

The Influence of H⁺ and Cl⁻ Ions on the Corrosion Inhibitive Effect of Poly(*para*-aminophenol) for Iron in Hydrochloric acid

P. Manivel[†]

Department of Chemistry, Thanthai Periyar Government Institute of Technology, Vellore-632002, Tamilnadu, India

(Received June 28, 2017; Revised August 11, 2017; Accepted August 21, 2017)

Polymer amines are found to show distinct corrosion inhibition effects in acidic media. The functional groups of organic compounds have a wide role in the physical and chemical properties, for the inhibition efficiency with respect to steric factors, aromaticity, and electron density. The influence of H⁺ ions and Cl⁻ ions on the corrosion inhibitive effect of poly(*p*-aminophenol) for iron in hydrochloric acid was studied using electrochemical methods such as impedance, linear polarization, and Tafel polarization techniques. The experiments were conducted with and without the inhibitor, poly(*p*-aminophenol). The concentration range of H⁺ ions and Cl⁻ ions are from 1 M to 0.05 M and 1 M to 0.1 M, respectively. With the inhibitor poly(*p*-aminophenol), this study shows that inhibition efficiency decreases with the reduction of H⁺ ion and Cl⁻ ion concentrations in aqueous solution. Further, it reveals that the adsorption of an inhibitor on the surface of iron is dependent on the concentrations of H⁺ and Cl⁻ ions in the solution and the adsorption of inhibitor on the iron surface through the cationic form of amine.

Keywords: poly(*p*-aminophenol) inhibition, corrosion, iron, H⁺ and Cl⁻ ions, HCl

1. Introduction

The greatest advantage of hydrochloric acid over the other acids in cleaning and pickling operations lies in its ability to form metal chlorides, which are extremely soluble in aqueous phase, compared to sulfate, nitrate, phosphate, etc. This higher rate of solubility of chloride salts causes the least polarizing effect and does not hamper the rate of reaction

The polymers of aromatic amines are effective inhibitors for iron in acid solutions and highly useful in chemical industries. Troch-Nagels *et al.* [1] have studied an electron conducting organic coating of mild steel by electro polymerization of poly pyrrole. They found that the film was conductive, ensured good corrosion resistance of the substrate, but they were brittle and adhesion to the substrate was not high. Similarly, poly aniline [2], which is obtained in nitric acid gave a good adhesion but were brittle and powdery on the surface.

Khalad and Hackerman [3] Luo *et al.* [4] and others [5-10] have studied anilines and its derivatives and found that they were effective inhibitors for iron in acid solutions. The functional groups of the organic compounds have a wide role in the physical chemical properties for the in-

hibition efficiency with respect to steric factors, aromaticity, and electron density [11,12]. The mechanism of corrosion of iron by HCl has been studied by Rajagopalan and Venkatachari [13]. For the present study, poly(*p*-aminophenol) has been chosen to study the effect of H⁺ and Cl⁻ ions on iron in various concentrations.

2. Experimental Details

2.1 Preparation of Polymer

Reagent grade *para*-aminophenol was used for the preparation of water-soluble poly(*p*-aminophenol) [6]. Freshly prepared 0.1 M solution of *p*-Toluene sulphonic acid was added with 0.1 M of *para*-aminophenol (in 0.1 M HCl) and cooled to 0.5 °C in a bath of ice and salt mixture. To this solution mixture, freshly prepared solution of Ammonium per sulphate (0.1 M) 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 two hours, to ensure the completion of the reactions.

The obtained Polymer was characterized by Fourier transform infrared (FTIR) Spectroscopy (Perkin Elmer Paragon500) and Ultraviolet-Visible (UV- vis) spectroscopy (Hitachi, Model U 3400, Tokyo, Japan) and the molecular weight determination was carried out by gel

[†] Corresponding author: mani_accet@yahoo.co.in

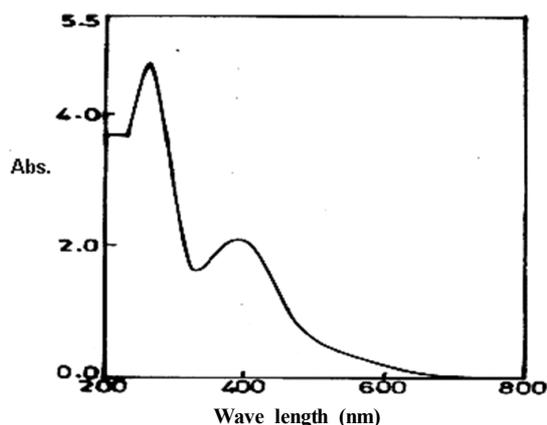


Fig. 1 UV-visible Spectrum for poly(*p*-aminophenol).

