Polyethelene Glycol-Anthranilic Acid Composite as Corrosion Inhibitor for Mild Steel in Acid Medium

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Abstract: The polymer PGA composite was prepared by chemical oxidative method of polyethylene glycol, anthranilic acid with ammonium persulphate in oxalic acid medium. The resulted polymer was characterized by FTIR spectroscopy. The performance of the polymer polyglycol anthranilic acid composite (PGA) as corrosion inhibitor for mild steel in 1 M HCl has been studied by weight loss, potentiodynamic and impedance spectroscopy methods. The maximum IE was found to be 97%. Experimental results were fitted to Langmuir adsorption isotherm. Electrochemical studies confirmed the inhibitive nature of the PGA composite and also the mixed nature of the inhibitor. The polymer is found to be highly efficient non-toxic and environmentally safe.

Keywords: PGA, HCl, Mild steel, Corrosion.

Introduction

Corrosion of metals in different environment is one of the serious problems facing the industries and its prevention has been approached from various angles like surface coating, plating and alloying. Technological and financial considerations may sometimes favour the addition of inhibitors to reduce the corrosion rate. Inhibition of corrosion of mild steel is a matter of theoretical as well as practical importance¹. Compounds containing nitrogen, sulphur and oxygen have been reported as inhibitors²⁻⁶. The most efficient organic inhibitors are organic compounds having unsaturated bonds in their structures⁷. Most of the conducting polymers have extensively delocalized π electrons, in abundance, should enable them to be good corrosion inhibitors. The adsorption of these compounds is influenced by various factors *viz.* (i) electronic structure of inhibiting molecules, (ii) steric factor, (iii) aromaticity, (iv) electron density at donor site, (v) presence of functional group such as $-\text{CHO}$, $-\text{N}=\text{N}$, $\text{R}-\text{OH}$ in the inhibitor molecule, (vi) molecular area and (vii) molecular weight of the inhibitor molecule⁸⁻¹².

Conducting polymers are becoming the most promising new materials for next generation electrical and electronic devices^{13,14}. These polymers have also been recognized as excellent corrosion inhibitors for metals in acid environment¹⁵⁻²⁰. Recently polymer amines^{21,22} were evaluated due to their higher inhibition efficiency on the corrosion of mild steel in acid solutions. Owing to the multiple adsorption sites, polymeric compounds adsorb more strongly on the metal surface compared with their monomer analogues²³. Polyaniline and its derivatives have versatile applications in plastic batteries, harmonic generators, display devices, solid state sensors and corrosion inhibitors²⁴⁻²⁶. Polyaniline and its derivatives are key effective corrosion inhibitors in acid chloride solution due to the presence of π electrons, quaternary nitrogen atom and large molecular size, which ensures greater coverage of the metallic surface, which leads to higher inhibition efficiency.

A study was undertaken with polyethelene glycol-anthranilic acid composite as an inhibitor for mild steel in acidic aqueous solution. The inhibition efficiency was estimated by Tafel extrapolation method, linear polarization resistance method, impedance spectroscopy and direct weight loss method. Before use, the characterization of polymer composite was carried out by recording FTIR spectrum.

Experimental

The polymer PGA composite was synthesized as described by Rupali Gangopadhyay *et.al*²⁷. The infrared spectra of the polymer was recorded on a Perkin Elmer FTIR. The evaluation of this polymer as corrosion inhibitor was carried by electrochemical techniques and direct weight loss method. Weight loss experiments were carried out in triplicate by using $1 \times 5 \text{ cm}^2$ mild steel strips for duration of $\frac{1}{2}$ h, 3 h, 6 h, 12 h and 24 h at 303K, 313K, 323K and 343K.

For electrochemical studies a three electrode cell with 1 cm^2 mild steel as working electrode, a saturated calomel electrode (SCE) as the reference electrode and platinum foil as the counter electrode was used. The working electrode was polished before use. Before starting the electrochemical experiments the test sample was allowed to reach steady state after immersion in the solution.

Impedance studies were performed for the mild steel in 1 M HCl at $26 \pm 2^\circ \text{C}$ in the absence and presence of polymer composite PGA at E_{corr} with the a.c.voltage amplitude 10 mV in the frequency range 10 KHz to 10 MHz. A time interval of a few minutes was given for the o.c.p to read a steady value.

