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

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The corrosion inhibitive effect of Poly (p-Anisidine) on iron in 1M HCl with various concentrations were studied by using electrochemical methods such as impedance measurements and polarization techniques. The inhibition efficiency (IE) of Poly (p- Anisidine) was compared with its monomer and it was observed that there is a remarkable increase for the polymer. Further, it is found that the value of IE increases with increasing concentrations for both monomer and polymer of p-Anisidine.

Keywords : anisidine, poly (p-Anisidine), inhibition, corrosion, iron, HCl.

1. Introduction

In recent years, studies have shown that the polymer amines have attracted a great deal of attention for the research interest, because they have good electrochemical properties due to the presence of extensive delocalization of π electrons. These polymers are highly useful in electrochemical industries as effective inhibitors for iron in acid solutions.

The inhibitive properties of soluble poly aniline films were studied by wei et.al.[1] and Jasty.[2] Similarly the corrosion inhibitive effect of poly acrylic acid and its derivatives,[3] poly ethoxy aniline,[4] poly methoxy aniline[5] and Poly (p- Phenylene diamine)[6] have been studied for their inhibitive effectiveness for Iron in acid chloride solutions. In this work, the inhibitive behavior of poly (p-Anisidine) on iron in 1M HCl, has been studied using Impedance and polarization techniques.

2.Experimental details

2.1 Preparation of polymer

Reagent grade p-Anisidine was used for the prepation of water-soluble poly (p-Anisidine). A fresh solution of 0.1M p-Toluene sulphonic acid was prepared using double distilled water. To this solution 0.1M of p-Anisidine dissolved in 0.1M HCl, was added and cooled to 0.5°C in a bath of ice and salt mixture. To this solutions, freshly prepared solution of 0.1M Ammonium per sulphate 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 reactions. The obtained Polymer was characterized by FTIR and UV spectra, and the molecular weight determination was carried out by GPC method. The molecular weight of the above polymer was found to be 43,767.

2.2 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 1cm². 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 electro chemical studies were carried out using a double walled glass cell of capacity 200ml 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 (15mts) 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) 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 corrosion potential with the A.C.amplitude of 20 mV for the frequency range of 10 KHZ to 10 mHZ. The real and ima-

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ginary 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.

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/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. 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 icorr values, R_p values and R_{ct} values using the following relationships.

(i) I.E. (%) = $\dfrac{i_{cor} - i_{corr(i)}}{i_{corr}}$ X 100

(ii) I.E. (%) = $\dfrac{1/R_{ct} - 1/R_{ct(i)}}{1/R_{ct}}$ X 100

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

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

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

$\theta = \dfrac{C_{dl} - C_{dl(i)}}{C_{dl}}$

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

3. Results and discussion

The impedance measurements for Iron in 1M HCl and 1M HCl with different concentrations of p-Anisidine in the Concentration range 1×10^{-3}M to 5×10^{-2}M and poly (p-Anisidine) in the concentration range 10 ppm to 100 ppm were conducted. Figs.(1) and (2) show the Nyquist Plots for iron in 1M HCl containing p-Anisidine and poly
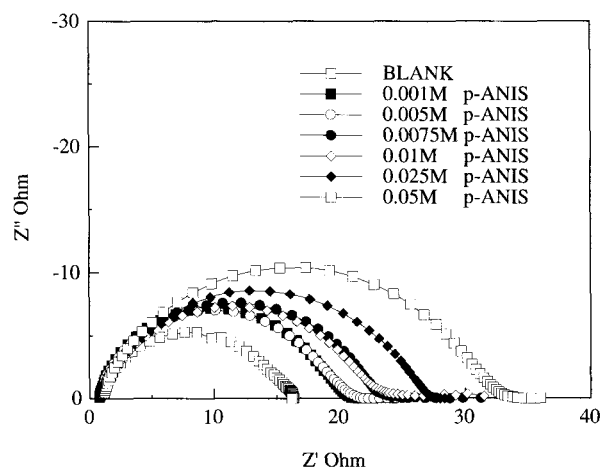