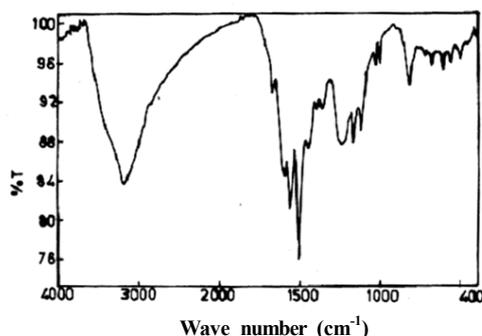


Fig. 2 FTIR Spectrum for poly(*p*-aminophenol).

permeation chromatography (GPC) (Shimadzu, Kyoto, Japan).

2.2 Poly(*p*-aminophenol)

The absorption peak at 260nm shows the p-p* transition in the benzenoid ring and 390 nm shows the donor-acceptor interaction of quinonoid ring Fig. 1. The IR adsorption Fig. 2 shows the band at 1562 cm⁻¹ and 1510 cm⁻¹ are the characteristic band due to nitrogen- quinonoid [14] ring structure and peaks for poly(*p*-aminophenol) is observed in 3191cm⁻¹, 1672 cm⁻¹ and 1562 cm⁻¹. For nitrogen benzenoid - quinonoid ring structure the peaks obtained at 1598 cm⁻¹and 1510 cm⁻¹. The other IR characteristics are observed at 1122 cm⁻¹, 1034 cm⁻¹, 1009 cm⁻¹ and 820 cm⁻¹.

2.3 Methodology

Pure iron (99.998%) was used as a test electrode and it was embedded in Araldite, so as to expose the 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 decreased with trichloroethylene. The electro-

chemical 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 min] at 30±1 °C. All the solutions were prepared using reagent grade chemicals in double distilled water.

The experiments were conducted using SOLARTRON ELECTRO CHEMICAL MEASUREMENT UNIT(1280B, Solatron Analytical, Hampshire, England) with a software package of Z plot 2 and CORR WARE2. This system includes a potentiostat and personal computer.

Impedance measurements were carried out at the 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 using Z view software.

In 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 1mV/Sec. 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*).

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 kinetic parameters such as *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 relationships,

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

$$(ii) \text{ I.E. (\%)} = \frac{1/R_{\text{ct}} - 1/R_{\text{ct}(i)}}{1/R_{\text{ct}}} \times 100$$

$$(iii) \text{ I.E. (\%)} = \frac{1/R_p - 1/R_{p(i)}}{1/R_p} \times 100$$

Table 1 Electrochemical parameters for iron in different H⁺ ion concentrations (Blank)

Conc. of [H ⁺]	R _{ct} (Ωcm ²)	C _{dl} (μF/cm ²)	E _{corr} (mV)	R _p (Ωcm ²)	ba (mV)	bc (mV)	i _{corr.} (μA/cm ²)
1.0 M	15.6	330.1	-488.4	17.4	99.7	133.07	1425.5
0.5 M	81.4	215.0	-511.8	119.9	89.6	100.9	185.4
0.1 M	92.9	146.8	-548.5	126.7	84.5	102.7	158.4
0.05 M	109.3	123.8	-559.2	153.9	86.4	116.2	140.0

Where i_{corr} and i_{corr(i)} are the corrosion current values in the absence and presence of inhibitor, R_{ct} & R_{ct(i)} are charge transfer resistance values in the absence and presence of inhibitor, and R_p & R_{p(i)} are the polarization resistance values in the absence and presence of inhibitor.