Results and Discussion

Effect of concentration and immersion time

Weight loss experiments showed the effective action of the polymer composite as corrosion inhibitor of MS in HCl solution. Values of IE of different concentration of the polymer for all test durations are given in Table 1. IE increased with increase in concentration of the polymer and maximum IE was noticed with 1.7% concentration. The IE increased with increase in immersion time up to 12 h, showing decrease at 24 h.

The inhibition of corrosion by the polymer in 1 M HCl may be due to the adsorption of polymer molecules on the metal surface thus preventing the dissolution of iron. An increase in number of additive molecules the blockage of active sites on the metal surface increases. Consequently the inhibition increased. It may be assumed that due to greater rate of adsorption during the first few hours of immersion the IE enhanced with time.

Table 1. Inhibition efficiency as a function of immersion time and concentration

Conc, %	IE, %					
	0.5 h	1 h	3 h	6 h	12 h	24 h
0.1	32.1	39.5	25.8	21.6	40.4	15.1
0.3	32.7	48.9	41.2	43.1	56.1	43.5
0.5	50.3	53.7	51.8	55.9	69.7	68.2
0.7	57.3	69.2	56.1	59.3	74.1	85.9
0.9	61.7	72.1	65.8	61.3	76.5	92.1
1.3	65.7	80.2	68.1	67.1	79.5	96.1
1.7	67.3	81.4	97.1	86.7	86.4	96.8
1.9	68.1	82.5	96.1	86.6	78.1	92.8

Influence of temperature

The loss in the weight of steel samples in 1 M HCl in the absence and presence of various concentrations of PGA composite at different temperatures were determined. The effect of temperature on the inhibition efficiency of the polymer is shown in Table 2. In all cases, increase in PGA composite concentration leads to a decrease in the corrosion rate of samples indicating that the presence of polymer composite retards the general corrosion of samples in 1 M HCl.

On the other hand, an increase in temperature from 333-343 K resulted in an increase in the corrosion rate for all polymer composite solution, probably as a result of desorption of inhibitor molecules from the metal surface.

Table 2. Variation of PGA at different temperature

S.No	Conc, %	Temperature, K									
		303		313		323		333		343	
		CR	IE, %	CR	IE, %	CR	IE, %	CR	IE, %	CR	IE, %
1	0.1	1115.53	32.1	929.8	41.6	518	21.6	5816.8	13.3	9119.6	11.9
2	0.3	1104.19	32.7	853.9	46.3	398	46.5	4826.7	28.1	7905.5	23.5
3	0.5	816.37	50.3	770.1	51.6	136	52.4	4232.7	36.9	8285.8	23.6
4	0.7	701.24	57.3	705.6	55.7	963	56.2	3584.7	46.6	7782.6	24.8
5	0.9	627.1	61.7	630.6	57.6	849	58.8	3530.6	47.3	66503.9	37.1
6	1.3	563.43	65.7	613.2	61.5	580	64.8	2665.4	60.3	6294.6	39.1
7	1.7	536.39	67.3	553.8	65.2	356	69.8	2599	61.2	6269.3	39.4
8	1.9	525.93	68.1	498.9	68.6	18.1	81.8	1721.7	74.3	4456	57.9

Adsorption isotherm

The phenomenon of interaction between the metal surface and inhibitor can be better understood in terms of adsorption isotherm. A plot of $\log \theta / (1 - \theta)$ Vs. $\log C$ Figure 1 gave a straight line with approximately unit slope indicating that the inhibitor under study obeys Langmuir adsorption isotherm. The deviation from unity may be explained on the basis of the interaction between the adsorbed species on the metal surface. It has been postulated in the derivation of Langmuir isotherm equation that the adsorption molecules do not interact with each other. This is not true in case of organic or polymer molecules having polar atoms or groups which are adsorbed on the anodic and cathodic sites of the metal surface. Such adsorbed species may interact by mutual repulsion or attraction²⁸.

Figure 1. Langmuir adsorption Isotherm

The regression co-efficients were calculated for Langmuir adsorption isotherm. The values of R^2 generally lie between 0 and 1. The closer the value of R^2 lies to 1, the better the regression line to data. The R^2 values were significant at one percent level.

