaviors of p-aminobenzoic acid and poly p-aminobenzoic acid on iron in 1 mol/L HCl have been studied by impedance and polarization techniques.

2. Experimental

2.1 Preparation of polymer

Reagent grade p-aminobenzoic acid was used for the preparation of water-soluble poly p-aminobenzoic acid. A fresh solution of 0.1 mol/L p-toluene sulphonic acid was prepared using double distilled water. To this solution 0.1 mol/L of p-aminobenzoic acid dissolved in 0.1 mol/L HCl, was added and cooled to 5°C in a bath of ice and salt mixture. Freshly prepared solution of 0.1 mol/L ammonium per sulphate was slowly added (to avoid warming) into the above solution, 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 Fourier transform infrared spectroscopy (FTIR) and ultraviolet (UV) spectra, and the molecular weight determination was carried out by gel permeation chromatography (GPC). The molecular weight of the above polymer was found to be 17,382.

2.2 Evaluation of inhibitor

The iron electrode with purity of 99.998% was used as a test electrode and it was embedded in araldite, so as to expose surface area of 1 cm². The electrode was polished successively on the emery papers of grade 1/0, 2/0, 3/0 and 4/0, and then degreased with trichloroethylene. The electrochemical studies were carried out using a double walled glass cell of capacity 200 ml having provisions for the working electrode, counter platinum electrode and luggin capillary. The potential of the working electrode was measured with respect to saturated calomel electrode (SCE) through the luggin capillary. The experiments were carried out after the steady state attainment of corrosion potentials (15 mts) at 30±1°C. All the solutions were prepared using reagent grade chemicals in double distilled water. Solartron Electro Chemical Measurement Unit (1280B) with a software package of Z plot 2 and CORR WARE 2 was used to conduct the experiments. This system includes a potentiostat and personal computer.

For impedance measurements, the experiments were carried out at corrosion potential with the AC amplitude of 20 mV in 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 linear polarization resistance studies 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

† To whom correspondence should be addressed,
  E-mail: mani_accet@yahoo.co.in.

Table 1 Impedance parameters of iron in 1 mol/L HCl without and with different concentrations of p-aminobenzoic acid

Conc./Molar	$R_{ct}/\Omega\cdot cm^2$	$C_{dl}/(\mu F/cm^2)$	$I.E./\%$	Surface coverage, θ
Nil	15.6	330.1	–	–
1×10^{-3}	22.3	149.8	30.3	0.55
5×10^{-3}	26.5	114.9	41.4	0.65
7.5×10^{-3}	27.5	114.5	44.0	0.65
1×10^{-2}	32.0	112.3	51.5	0.66
2.5×10^{-2}	34.1	110.0	54.4	0.67
5.0×10^{-2}	35.1	108.2	55.7	0.67

Table 2 Impedance parameters of iron in 1 mol/L HCl without and with different concentrations of poly p-aminobenzoic acid

Conc./10^{-6}	$R_{ct}/\Omega\cdot cm^2$	$C_{dl}/(\mu F/cm^2)$	$I.E./\%$	Surface coverage, θ
Nil	15.6	330.1	–	–
50	70.9	220.8	78.0	0.33
100	102.7	208.1	84.8	0.37
250	124.9	201.6	87.5	0.39
500	155.2	188.0	89.9	0.43
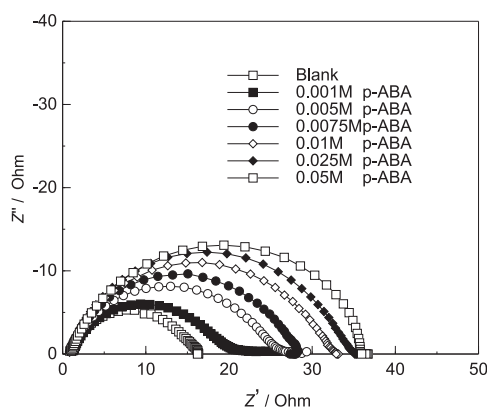
Fig.1 Nyquist plots for iron in 1 mol/L HCl with different concentrations of p-aminobenzoic acid
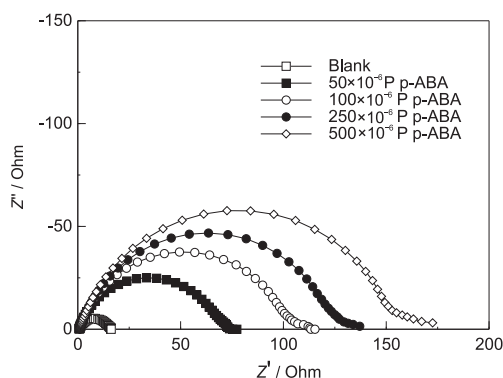
Fig.2 Nyquist plots for iron in 1 mol/L HCl with different concentrations of poly p-aminobenzoic acid