3. Results and Discussion

3.1 Effect of H⁺ and Cl⁻ ions on iron in absence of inhibitor (Blank)

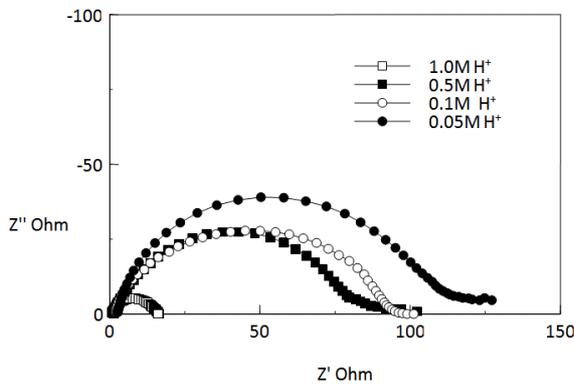


Fig. 3 Nyquist plots for iron in different H⁺ ion concentrations (Blank).

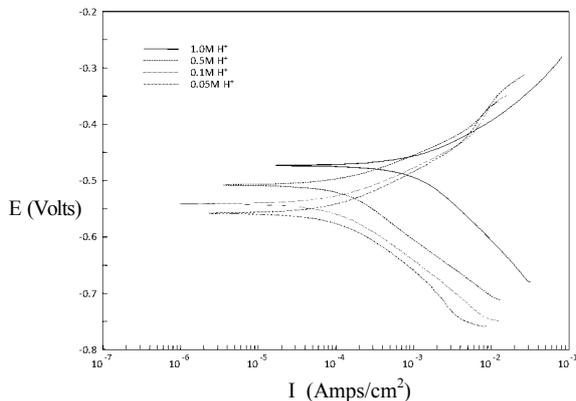


Fig. 4 Polarization curves for iron in different H⁺ ion concentrations (Blank).

The effect of H⁺ and Cl⁻ ions on iron was studied through impedance measurements, linear polarization and Tafel polarization methods. For the effect of H⁺ and Cl⁻ ions, the studies were carried out with and without inhibitor. The concentration range of H⁺ ions and Cl⁻ ions are from 1 M to 0.05 M and 1 M to 0.1 M respectively.

The iron dissolution in 0.05 M to 1 M HCl was studied through the electrochemical measurements for the H⁺ ion concentrations from 0.05 M to 1 M. The impedance data for iron in various [H⁺] ion concentrations, at [Cl⁻] = 1 M are given in Fig. 3 and the values are given in Table 1. The values of R_{ct} found to increase from 15.6 Ωcm² to 109.3 Ωcm² with subsequent decrease in C_{dl} values from 330.1 μF/cm² to 123.8 μF/cm² with decrease of H⁺ ion concentrations. It showed that the dissolution of iron decreases with decrease in H⁺ ion concentrations.

The Fig. 4 shows the corresponding Tafel polarization curves for various [H⁺] ion concentrations. It is observed that the R_p values increased from 17.4 Ωcm² to 153.9 Ωcm² and the E_{corr} values from -488.4 mV to -559.2 mV with a decrease in concentration of H⁺ ions from 1 M to 0.01 M. From the Tafel polarization studies, it is found that the i_{corr} values are decreased from 1425.5 μA/cm² to 140.0 μA/cm² and it shows the rate of iron dissolution is decreased with decrease of H⁺ ions concentrations.

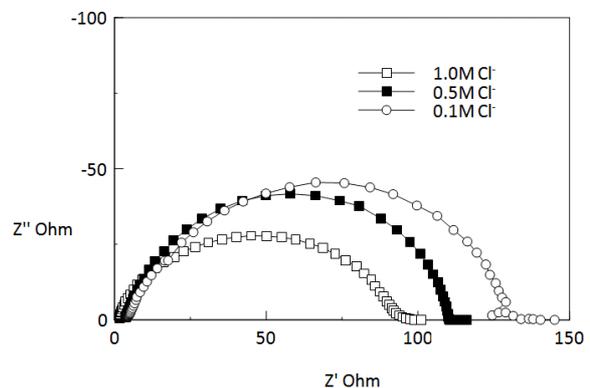
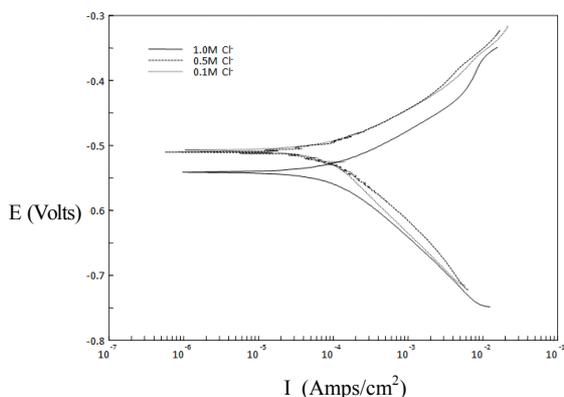
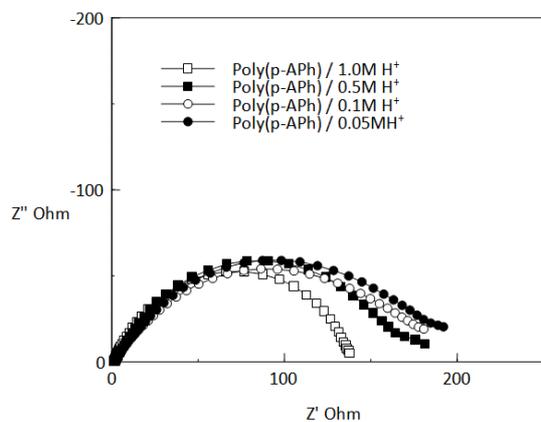