Activation energy (E_a)

Corrosion rate of mild steel in presence of PGA composite by weight loss method are plotted against temp ($\log CR$ vs. $1/T$). Activation energies are calculated from the slope. It was observed for HCl solution the E_a as 44.128 kJ/mole. In the presence of the inhibitor the activation energies are increased compared to the acid solution revealing the retardation of the corrosion reaction. The marked changes in E_a suggest that the inhibitor may either participate in the electrode or may change the potential difference of the metal solution interface by adsorption.

Thermodynamic parameters

Free energy change

The values of free energy of adsorption (ΔG) were calculated using the standard equation

$$\log C = \log \frac{\theta}{(1-\theta)} - \log B$$

$$\text{where, } \log B = -1.74 - (-\Delta G / 2.303 RT)$$

θ = Surface coverage

C = Concentration

R = Gas Constant

T = Temperature

The calculated free energy of adsorption (Table 3) ranged between -27.5 kJ to -21.8 kJ. The negative free energy values indicate the spontaneous adsorption of inhibitor and the strong interaction between the metal surface and the inhibitor molecule. The increase in $-\Delta G$ with increasing concentration is an evidence for repulsive forces in the adsorption layer. Similar observations have been reported by Lillard R.S. *et al*²⁹.

The values of $-\Delta G_{\text{ads}} \leq 20 \text{ kJ mol}^{-1}$ are consistent with electrostatic interaction between the charged molecules and the charged metal surface. This is substantiated by the observation reported by Khamis *et.al* (1991)³⁰.

Table 3. Thermodynamic and kinetic parameters for adsorption of PGA on MS surface

Conc, %	Ea, kJ/mol	- ΔG , kJ/mol				ΔH , kJ/mol	ΔS , kJ/mol
		313K	323K	333K	343K		
0.1	51.990	27.5499	25.8787	25.0585	25.4481	-49.3566	0.071258
0.3	48.6277	25.1875	26.0138	24.6059	24.6581	-34.9435	0.029961
0.5	54.4282	24.4105	25.2765	24.3073	23.2169	-39.2259	0.045497
0.7	55.2966	23.9641	24.7842	24.4841	22.4439	-39.8628	0.048609
0.9	55.0532	23.5114	24.3951	23.866	23.3853	-26.7658	0.009074
1.3	54.0653	22.976	24.0911	24.3045	22.5784	-26.6998	0.009794
1.7	55.4177	22.6928	23.9817	23.6662	21.8491	-32.384	0.009794
1.9	46.995	22.8032	25.4693	25.036	23.6687	-17.1484	-0.02163

Heat of adsorption

The change in heat of adsorption ΔH and change in Entropy ΔS can be calculated using Gibbs Helmholtz equation

$$\Delta G = \Delta H - T\Delta S$$

A plot of ΔG versus T will be a straight line with intercept ΔH and slope ΔS . All the obtained values of ΔH and ΔS for the inhibitor adsorption on the mild steel surface were listed in Table 3.

The negative values indicated the exothermic adsorption behavior of the inhibitor at the experimental temperatures studied. The average value of ΔH is about 33.29 kJ/mol which is larger than common physical adsorption heat but smaller than the common chemical adsorption heat³¹ probably meaning comprehensive adsorption (physical and chemical). That is to say, since the adsorption heat approached the general chemical reaction heat, the chemical adsorption might occur accompanied by physical adsorption (electrostatic interaction)³².

Entropy change

When adsorption increases the entropy will decrease. For an exothermic adsorption process also the entropy will decrease. The decrease in positive value of ΔS with increase in concentration of the inhibitor (Table 3) proved the exothermic adsorption of the inhibitor on the metal surface.

Electrochemical measurements*Polarization studies*

Typical potentiodynamic polarizing curve showing the inhibitive action of PGA is given in Figure 2. The corrosion parameters calculated from the polarization curves are tabulated in Table 4. I_{corr} was found to decrease as the inhibitive action of PGA composite on metal surface. The E_{corr} values and observation of curve infers that there is change in both anodic and cathodic polarization with the addition of inhibitor. This indicates that the inhibitor acts through mixed mode of inhibition. The decrease in both Tafel constants b_a and b_c value of concentration with increase in concentration of the inhibitor up to 0.5%, suggest that both anodic dissolution and cathodic hydrogen evolution mechanism are affected in presence of the inhibitor. It can be concluded from the results obtained that PGA act as a mixed inhibitor. In addition, no significant change in E_{corr} value was observed, which suggests a mixed type of inhibition effect of polymer³³.

