Poly (orthomethoxyaniline) as Corrosion Inhibitor for Carbon Steel in 1N HCl Medium

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Abstract

Poly(o-methoxyaniline) doped with phenylphosphonic acid (POMA-PPA) has been prepared by chemical polymerization method. It was then characterized by UV-Visible and IR spectroscopic methods. The corrosion inhibiting effect of POMA-PPA was studied for carbon steel in 1N acid chloride medium by weight loss, potentiodynamic polarization and electrochemical impedance methods. It was found that 100 ppm of doped polymer offers nearly 82-87% inhibition efficiency (IE) to carbon steel immersed in 1N HCl medium. Polarization study reveals that both monomer and doped polymer are of mixed type inhibitor.

Keywords: carbon steel, poly(o-methoxyaniline), conducting polymers, corrosion inhibition.

Introduction

Corrosion is a common phenomenon associated with almost all the metals except noble metals and is particularly severe in the case of iron that forces the many industries to invest more for the control of corrosion by various techniques. The use of inhibitors for corrosion control is the most common method. Recently, it has been shown that conducting polymers, when deposited onto the surface of corrosion – susceptible materials can inhibit corrosion [1, 2]. Although it has been known for several decades, aniline polymerization has recently a great deal of attention because aniline-based polymers constitute one of the most complex and thoroughly studied families in the area of conducting polymers [3-7]. Among the conducing polymers, those derived from aniline and its derivatives have been predicted to be the futuristic materials because of their greater environmental stability, highly favourable economics, easy synthesis and simple non-redox doping by protonic acids. During doping all the hetero atoms in polymer, namely nitrogen, become protonated. This protonated form is electronically conducting and the magnitude of increase in conductivity is a function of level of protonation as well as functionalities present in the dopant. The functional group present in the doping acid, its structure and orientation play an important role in the solubility of a conducting form of polyaniline or for obtaining aqueous dispersion and compatibility with other polymers [8-15]. The alkoxy group attached to the aniline ring helps in achieving solubilization of the resultant polymer in common organic solvents like ethanol, methanol, acetone etc [16]. There are reports that the corrosion performance of coatings with the conducting polyaniline is not as good as that of non-conducting polyaniline[17,18].

The present work is undertaken

- To synthesis the Poly(o-methoxyaniline) (doped polymer) using phenylphosphonic acid by chemical polymerization method.
- To characterize the synthesized doped polymer by FTIR spectra and UV-visible study.
- To study the corrosion inhibition efficiency of the monomer (omethoxyaniline) and doped polymer for carbon steel in 1N HCl solution.
- To compare the Inhibition efficiency of monomer and doped polymer.

Experimental

Chemical Synthesis of Doped Polymer (Poma-Ppa)

Ice cooled 0.1M aqueous solution of ammonium peroxydisulphate is added dropwise to a stirred ice cold 0.1M solution of o-methoxyaniline dissolved in 1M aqueous phenylphosphonic acid pre-cooled to 0-5°C. Ammonium peroxydisulphate solution is added very slowly to prevent the warming of the solution. After completion of the addition (30 minutes), stirring is continued for 2 hours to ensure completion of the reaction. The precipitated POMA-PPA (doped polymer) is filtered and washed repeatedly with distilled water until the filtrate is colourless. Finally the doped polymer is transferred to a beaker containing 1M aqueous solution of a phenylphosphonic acid. After keeping overnight, the precipitates are filtered and dried at 80°C under reduced pressure until it shows constant weight.

Characterization of poly(o-methoxyaniline)

Characterization of poly(o-methoxyaniline) was carried out after thorough washing with distilled water and drying under dynamic vacuum for 8 h at 70°C. The following methods were used for the characterization.

Electronic spectra

The absorption spectra of the solution was recorded using Hitachi-U-3400 UV-Vis near -IR spectrophotometer in the range of 250 to 1200 nm.

Infrared spectra

Infrared spectra in KBr pellets were recorded in the 4000 to 400 cm⁻¹ range on a Toshniwal-Simadzu FT-IR spectrophotometer 8000 series.