Fig. 5 Nyquist plots for Iron in different Cl⁻ ion concentrations (Blank).

Table 2 Electrochemical parameters for iron in different Cl⁻ ion concentrations (Blank)

Conc. of [Cl ⁻]	R _{ct} (Ωcm ²)	C _{dl} (μF/cm ²)	E _{corr} (mV)	R _p (Ωcm ²)	ba (mV)	bc (mV)	i _{corr.} (μA/cm ²)
1.0 M	92.9	146.8	-548.5	126.7	84.5	102.7	158.2
0.5 M	107.1	134.1	-535.5	152.9	83.7	111.7	140.1
0.1 M	127.0	124.5	-522.2	158.3	89.6	105.8	131.7

**Fig. 6 Polarization curves for iron in different Cl⁻ ion concentrations (Blank).****Fig. 7 Nyquist plots for iron in different H⁺ ion concentrations in presence of 100 ppm poly(*p*-aminophenol).****Table 3 Impedance parameters for iron in different H⁺ ion concentrations in presence of 100 ppm poly(*p*-aminophenol)**

Conc. of [H ⁺]	R _{ct} (Ωcm ²)	C _{dl} (μF/cm ²)	% I.E
1.0 M	138.0	211.7	88.7
0.5 M	166.2	155.4	51.0
0.1 M	186.0	109.0	50.1
0.05 M	189.2	84.4	42.2

The effect of chloride ions on the corrosion reactions can be seen from the impedance plots shown in Fig. 5 and the values are given in Table 2. It is found that the R_{ct} values are increased from 92.9 Ωcm² to 127.0 Ωcm² with subsequent decrease in C_{dl} values from 146.8 μF/cm² to 124.5 μF/cm² for the concentration range from 1 M to 0.1 M Cl⁻ ions.

The polarization behaviour is shown in Fig. 6. It is observed that the linear polarization (R_p) values are found to increase from 126.7 Ωcm² to 158.3 Ωcm² with subsequent decrease in E_{corr} from -548.5 mV to -522.0 mV for the concentration of Cl⁻ from 1 M to 0.1 M. Similarly, from the Tafel polarization it is observed that the i_{corr} values have decreased from 158.2 to 131.7 μA/cm² as the concentration of Cl⁻ decreased from 1.0 M to 0.1 M. From this study, it is observed that the rate of iron dissolution increases with increase of Cl⁻ ions concentrations.

3.2 Effect of H⁺ and Cl⁻ ions on iron in presence of inhibitor

The impedance behaviour of iron in the concentration of 1 M to 0.1 M H⁺ ions solutions in the presence of 100 ppm poly(*p*-aminophenol) is shown in Fig. 7. The charge transfer resistance [R_{ct}] values and double layer capacitance [C_{dl}] values obtained from the impedance diagrams are given in Table 3. It shows that a decrease in inhibitor efficiency is obtained from R_{ct} values with a decrease in concentration of H⁺ ions from 1.0 M to 0.05 M.