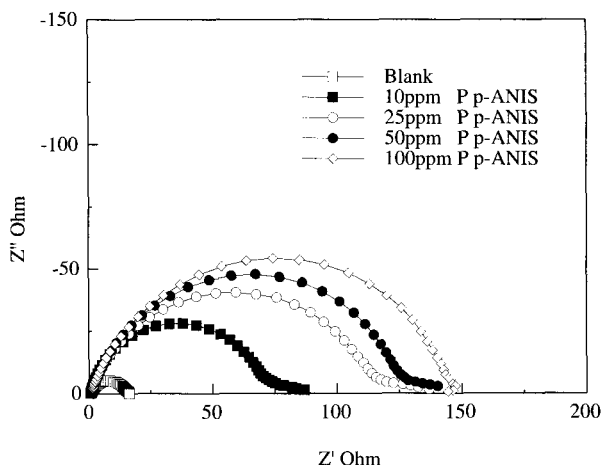Fig. 1. Nyquist plots of Iron in 1M HCl with different concentrations of p-Anisidine

Fig. 2. Nyquist plots of Iron in 1M HCl with different concentrations of poly (p-Anisidine)

Table 1. Electrochemical parameters of iron in 1M HCl Without and with different concentrations of p-Anisidine

Conc. (ppm)	$R_{ct.}$ (Ωcm^2)	$C_{dl.}$ ($\mu F/cm^2$)	% I.E	Surface Coverage (θ)
Nil	15.6	330.1	-	-
1×10^{-3}	21.0	117.4	26.09	0.64
5×10^{-3}	21.7	114.5	28.28	0.65
7.5×10^{-3}	24.1	92.1	35.37	0.72
1×10^{-2}	25.3	92.1	38.43	0.72
2.5×10^{-2}	28.2	83.6	44.84	0.75
5.0×10^{-2}	33.1	80.0	53.05	0.76

(p-Anisidine) respectively. The charge transfer resistance (R_{ct}) values, the double layer capacitance(C_{dl}) values, and surface coverage(θ) values calculated from the impedance

Table 2. Electrochemical parameters of iron in 1M HCl Without and with different concentrations of poly (p-Anisidine)

Conc. (ppm)	Rct. (Ωcm^2)	$C_{dl.}$ ($\mu F/cm^2$)	% I.E	Surface Coverage (θ)
Nil	15.6	330.1	-	-
10	72.5	258.3	78.5	0.22
25	116.2	240.1	86.6	0.27
50	126.4	223.8	87.6	0.32
75	134.0	217.0	88.4	0.34
100	145.7	205.9	89.3	0.38

Table 3. Electrochemical parameters of iron in 1M HCl Without and with different concentrations of p-Anisidine

Conc (ppm)	E_{corr} mV	R_p (Ωcm^2)	% I.E	ba mV	bc mV	$I_{corr.}$ ($\mu A/cm^2$)	% I.E
Nil	-488.4	17.4	-	99.7	133.1	1425.5	-
$1x10^{-3}$	-453.4	24.77	29.80	83.35	135.14	865.55	39.28
$5x10^{-3}$	-457.4	30.59	43.15	82.4	114.20	669.59	53.03
$7.5x10^{-3}$	-459.9	45.82	62.05	75.14	133.15	441.75	69.01
$1x10^{-2}$	-459.9	45.84	62.07	69.9	136.97	414.4	70.93
$2.5x10^{-2}$	-460.1	62.64	72.24	74.44	132.21	322.11	77.40
$5.0x10^{-2}$	-463.1	67.67	74.31	79.64	136.89	316.49	77.80

Fig. 3. Polarisation curves plots of Iron in 1M HCl with different concentrations of p-Anisidine

Table 4. Electrochemical parameters of iron in 1M HCl Without and with different concentrations of poly (p-Anisidine)