plots and the slope of the plots gave the polarization resistance (R_p). Similarly, for the potential 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 kinetic parameters, e.g. I_{corr}, b_a and b_c, have been obtained from the polarization curves.

The inhibitor efficiencies ($I.E.$) were calculated from the I_{corr} values, R_p values and R_{ct} values using the following relations.

$$(1) \text{ Inhibitor efficiency } (\%)=\frac{I_{corr}-I_{corr(i)}}{1/R_{ct}}\times100$$

$$(2) \text{ Inhibitor efficiency } (\%)=\frac{1/R_{ct}-1/R_{ct(i)}}{1/R_{ct}}\times100$$

$$(3) \text{ Inhibitor efficiency } (\%)=\frac{1/R_p-1/R_{p(i)}}{1/R_p}\times100$$

where I_{corr} and $I_{corr(i)}$ are the corrosion current in the absence and presence of inhibitors; R_{ct} and $R_{ct(i)}$ are charge transfer resistance values in the absence and presence of inhibitors; R_p and $R_{p(i)}$ are the polarization resistance values in the absence and presence of inhibitors. Since R_{ct} and R_p are related to I_{corr} as R_p or $R_{ct}=k/I_{corr}$[9], the $(1/R_p)$ and $(1/R_{ct})$ are used to calculate the inhibition efficiency.

The surface coverage values (θ) were calculated from the C_{dl} values according to the following equation.

$$\text{Surface coverage } (\theta) = \frac{C_{dl} - C_{dl(i)}}{C_{dl}}$$

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

3. Results

The experiments were conducted for iron in 1 mol/L HCl and 1 mol/L HCl with p-aminobenzoic acid in the concentration range of 1×10^{-3} to 5×10^{-2} mol/L and poly p-aminobenzoic acid in the concentration range of 50 to 500×10^{-6}. Figures 1 and 2 show the Nyquist plots obtained from impedance measurements for iron in 1 mol/L HCl containing p-aminobenzoic acid and poly p-aminobenzoic acid, respectively. 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 Tables 1 and 2. It is found that the R_{ct} are increased from 15.6 to 35.1 $\Omega\cdot cm^2$ steadily with increasing inhibitor concentrations. The inhibition efficiency increased from 30.3% at 1×10^{-3} mol/L concentration to 55.7% at 5×10^{-2} mol/L concentration for the p-aminobenzoic

Table 3 Electrochemical parameters of iron in 1 mol/L HCl without and with different concentrations of p-aminobenzoic acid

Conc/Molar	E_{corr}/mV	R_p/$\Omega\cdot$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}	−456.5	34.1	49.1	80.8	145.4	661.9	53.6
5×10^{-3}	−460.6	37.0	53.0	75.0	145.2	580.9	59.3
7.5×10^{-3}	−465.7	38.5	54.8	82.6	138.8	499.7	65.0
1×10^{-2}	−464.1	39.9	56.4	71.6	141.7	459.3	67.8
2.5×10^{-2}	−464.1	40.8	57.4	76.1	127.2	445.4	68.8
5.0×10^{-2}	−473.2	57.8	69.9	74.1	127.2	326.1	77.1

Table 4 Electrochemical parameters of iron in 1 mol/L HCl without and with different concentrations of poly p-aminobenzoic acid