Table 4 gives the electrochemical parameters obtained from polarization resistance and Tafel polarization resistance studies for the same concentrations of Cl⁻ ions and inhibitor for iron and Fig. 8 shows the polarization behaviour. It is found that inhibitor efficiency obtained from the R_p values decreases gradually from 88.4 to 32.4%.

The effect of Cl⁻ ions on the inhibitory effect of iron by 100 ppm of the poly(*p*-aminophenol) has been carried out through the electrochemical techniques. Table 5 shows the results of impedance study of iron in 1 M to 0.1 M Cl⁻ ions with 100 ppm poly(*p*-aminophenol). The polarization behaviour of iron is given in Fig. 9. It is found that the R_{ct} value shows a decrease in inhibitor efficiency

Table 4 Electrochemical parameters for iron in different H⁺ ion concentrations in presence of 100 ppm poly(*p*-aminophenol)

Conc [H ⁺]	E _{corr} mV	R _p (Ωcm ²)	% I.E	ba mV	bc mV	i _{corr.} (μA/cm ²)	% I.E
1.0 M	-490.1	150.2	88.4	51.0	95.6	54.9	96.1
0.5 M	-495.4	206.7	42.0	78.1	107.3	54.7	70.5
0.1 M	-521.2	208.8	39.3	69.5	109.7	53.3	66.3
0.05 M	-524.7	227.7	32.4	56.2	116.2	51.4	63.3

from 50.1 to 35.9%.

Table 6 shows the parameters of polarization studies for 1M to 0.1 M concentrations of Cl⁻ ions in presence of inhibitor. Tafel polarization behaviour for this system is shown in Fig. 10. It is observed that the inhibitor efficiency obtained from R_p and i_{corr} values shows a decrease with decrease in Cl⁻ ions concentrations. From this study [Fig. 11], it is observed that the adsorption of inhibitor on iron surface decreases with decrease in concentration of Cl⁻ ions [13].

In the case of H⁺ ions concentrations, it is observed that the lowering of the inhibitor efficiency with decrease of H⁺ ion concentration [Fig. 12] is due to the decrease in the concentration of cationic formation of poly(*p*-ami-

nophenol). 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 [15].

In higher concentration of H⁺ ion solutions they predominantly exist as cations and adsorb through electrostatic interaction between the positively charged anilinium cation and negatively charged metal surface. The stronger

Table 5 Impedance parameters for iron in different Cl⁻ ion concentrations in presence of 100 ppm poly(*p*-aminophenol)

Conc. of [Cl ⁻]	R _{ct} (Ωcm ²)	C _{dl} (μF/cm ²)	% I.E
1.0 M	186.0	109.0	50.1
0.5 M	188.7	94.1	43.2
0.1 M	198.4	86.2	35.9

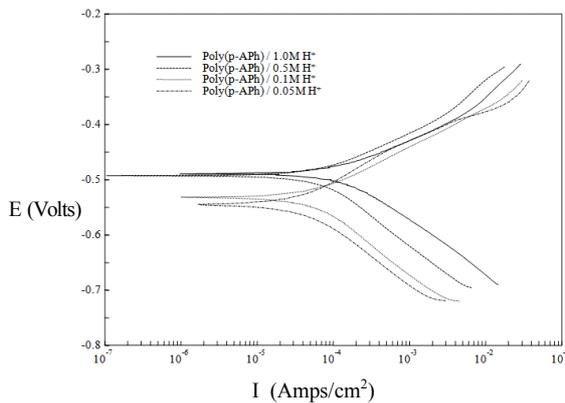


Fig. 8 Polarization curves for iron in different H⁺ ion concentrations in presence of 100 ppm poly(*p*-aminophenol).

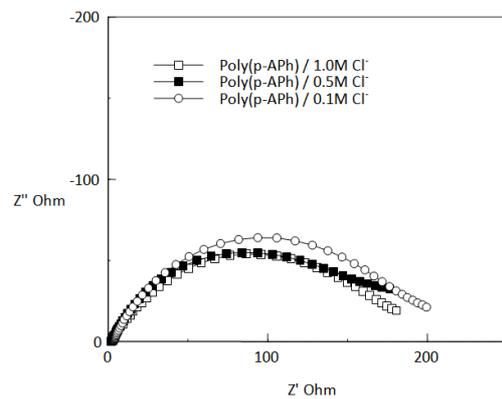


Fig. 9 Nyquist plots for iron in different Cl⁻ ion concentrations in presence of 100 ppm poly(*p*-aminophenol).