Preparation of specimens

The carbon steel specimens were chosen from the same sheet of the following composition 0.15 % C, 0.026 %S, 0.06 %P, 0.4 %Mn and the rest being Fe. Carbon steel specimen of the dimensions 1.0 x 4.0 x 0.2 cm were polished to mirror finish using emery sheets, (No. 0/2 and 0/3) washed with double distilled water, degreased with trichloroethylene, dried and were used for weight-loss and electrochemical studies.

Weight loss method

Three carbon steel specimens were suspended by means of glass hooks in 100 ml beakers containing 100 ml of various test solutions and after 2 hours of immersion, the specimens were taken out, washed in running water, dried and weighed. From the change in weights of the specimen, corrosion inhibition efficiency (IE) were calculated using the following relationship

I.E. = $100 [1 - (W_2/W_1)] \%$

Where

 W_1 = Loss of weight in the absence of the inhibitor.

 W_2 = Loss of weight in the presence of the inhibitor.

Potentiodynamic Polarization Study

Potentiodynamic polarization studies were carried out using CHI electro chemical Impedance analyzer, Model 660 A. A conventional three electrode cell assembly was used. The working electrode was a rectangular specimen of carbon steel with one face of exposed area 1 cm² and the another is shielded with red lacquer. A saturated calomel electrode (SCE) was used as the reference electrode and a rectangular platinum foil was used as the counter electrode. The experiments were carried out over a potential range of -200 mV to +1500 mV with respect to open circuit potential at a scan rate of 1 mVsec⁻¹. The working electrode and platinum electrode were immersed in test solution in the absence and presence of inhibitor. Saturated Calomel Electrode was connected with the test solution through a salt bridge. Tafel plots were then recorded. Corrosion potential (E_{corr}) and Tafel slopes b_a and b_c were determined from these plots. The inhibition efficiency was obtained from the equation

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

 I_{corr} = Corrosion current in the absence of inhibitor. $I_{corr(i)}$ = Corrosion current in the presence of inhibitor.

AC impedance measurements

The instrument used for polarization was also used for AC impedance study. The cell set up was the same as that used for polarization measurements. The AC sine wave potential with an amplitude of 10 mV was imposed on open circuit in the frequency range 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 inhibition efficiencies were obtained from R_{ct} values as follows

I.E. =
$$\frac{R_{ct(i)} - R_{ct}}{R_{ct(i)}} \times 100$$

 R_{ct} = Charge transfer resistance in the absence of inhibitor. $R_{ct(i)}$ = Charge transfer resistance in the presence of inhibitor.

Results and Discussion

Spectral characterisation

UV-Vis-NIR spectroscopic studies

The electronic spectra of POMA-PPA chemically synthesized in DMSO and ethanol are shown by curves a and b in Fig.1. A DMSO solution of chemically synthesized POMA-PPA shows absorption peaks at 335 and 602 nm, whereas an ethanol solution of chemically synthesized POMA-PPA shows absorption peaks at 326 and 581 nm. The absorption peaks observed at 326 nm to 335 nm are due to $\pi - \pi$ * transition associated with benzenoid ring. The peaks due to cation radicals lies at 581 nm to 602 nm. [19-22].



Figure 1: UV – Vis – NIR solution absorption spectra of POMA-PPA in a) C_2H_5OH b) DMSO

FT-IR Spectroscopic Studies

Infrared spectroscopy is a powerful tool to determine the structural changes that occur during doping process. It has been shown that the absorption frequencies are strongly influenced by the dopant [23-25]. The principle absorption bands observed in the FT-IR spectra in the region of 4000 - 400 cm⁻¹ for POMA doped with PPA are presented in Fig. 2.

The band observed at 847.1 cm⁻¹ for POMA-PPA (doped polymer) indicates head to tail coupling in the polymer i.e. the monomeric units are linked at 1,4 positions. The absorption band at 1120.3 cm⁻¹ observed for chemically synthesiszed phosphonic acid doped POMA is due to the charge delocalization on the polymer backbone. The band observed at 1027.3 cm⁻¹ in the doped polymer is due to symmetric stretching of PO4⁻³ group present in the dopant. The bands observed at 1459.9 is due to the characteristics of Nitrogen benzenoid band. The Nitrogen quinonoid band was observed at 1585.7 cm⁻¹. The aromatic C-H stretching was observed at 2926.9 cm⁻¹ for doped polymer. The N-H stretching was observed at 3415 cm⁻¹.