Conc./10^{-6}	E_{corr}/mV	R_p/$\Omega\cdot$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	−482.6	95.1	81.7	52.9	97.3	141.4	90.1
100	−483.9	132.9	86.9	52.2	90.9	107.6	92.5
250	−487.1	153.2	88.6	55.2	94.2	83.9	93.8
500	−488.9	197.5	91.1	52.3	94.3	77.6	94.8
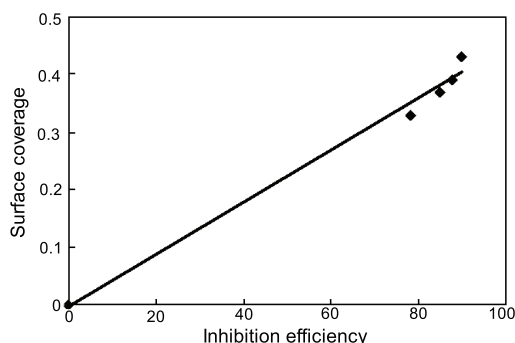
Fig.3 Plot of surface coverage *vs* inhibition efficiency for poly p-aminobenzoic acid
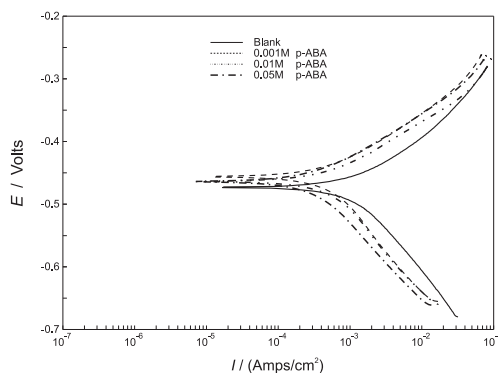
Fig.4 Polarisation curves for Iron in 1 mol/L HCl with different concentrations iron of p-aminobenzoic acid
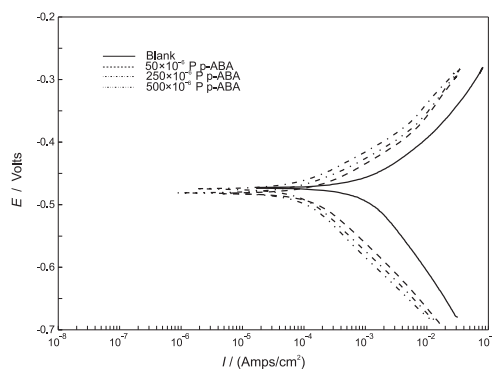
acid monomer. In the case of poly p-aminobenzoic acid, the R_{ct} values are increased from 15.6 to 155.2 $\Omega\cdot$cm^2 and the inhibition efficiency (*I.E.*) increased from 78.0% at 50×10^{-6} concentration to 89.9% at 500×10^{-6} concentration. It is observed that the R_{ct} values are increased steadily with increasing inhibitors concentrations.

The C_{dl} values are found to decrease from blank value in the presence of inhibitors. This decrease in C_{dl} values, which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, shows that
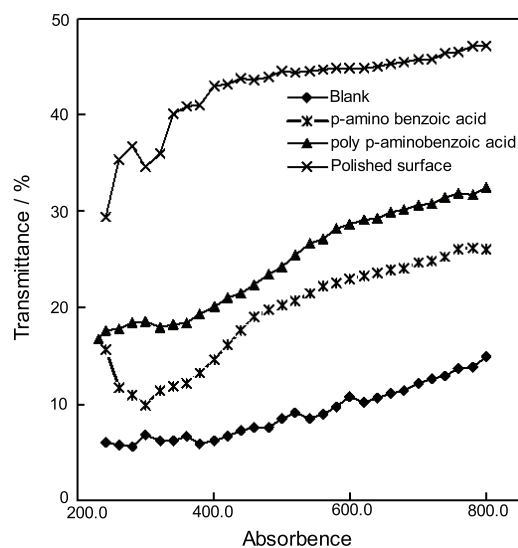
p-aminobenzoic acid molecules acts by adsorption at the solution interface[10]. The θ values are in the range of 0.55 to 0.67 in the presence of various concentrations of p-aminobenzoic acid. On comparing inhibitor efficiencies with that of surface coverage for poly p-aminobenzoic acid (Fig.3), there exists a linear relation.