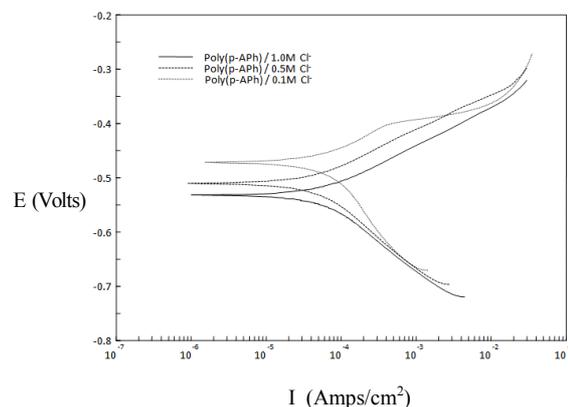


Fig. 10 Polarization curves for iron in different Cl⁻ ion concentrations in presence of 100 ppm poly(*p*-aminophenol).

Table 6 Electrochemical parameters for iron in different Cl⁻ ion concentrations in presence of 100 ppm poly(*p*-aminophenol)

Conc. [Cl ⁻]	E _{corr} mV	R _p (Ωcm ²)	% I.E	ba mV	bc mV	i _{corr.} (μA/cm ²)	% I.E
1.0 M	-521.2	208.8	39.3	69.5	109.7	53.3	66.3
0.5 M	-498.0	227.2	32.7	66.1	118.1	48.3	65.5
0.1 M	-471.9	228.5	30.7	76.7	90.4	45.8	62.5

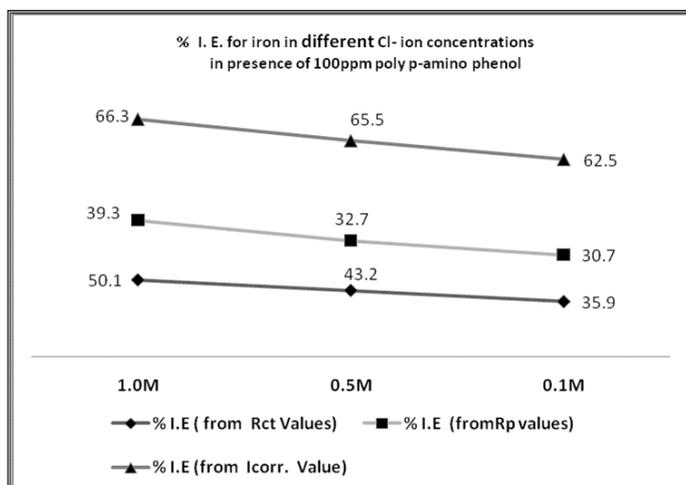


Fig. 11 The percentage of I. E. for iron in different Cl⁻ ion concentrations in presence of 100 ppm poly(*p*-aminophenol).

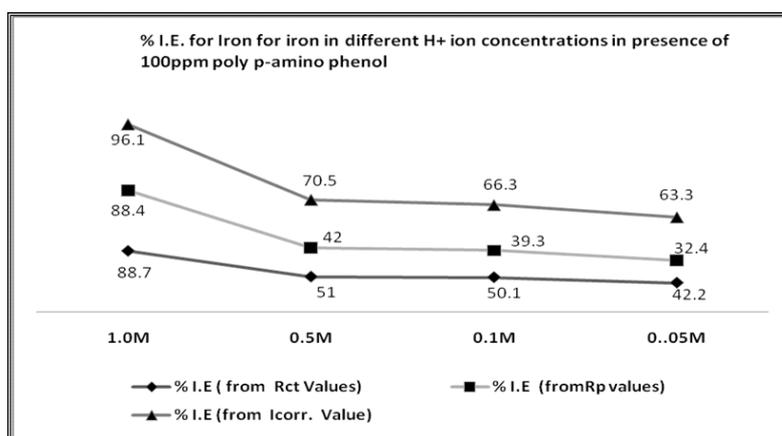


Fig. 12 The percentage of I. E. for iron in different H⁺ ion concentrations in presence of 100 ppm poly(*p*-aminophenol).

adsorption of the organic molecules with the metal surface is with increase in concentration of H⁺ ions [16,17].