Figure 2: FT - IR spectra of POMA-PPA in the region 4000 cm⁻¹ to 400 cm⁻¹ in KBr medium.

Corrosion inhibition by o-methoxyaniline Analysis of the results of the weight-loss method

The calculated inhibition efficiencies (IE) of o-methoxyaniline in controlling the corrosion of carbon steel immersed in 1N HCl have been tabulated in Table 1. From table 1, it has been observed that, the inhibition efficiency values increase from 11% to 80% with increase in inhibitor concentration. The maximum inhibition efficiency of 80% was observed at 20000 ppm of o-methoxyaniline.

Concentration of	Weight Loss	IE
monomer (ppm)	(gm / h)	(%)
1N HCl	0.0066	-
100	0.0059	11
1000	0.0058	12
5000	0.0046	30
10000	0.0024	64
20000	0.0013	80

Table 1: Corrosion inhibition efficiencies evaluated by weight loss method

Analysis of the Results of Potentiodynamic Polarization Studies

The polarization behaviour of carbon steel in 1N HCl with the addition of various concentrations of o-methoxyaniline in the Tafel region is shown in Fig.3. The corrosion kinetic parameters derived from these curves are given in Table 2. From this table, it is found that the addition of o-methoxyaniline in the concentration range 100 ppm to 20000 ppm decreases the dissolution rate of carbon steel in 1N HCl. The corrosion current value (i_{corr}) is decreased from 560 μ Acm⁻² (for blank) to 78 μ Acm⁻² at 20000 ppm o-methoxyaniline. The maximum efficiency of 86% is obtained at 20000 ppm o-methoxyaniline. It is clear from the tafel plots that the cathodic and anodic polarizations increase with the addition of inhibitor suggesting mixed type of control.

Table 2: Corrosion inhibition efficiencies evaluated by Tafel polarization method.

Concentration of	E _{corr}	I _{corr}	ba	bc	IE (%)
monomer (ppm)	mV SCE	µAcm ⁻²	mVdec ⁻¹	mVdec ⁻¹	
1N HCl	-517	560	46	112	-
100	-513	487	47	110	13
1000	-507	403	49	114	28
5000	-507	296	53	119	47
10000	-508	174	61	113	69
20000	-509	78	75	109	86



Figure 3: Polarization curves for carbon steel in 1N HCl with different concentration of o-methoxyaniline a) 100 ppm b) 1000 ppm c) 5000 ppm d) 10000 ppm e) 20000 ppm.

Analysis of the results of AC impedance studies

The Nyquist representation of the Impedance behaviour of carbon steel in 1N HCl with and without the addition of various concentrations of o-methoxyaniline is shown in Fig.4. The AC Impedance parameters namely charge transfer resistance and the double layer capacitance are given in Table 3. From table 3, it has been observed that the charge transfer resistance (R_{ct}) value increases from 33 Ωcm^2 to 165 Ωcm^2 , with subsequent decrease in C_{dl} value from 971 μFcm^{-2} to 188 μFcm^{-2} showing the good coverage of carbon steel surface by the monomer.

Concentration of	R _{ct}	C _{dl}	Surface	IE (%)
monomer (ppm)	$\Omega \text{ cm}^2$	µFcm ⁻²	coverage θ	
1N HCl	33	971	-	-
100	35	920	0.0521	5
1000	38	841	0.1334	13
5000	53	607	0.3751	38
10000	118	271	0.7210	72
20000	165	188	0.8062	80

Table 3: Corrosion inhibition efficiencies evaluated by AC impedance spectroscopy



Figure 4: Nyquist plot for carbon steel in 1N HCl with different concentration of omethoxyaniline a) 100 ppm b) 1000 ppm c) 5000 ppmd) 10000 ppm e) 20000 ppm.

Corrosion inhibition by POMA-PPA

Analysis of the results of the weight-loss method

The calculated inhibition efficiencies (IE) of poly(o-methoxyaniline) doped with PPA in controlling the corrosion of carbon steel immersed in 1N HCl, both in the absence and presence of inhibitor have been tabulated in Table 4. The calculated values indicate the ability of POMA-PPA to be a good corrosion inhibitor. The inhibition efficiency is found to be enhanced in the presence of inhibitor. From Table 4, it has been observed that the inhibition efficiency (I.E.) value increases from 50% to 82% with increase in inhibitor concentration. The maximum inhibition efficiency of 82% is observed at 100 ppm of POMA – PPA.