Figures 4 and 5 show the polarization behavior of iron in 1 mol/L HCl and 1 mol/L HCl containing p-aminobenzoic acid and poly p-aminobenzoic acid at different concentrations. The electrochemical parameters obtained from these diagrams are given in Tables 3 and 4. It is found that there is no significant variation in the E_{corr} value in the presence of inhibitors, which suggests that this monomer and polymer behave as mixed type of inhibitors. It is observed that, there is a steady increase in R_p values with concentrations from 17.4 to 57.82 $\Omega\cdot$cm^2 and *I.E.* from 49.1 to 69.9% for the p-aminobenzoic acid monomer. Similarly, for the poly p-aminobenzoic acid the R_p value was increased from 17.4 to 197.5 $\Omega\cdot$cm^2 and *I.E.* from 49.1% to 91.1%. The Tafel slopes remained unaffected in the presence of inhibitors p-aminobenzoic acid and poly p-aminobenzoic acid. The data obtained from Tafel polarization show that for p-aminobenzoic acid the I_{corr} values decreases from 1425.5 to 326.1 μA/cm^2 with the increase in *I.E.* value as 77.1% at the concentration of 5×10^{-2} mol/L from 53.6% at 1×10^{-3} mol/L concentration. Similarly, in the case of poly p-aminobenzoic acid, the I_{corr} value was reduced steadily from 1425.5 to 77.6 μA/cm^2 with increase of *I.E* as 94.8% at the concentration of polymer 500×10^{-6}. As in the case of monomer, the C_{dl} values decreases in the presence of poly p-aminobenzoic acid. However, the inhibitive efficiencies are high even at lower coverage.

It shows that these inhibitors inhibit by adsorption. The inhibitor efficiencies obtained by polarization resistance, impedance and Tafel polarization methods agree very well. Figure 6 shows the UV reflectance curve for iron surface exposed to acid containing poly p-aminobenzoic acid. The shift in the absorption band indicates the stronger adsorption of poly p-aminobenzoic acid. The nature of interaction between the inhibitor and iron surface can be provided

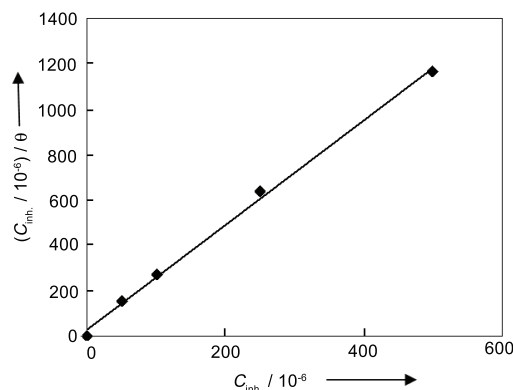Fig.5 Polarization curves for iron in 1 mol/L HCl with different concentrations of poly p-aminobenzoic acid

Fig.8 Langmuir isotherm plot for poly p-aminobenzoic acid

poly p-aminobenzoic acid is mainly due to the adsorption on iron surface.

4. Discussions

The studies have shown that, p-aminobenzoic acid and poly p-aminobenzoic acid inhibit corrosion of iron in 1 mol/L HCl by adsorption and retards anodic dissolution and hydrogen evolution reaction according to Langmuir adsorption isotherm. Previous studies[7~10] have shown that, adsorption of organic compound depends mainly on functional groups, steric factor aromaticity, electron density and the electronic structure of molecules.

Amines in aqueous acidic solutions may exist as either neutral molecules or in the form of cations depending on the concentration of H^+ ions in the solutions[7,8]. In acidic solutions they predominantly exist as cations and adsorb through electrostatic interaction between the positively charged anilinium cation and negatively charged metal surface. Hence adsorption of the p-aminobenzoic acid molecules with the metal surface takes place through the adsorbed chloride ions[10,11].