Further, it is observed that at higher Cl⁻ ion concentration the inhibiting effect of poly(*p*-aminophenol) is found to be higher and it is due to the presence of Cl⁻ ions, which are preferentially adsorbed on the iron electrode surface and makes the surface more negative [18].

Therefore, Cl⁻ ions act as catalyst to promote the adsorption of poly(*p*-aminophenol) and improves the inhibiting effect to a considerable extent [19-22].

Besides, at higher Cl⁻ ion concentration, the Cl⁻ ions and amine cations co-exist in solution and co-adsorbed on the ion surface in terms of electrostatic attraction of these species and adsorption of amine cation is strengthened.

The most pronounced effect of Cl⁻ ions is due to a small degree of hydration. The decrease in efficiency of poly(*p*-aminophenol) at lower concentrations of Cl⁻ is due to lesser adsorption of poly(*p*-aminophenol) at the electrode surface.

4. Conclusion

The inhibition efficiency of poly(*p*-aminophenol) on iron in hydrochloric acid, increases with an increase in the concentrations of H⁺ ions and Cl⁻ ions. The adsorption of inhibitor on the surface of iron is dependent on the concentrations of H⁺ and Cl⁻ ions in the solution, and the adsorption of inhibitor on the iron surface through the cationic form of amine.

Acknowledgements

I express my sincere gratitude to Dr. G. Venkatachari, Deputy Director [Retd.] Corrosion Testing and Evaluation Division, CECRI, Karaikudi, for suggesting this interesting problem with his valuable guidance, suggestions to carry out this research work.

References

1. G. Troch-Nagels, R. Winand, A. Weymeersch, and L. Renard, *J. Appl. Electrochem.*, **22**, 756 (1992).
2. D. W. Hatchett, M. Josowicz, and J. Janata, *J. Electrochem. Soc.*, **146**, 4535 (1999).
3. K. F. Khaled and N. Hackerman, *Mater. Chem. phys.*, **82**, 949 (2003).
4. H. Luo, Y. C. Guan, and K. N. Han, *Corrosion*, **54**, 721 (1996).
5. P. Manivel and G. Venkatachari, *J. Met. Mater. Sci.*, **46**, 173 (2004).
6. P. Manivel and G. Venkatachari, *J. Met. Mater. Sci.*, **46**, 263 (2004).
7. P. Manivel and G. Venkatachari, *Corros. Sci. Tech.*, **4**, 51 (2005).
8. E. Mc Cafferty and N. Hackerman, *J. Electrochem. Soc.*, **119**, 999 (1972).
9. K. F. Khaled and N. Hackerman, *Mater. Chem. Phys.*, **82**, 949 (2003).
10. S. Rangamani, S. Muralidharan, M. Ganesan, and S. V. K. Iyer, *Indian J. Chem. Techn.*, **1**, 168 (1994).
11. F. Bentiss, M. Lagrenee, M. Traisnel, and J. C. Hornez, *Corros. Sci.*, **41**, 789 (1999).
12. G. Thenmozhi, P. Arockiasamy, and R. Jaya Santhi, *Int. J. Electrochem.*, Article ID 961617 (2014).
13. K. S. Rajagopalan and G. Venkatachari, *Corrosion*, **36**, 320 (1980).
14. D. W. Hatchett, M. Josowicz, and J. Janata, *J. Electrochem. Soc.*, **146**, 4535 (1999).
15. C. A. Mann, *Trans. Electrochem.*, **69**, 105 (1936).
16. B. Ramesh Babu and R. Holze, *Br. Corros. J.*, **35**, 204 (2000).
17. R. C. Ayers and N. Hackerman, *J. Electrochem. Soc.*, **119**, 146 (1972).
18. Z. A. Iofa and G. N. Tomasov, *Zh. Fiz. Khim.*, **34**, 1036 (1960).
19. P. Manivel and G. Venkatachari, *J. Mater. Sci. Technol.*, **22**, 301 (2006).
20. S. Rangamani and S. V. K. Iyer, *J. Appl. Electrochem.*, **24**, 355 (1994).
21. Y. Wei, F. K. Hsuch, and G. W. Tang, *Macromolecules*, **27**, 518 (1994).
22. P. Priori and P. Ranno, *Prog. Polym. Sci.*, **27**, 135 (2002).