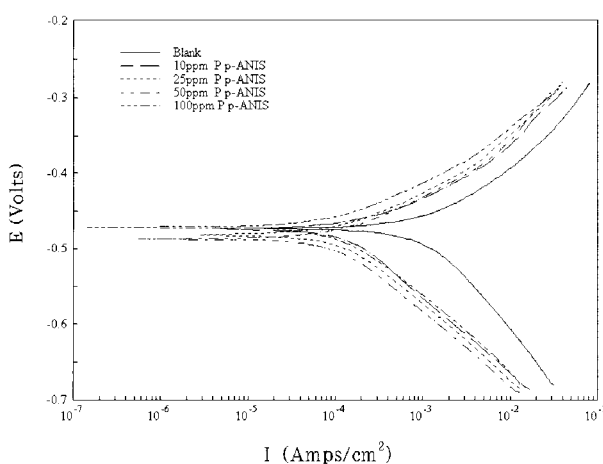| Conc (ppm)	E_{corr} mV	R_p (Ωcm^2)	% I.E	ba mV	bc mV	$I_{corr.}$ ($\mu A/cm^2$)	% I.E
Nil	-488.4	17.4	-	99.7	133.1	1425.5	-
10	-479.7	96.4	81.9	59.6	101.3	178.9	87.4
25	-486.7	161.7	89.2	53.2	94.9	95.7	93.2
0	-487.1	166.2	89.3	54.3	94.5	94.1	93.4
75	-488.5	168.4	89.7	50.3	89.2	86.9	93.9
100	-489.9	168.7	89.7	51.6	88.2	81.1	94.4

Fig. 4. Polarisation curves plots of Iron in 1M HCl with different concentrations of poly (p-Anisidine)

diagrams are given in Tables(1) and (2). It is found that the Rct values are increased steadily with increase of inhibitors concentrations.

The polarization behavior of iron in 1M HCl and 1M HCl containing p-Anisidine and poly (p-Anisidine) are shown in Figs(3) and (4). The electro chemical parameters obtained from these diagrams are shown given in Tables(3) and (4). It is found that, there is no significant variation in the $E_{Corr.}$ values in the presence of inhibitors suggesting that this monomer and polymer behave as mixed type of inhibitors. It is observed that, there is a steady increase of inhibitors efficiencies with concentration as observed in the impedance results.

The Tafel slopes are remained unaffected in the presence of inhibitors p-Anisidine and poly (p-Anisidine). It shows that these inhibitors inhibit by adsorption. It is observed that, there is a steady increase of inhibitors efficiencies with concentration as observed in the impedance results. Further the inhibitors efficiencies obtained by Polarization resistance, Impedance and Tafel polarization methods agree very well. Figs.(5) and (6) show the adsorption isotherm of the p-Anisidine and poly(p-Anisidine) has been found that the inhibitors obey Languimer's isotherm.

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] In acidic
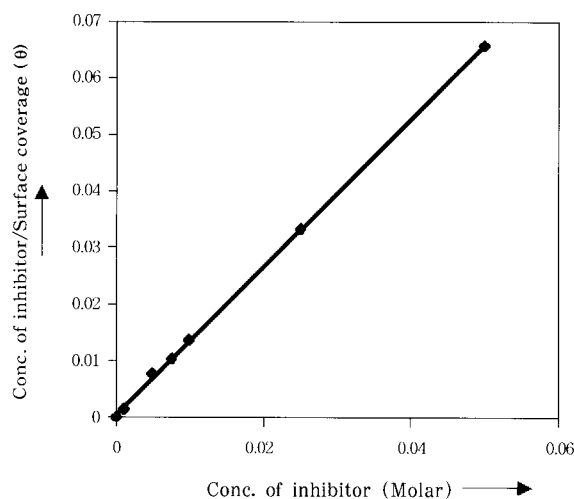
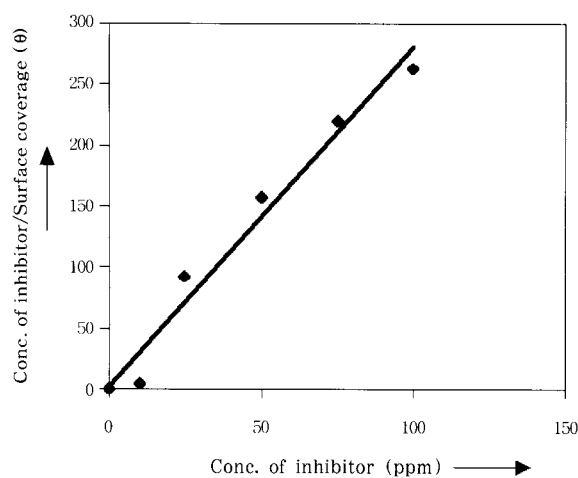**Fig. 5.** Langmuir's Isotherm Plot for p-Anisidine