Concentration of	Weight Loss	IE (%)
POMA-PPA (ppm)	(gm / h)	
1N HCl	0.0066	-
10	0.0033	50
25	0.0025	62
50	0.0020	70
75	0.0017	74
100	0.0012	82

Table 4: Corrosion inhibition efficiencies evaluated by weight loss method

Analysis of The Results of Potentiodynamic Polarization Studies

The potentiodynamic polarization curves of carbon steel immersed in 1N HCl in the presence and absence of POMA-PPA are given in Fig.5. The corrosion parameters of

carbon steel immersed in 1N HCl in the presence and absence of inhibitor are given in Table. 5. From table 5, it is observed that, the corrosion current (i_{corr}) value decreases from 560 μ Acm⁻² to 73 μ Acm⁻² with increase in POMA-PPA concentration and the highest inhibition efficiency of 87% was observed at 100ppm of poly(o-methoxyanline) doped with PPA. The Tafel constants b_a and b_c are in the range of 46-68 mVdec⁻¹ and 112-114 mVdec⁻¹ respectively. The addition of POMA-PPA does not change the values of open circuit potentials and the values of b_a and b_c indicate the corrosion process involved is under mixed control and the addition of inhibitor does not modify the charge transfer mechanism.

Table 5: Corrosion inhibition efficiencies evaluated by Tafel polarization method

Concentration of	Ecorr	I _{corr}	b _a	b _c	IE (%)
POMA-PPA (ppm)	mV SCE	µAcm ⁻²	mVdec ⁻¹	mVdec ⁻¹	
1N HCl	-517	560	46	112	-
10	-500	213	56	110	62
25	-510	162	50	107	71
50	-511	84	57	120	85
75	-507	73	64	119	87
100	-498	73	68	114	87



Figure 5: Polarization curves for carbon steel in 1N HCl with different concentration of POMA-PPA a) 10 ppm b) 25 ppm c)50 ppm d)75 ppm e) 100ppm

Analysis of the results of AC impedance studies

The AC Impedance spectra of carbon steel immersed in 1N HCl in the presence and absence of POMA-PPA are given in Fig.6. The AC Impedance parameters of carbon

steel immersed in 1N HCl in the presence and absence of inhibitor are given in Table. 6.

The charge transfer resistance (R_{ct}) value increases from 33 Ωcm^2 for free solution (Blank) to 236 Ωcm^2 with the addition of 100 ppm of POMA-PPA resulting in 86% inhibition efficiency. The double layer capacitance (C_{dl}) is decreased from 971 μ Fcm² to 139 μ Fcm² for 100 ppm of POMA-PPA concentration. Decrease in the C_{dl} is due to a decrease in local dielectric constant and or an increase in the thickness of the electrical double layer[26]. This confirms that a protective film is formed on the carbon steel surface.

 Table 6: Corrosion inhibition efficiencies evaluated by AC impedance spectroscopy

Concentration of	R _{ct}	C_{dl}	Surface coverage θ	IE (%)
POMA-PPA(ppm)	$\Omega \text{ cm}^2$	µFcm ⁻²	6	
1N HCl	33	971	-	-
10	79	412	0.5762	58
25	110	288	0.7037	70
50	174	182	0.8121	81
75	206	153	0.8424	84
100	236	139	0 8570	86



Figure 6: Nyquist plot for carbon steel in 1N HCl with different concentration of POMA-PPA a) 10 ppm b) 25 ppm c)50 ppm d)75 ppm e) 100ppm

Conclusion

- The following important conclusions have been arrived in the present study.
- The obtained results show the synthesized doped polymer can act as good inhibitor for the corrosion of carbon steel in 1N HCl solution.

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- Doped polymer was found to be effective corrosion inhibitor for carbon steel in 1N HCl when compared with monomer. It shows maximum inhibition efficiency of 87 % even at very low concentration of 100 ppm.
- Polarization study reveals that both monomer and doped polymer are of mixed type.
- AC impedance spectra reveal that a protective film is formed on the carbon steel surface.

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