Figure 2. Polarization curve of MS in presence of PGA in 0.1 M HCl

Table 4. Electrochemical and corrosion parameters for MS in the presence of PGA in 1 M HCl

Conc, %	E_{corr} Amp/cm)	I_{corr}^* 10^{-4}	Ba, mV	Ba(mV)	IE%	R_p (ohm/cm)	IE%
Blank	522	54.7	265	190	-	4.77	-
0.1	517	48.9	202	183	10.6	5.33	10.5
0.3	519	47.9	192	180	12.4	5.43	12.2
0.5	512	34.6	151	156	36.7	7.53	36.7
0.7	513	30.3	154	162	44.6	8.60	44.5
0.9	501	14.7	126	117	73.1	17.6	72.9

Impedance studies

The inhibitive action is enhanced by the protective barrier on the metal surface which is indicated from the increase of R_{ct} values with increase in inhibitor concentration. The existence of single semi circle showed the single charge transfer process during dissolution which is unaffected by the presence of inhibitor molecules. The decrease in C_{dl} values for higher concentrations is attributed to increase in thickness of electronic double layer³⁴. The increase in R_{ct} value is attributed to the formation of protective film on the metal/solution interface^{35,36}. The charge transfer resistance (R_{ct}) and the interfacial double layer capacitance (C_{dl}) derived from these curves are given in Table 5.

Table 5. Electrochemical and Impedance parameters of MS in the presence of PGA

Conc, ppm	R_{ct} , ohm cm	IE, %	$C_{dl} \times 10^{-4}$, $\mu F/cm$
Blank	14.79	-	3.43
0.1	17.43	15.2	4.10
0.3	22.04	32.9	4.32
0.5	40.46	63.5	2.33
0.7	43.74	66.1	2.99
0.9	72.32	78.5	1.18

The probable mechanism is adsorption of the active species on the metal surface is revealed from the Cdl values which were found to decrease with increase in concentration of PGA. The depressed semicircle in Nyquist plot Figure 3 indicates that adsorption of the inhibitor molecule is charge transfer controlled. Maximum IE using Rct values was found to be 78.5% with 1.9% of concentration.

Figure 3. Nyquist Plot of MS in presence of PGA

Mechanism of Inhibition process

The mechanism of corrosion inhibition may be explained on the basis of adsorption behaviour³⁷. The inhibitive behaviour of self doped polyethelene glycol anthranilic acid (*ortho* carboxylated polyethelene glycol aniline) is reported for the first time.

Corrosion inhibition of mild steel in hydrochloric acid solution by polyanthranilic acid had been explained on the basis of molecular adsorption. The compound inhibits corrosion by controlling both the anodic and cathodic reactions. In acidic solution the polyglycol anthranilic acid exists as protonated species. These protonated species adsorb on the cathodic sites of the mild steel and decrease the evolution of hydrogen. The adsorption on anodic sites occurs through long π electrons of aromatic rings (benzenoid and quinoid) and lone pair of electrons of nitrogen atoms, which decreases anodic dissolution of mild steel³⁸. The high performance of the polymer is attributed to the presence of long π -electrons conjugation, quaternary nitrogen atom and the larger molecular size.

Conclusion

The PGA was proved to be a good inhibitor for MS in 1 M HCl. The IE increase with inhibitor concentration, time and temperature. It obeys Langmuir adsorption isotherm. Kinetic and thermodynamic parameters infer the strong adsorption of inhibitor molecule on MS surface also the inhibition is by spontaneous physical adsorption of inhibitor on MS surface. Electrochemical measurements indicate the mixed mode of inhibition. Thus the polymer PGA inhibitor was proved to be an effective eco friendly inhibitor.