Fig. 6. Langmuir's Isotherm Plot for Poly(p-Anisidine)

solutions they predominantly exist as cations and adsorb through electrostatic interaction between the positively charged anilinium cation and negatively charged metal surface. The stronger adsorption of the p-Anisidine molecules with the metal surface is usually through the already adsorbed chloride ions, which will interfere with the adsorption of p-Anisidine molecules. The inhibitive effect of aniline is mainly due to the delocalization of lone pair electrons of nitrogen atom by inductive effect.[9] In the case of p-Anisidine the higher inhibition efficiency may be due to increased electron density on nitrogen atom or phenyl ring. The presence of -OCH3 group may increase the electron density on the phenyl ring, due to the inductive effect. The inhibition action of organic inhibitors increased with the increase of electron density[9] at the nitrogen atom

constituting the reaction centre for pyridine and its derivative.[10] The inhibitive properties of organic compounds depend on the electron densities around the chemisorptions centre; the higher the electron density the more effect is inhibitor.[11,12]

For the polymer amines, earlier studies showed that, the inhibitive properties of substituted poly aniline for mild steel in acid chloride solutions[5,6] as well as in sulphuric acid solutions are very effective, due to the presence of (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.

The inhibitive property of poly (p-Anisidine)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 (i) a neutral molecule via chemisorption mechanism[5] involving the sharing of electrons between nitrogen and iron atoms (or), (ii) the adsorption occurs through π electrons interaction with the metal surface.

4. Conclusions

(1) The inhibition efficiency for both monomer and polymer of p-Anisidine increases with increase in concentrations.

(2) Poly (p-Anisidine) has shown a remarkable performance of inhibition efficiency for iron
in 1M HCl solutions when compared with its monomer.

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

(4) The adsorption of both monomer and polymer of p-Anisidine on iron surface in 1M HCl obey Langmuir's adsorption isotherm.

References

1. Y. Wei., J. M. Yeh., H. Wang., X. Jia., C. Yang., and D. Jin., *Polymer Mater. Sci. Eng.*, **74**, 202 (1996),
2. S. Jasty. and A. J. Epstein., *Polymer Mater. Sci. Eng.*, **72**, 565, (1995).
3. T. Grehev., M. Cvetovska., and J. W. Schultze., *Corr. Sci.*, **32**(1), 103 (1991).
4. S. Sathyanarayanan., S. K. Dhawan., D. C. Trivedi., and K. Balakrishnan., *Corr. Sci.*, **33**, 1831 (1992).
5. S. Sathyanarayanan., K. Balakrishnan., S. K. Dhawan., and D. C. Trivedi., *Electrochim. Acta*, **39**, 831 (1994).
6. P. Manivel. and G. Venkatachari., 'Inhibition of Corrosion iron in 1M HCl by Poly p-Phenylene diamine' , Presented in Twelfth National Corrosion Congress of India, held

at Vishakapatinum, India, 20-22, Sept.2004.

7. C. A. Mann., *Trans Electrochem*, **69**, 105 (1936).

8. C. Jeyaprabha, 'Ph.D., Thesis', Bharathidasan University, (2001).

9. B. Ramesh Babu. and R. Holze., *British Corros. J.*, **35**, 204 (2000).

10. R. C. Ayers. and N. Hackerman., *J. Electrochem. Soc.*, **119**, 146 (1972).

11. F. Bentiss., M. Traisnel., and M. Lagrnee., *J. Applied Electrochem.*, **31**, 41 (2001).

12. G. Moretti., G. Quartarone., A. Tassan., and A. Zingales, *Werkst, Korros.*, **45**, 641 (1994).