For the polymer amines, earlier studies[2~8] showed that the inhibitive properties of substituted polyaniline for mild steel in acid chloride solutions are very effective, 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. Hence the inhibitive property of poly p-aminobenzoic acid 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. The adsorption of polymer molecules on the metal surface in the form of a neutral molecule *via* chemisorption's mechanism involving the sharing of electrons between nitrogen and iron atoms and by the adsorption occurs through π electrons interaction with the metal surface[12~18].

5. Conclusions

(1) The inhibition efficiency for both monomer and polymer of p-aminobenzoic acid increases with the in-

Fig.6 UV reflectance plot for poly p-aminobenzoic acid

Fig.7 Langmuir isotherm plot for p-aminobenzoic acid

by adsorption isotherm. The degree of coverage θ obtained from C_{dl} is tested graphically for fitting a suitable adsorption isotherm as indicated in Figs.7 and 8. The plot of C_{inh}/θ *vs* C_{inh} yields a straight line with the correlation coefficient more than 0.98, which shows that the adsorption of inhibitor can be fitted to Langmuir adsorption isotherm. These plots indicate that the inhibition of iron by p-aminobenzoic acid and

crease in concentrations.

(2) Poly p-aminobenzoic acid has high inhibition efficiency for iron in 1 mol/L HCl solution when compared with its monomer.

(3) Both p-aminobenzoic acid and poly p-aminobenzoic acid were found to be mixed type inhibitor.

(4) The adsorption of both monomer and polymer of p-aminobenzoic acid on iron surface in 1 mol/L HCl obeys Langmuir adsorption isotherm.

REFERENCES

[1] P.J.Kinlen, V.Menon and Y.W.Ding: *J. Electrochem. Soc.*, 1999, **146**, 3690.

[2] Y.Wei, J.M.Yeh, H.Wang, X.Jia, C.Yang and D.Jin: *Poly. Mater. Sci. Eng.*, 1996, **74**, 202.

[3] S.Jasty and A.J.Epstein: *Poly. Mater. Sci. Eng.*, 1995, **72**, 565.

[4] K.Aramaki and N.Hackerman: *J. Electrochem. Soc.*, 1969, **116**, 568.

[5] S.Sathyanarayanan, S.K.Dhawan, D.C.Trivedi and K.Balakrishnan: *Corros. Sci.*, 1992, **33**, 1831.

[6] S.Sathyanarayanan, K.Balakrishnan S.K.Dhawan and D.C.Trivedi: *Electrochim. Acta*, 1994, **39**, 831.

[7] P.Manivel and G.Venkatachari: *Corr. Sci. Tech.*, 2005, **4**(2), 51.

[8] P.Manivel and G.Venkatachari: *J. Met. & Mat. Sci.*, 2004, **46**(3), 165.

[9] P.Manivel and G.Venkatachari: *J. Met. & Mat. Sci.*, 2004, **46**(4), 263.

[10] M.Stern and A.I.Geary: *J. Electrochem. Soc.*, 1957, **104**, 56.

[11] E.McCafferty and Norman Hackerman: *J. Electrochem. Soc.*, 1972, **119**, 146.

[12] C.A.Mann: *Trans. Electrochem.*, 1936, **69**, 105.

[13] C.Jeyaprabha: Ph.D. Thesis, Bharathidasan University, Trichy, India, 2001.

[14] K.F.Khalad and N.Hackerman: *Electrochim. Acta*, 2003, **48**, 2715.

[15] S.Muralidharan, K.L.N.Phani, S.Pitchumani, S.Ravichandran and S.V.K.Iyer: *J. Electrochem. Soc.*, 1995, **142**, 1478.

[16] S.L.Granese, B.M.Roseles, C.Oviedo and J.O.Zerbino: *Corros. Sci.*, 1992, **33**, 1439.

[17] D.Schweinsberg, G.George, A.Nanayakkara and D.Steiner: *Corros. Sci.*, 1988, **28**, 33.

[18] F.Bentiss, M.Traisnel and M.Lagrnee: *J. Appl. Electrochem.*, 2001, **31**, 41.