References

1. Ali S A, Saeed M T and Rahman S V, *Corros Sci.*, 2003, **45**, 253-266.
2. Lagrenée M, Mernari B, Bouanis M, Traisnel M and Bentiss F, *Corros Sci.*, 2002, **44**, 573-588.
3. Quraishi M A and Sardar R, *Corrosion*, 2002, **58**, 747-756.
4. Quraishi M A, Athar M and Ali H, *Brit Corros J.*, 2002, **37**, 155-158.
5. Quraishi M A and Ansari F A, *J Appl Electrochem.*, 2003, **33(3-4)**, 233-238.
6. Quraishi M A and Khan S, *J Appl Electrochem.*, 2006, **36**, 539-544.
7. Schmitt G, *Brit Corros J.*, 1984, **19**, 165-176.
8. Bentiss F, Lagrenée M, Traisnel M and Hornez J C, *Corros Sci.*, 1999, **41**, 789-803.
9. McCaerty E, Pravdic V and Zettlemoyer A C, *Trans Faraday Soc.*, 1999, **66**, 237.
10. Growcock F B, Frenier W W and Andrezzi P A, *Corrosion*, 1989, **45**, 1007.
11. Lukovits L, Kalman E and Palinkas G, *Corrosion*, 1995, **51**, 201.
12. Ayers Jr R C and Hackerman N, *J Electrochem Soc.*, 1963, **110(6)**, 507-513.
13. Skotheim T A, Elsenbaumer R L and Reynolds J R, *Handbook of Conducting Polymer*, Second Ed., Marcel Dekker Inc., New York, 1998.
14. Wang H L, MacDiarmid A G, Wang Y Z, D D Gebier and Epstein A J, *Synth Met.*, 1996, **78**, 33.
15. Rohwerder M and Michalik A, *Electrochim Acta*, 2007, **53**, 1300-1313.
16. Riaz U, Ashraf S M and Ahmad S, *Prog Org Coat.*, 2007, **59(2)**, 138-145.
17. Jeyaprabha C, Sathiyarayanan S and Venkatachari G, *Appl Surf Sci.*, 2006, **253**, 432-438.
18. De Souza S, *Surf Coat Technol.*, 2007, **201**, 7574-7581.
19. Armelin E, Oliver R, Liesa F, Iribarren J I, Estrany F and Alemán C, *Prog Org Coat.*, 2007, **59**, 46-52.
20. da Silva J E P, de Torresi S I C and Torresi R M, *Prog Org Coat.*, 2007, **58**, 33-39.
21. Kusch P, Knupp G, Hergarten M, Kozupa M and Majchrzak M, *Int J Mass Spectrom.*, 2007, **263(1)**, 45-53.
22. Alsabagh A M, Migahed M A and Awad H S, *Corros Sci.*, 2006, **48**, 813-828.
23. Ali S A and Saeed M T, Synthesis and corrosion inhibition study of some 1,6-hexanediamine-based *N,N*-diallyl quaternary ammonium salts and their polymers, *Polymer* 2001, **42**, 2785-2794.
24. Kitani A, Kaya M and Saski K, *J Electrochem Soc.*, 1986, **133**, 1069.
25. Huang J, Virji S, Weiller B H and Kaner R B, *J Am Chem Soc.*, 2003, **125(2)**, 314.
26. Lu W K, Elsenbeumer R L and Wesiling B, *Synth Met.*, 1995, **71**, 2163.
27. Rupali Gangopadhyay, Amitabha De and Gowtram Ghosh, *Synth Met.*, 2001, **123**, 21-31
28. Fouda A S and El-Dafrawy H, *Int J Electrochem Sci.*, 2007, **2**, 721 – 733
29. Lillard R S and Butt D P, *Corr Sci.*, 1997, **39(9)**, 1605-1624.
30. Khamis E, Bellucci F, Latanision R M and El-Ashry E S H, *Corrosion*, 1991, **47**, 67.
31. Mu G, Li X and Liu G, *Corros Sci.*, 2005, **47**, 1932.
32. E A Noor, *Int J Electrochem Sci.*, 2007, **2**, 996-1017.
33. Jayaprabha C, Sathiyarayanan S, Phani K L N and Venkatachari G, *J Electroanal Chem.*, 2005, **358**, 250-255.
34. McCafferty E, Hackerman N and Tsai S, *Corrosion*, 1982, **38**, 57-62.
35. Bentiss F, Traisnel M and Lagrenée M, *Corros Sci.*, 2000, **42**, 127-146.
36. Murlidharan S, Phani K L N, Pitchumani S, Ravichandran S and Iyer S V K, *J Electrochem Soc.*, 1995, **142**, 1478-1483.
37. Hirozawa S T, in: *Proceedings of the 8th Eur Symp Corrosion Inhibition*, Ann University, Ferrara, Italy, 1995, **1**, 25.
38. Quraishi M A, Rawat J and Ajmal M, *J Appl Electrochem.*, 2000, **30**, 745-751.