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Research Article

Corrosion Mitigation Effect of Water Soluble Poly (Ethylene Glycol–Ethoxy Aniline) Composite on Mild Steel in Acidic Medium

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Abstract

The polymers as corrosion inhibitors have attracted considerable attention nowadays. In recent years, Polyaniline and Polyethyleneglycol have been reported as efficient corrosion inhibitors for iron in acidic media. A polymer composite polyethylene glycol methoxyaniline (PGeAni) was prepared via chemical method. The characterisation of PGeAni have been carried out using Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy(SEM).The corrosion inhibition of PGeAni composite on mild steel in hydrochloric acid has been evaluated by weight loss measurements, potentiodynamic polarisation and electrochemical impedance spectroscopy. The inhibition efficiencies of this polymer composite increase with increasing concentration and immersion time. Adsorption followed the Langmuir isotherm with negative values of free energy of adsorption (ΔG_{ads}) suggesting a spontaneous inhibition process. The activation energy (Ea) and other thermodynamic parameters (ΔH_{ads} and ΔS_{ads}) have also obtained from temperature studies clearly shows strong inhibition between inhibitor and mild steel surface. The electrochemical studies indicated the mixed nature of the composite.

Keywords: PGeAni, Composite, mild steel, corrosion, inhibition.

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Introduction

Mild steel is widely used as the constructional material in most of the major industries particularly in food, petroleum, power production, chemical and electrochemical industries, especially due to its excellent mechanical properties and low cost. The major problem of mild steel is its dissolution in acidic medium. Corrosion of iron and mild steel in acidic aqueous solutions is one of the major area of concern in many industries where in acids are widely used for applications such as acid pickling, acid cleaning, acid descaling, and oil well acidizing. Because of general aggressiveness of acid solution the material of construction are getting corroded easily.

To prevent unexpected metal dissolution and excess acid consumption in pickling processes of mild steel, inhibitors are added to the acid [1, 2]. Most of the commercial inhibitors are toxic in nature; therefore replacements by eco-friendly inhibitors are necessary. Few non-toxic compounds have been investigated as corrosion inhibitors by some researchers [3 – 6]. Polymer gives better inhibitor efficiency with minimum concentration compared to organic compounds. Literature survey revealed the acid corrosion inhibitive nature of polyaniline (Pani) and substituted polyaniline [7, 8]. Inspite of being its high inhibitive nature, they could not be used effectively because of unstability and insolubility in water. Ethanol soluble polyethoxy aniline as corrosion inhibitor for iron in HCl is reported [9]. If Pani derivatives are made water soluble composite with polyethylene glycol, it could be used effectively as corrosion inhibitor on mild steel in acidic medium. The use of polymer composite offer interesting possibilities for corrosion inhibition due to the presence of hetero atoms like nitrogen and oxygen in their structure and are of particular interest because of their safe use, high solubility in water and high molecular size.

Therefore in present study, poly (ethylene glycol - ethoxy aniline) composite was synthesised by free radical solution polymerization technique as alternative to PANi and characterized using FT-IR spectroscopy and scanning electron microscopy methods. The corrosion behaviour of mild steel specimen have been evaluated by weight lose method, potentiodynamic polarization and electrochemical impedance spectroscopic (EIS) methods.

Experimental methods

Materials

The composition of the sample has been analysed by using ARL 3460 metal analyzer (Optical emission spectrometer).The composition of the specimen was found to be Fe, 99.677; C, 0.035; Mn, 0.196; Si, 0.003; S,0.011; P,0.030; Ni,0.010; Mo,0.014; Cr,0.024. The mild steel specimens were cut into 5cm x 1cm coupons for immersion studies and were lacquered so as to expose an area of 1 cm^2 for electrochemical studies. The specimens were mechanically polished, abraded with fine grade of emery papers, degreased, dried in acetone and stored in desiccators and used for all the studies.

Synthesis and Characterisation of PGeAni composite

The polymer PGeAni composite was synthesized as described by Rupali Gangopadhayan et.al [10]. The polymer composite was characterized by FTIR spectroscopic techniques. The FTIR spectrum of the polymer composite was recorded with a Nicolet- spectrometer (Madison, W I) in the 4000 – 500 cm^{-1} range. Morphological studies of composite samples were performed by Scanning Electron Microscopy (SEM) technique with JEOL scanning electron microscope (model JSM-840).

Weight loss experiment

Stock solutions of polyethylene glycol ethoxyaniline composites were prepared and diluted to appropriate concentrations (0.01% to 0.19%) with 1M HCl. Mild steel specimens in triplicate in the absence and presence of various concentrations of PGeAni were immersed in 1M HCl for ½,3,6,12 and 24hr at 298K. Weight loss measurements were carried out using analytical balance. From the values and inhibitor efficiency were determined.

Electrochemical experiment

Corrosion monitoring techniques like Potentiodynamic polarization (Tafel Polarisation) and electrochemical impedance spectroscopy (EIS) have been carried out using Solartron Electrochemical measurement unit (1284 Z) model with a software package of Z plot and corrware. For polarization and impedance studies the period of immersion was for 30 minutes. The potentiodynamic polarization studies were carried out over a potential range from-0.1 V of cathodic potential to -1 V of anodic potential with respect to corrosion potential at a sweep rate 2 mV sec^{-1}. These measurements were carried out at corrosion potential. The A.C. amplitude of 10 mV was applied and frequency was varied from 20 Hz to 0.1Hz. The real and imaginary parts of the impedance were plotted as Nyquist plot. From the Nyquist plots, the Charge Transfer Resistance (Rct) and Double Layer Capacitance (Cdl) values were derived. The charge transfer resistance values were obtained from the plots of Z' Vs Z''.

Results and discussion

FTIR Spectroscopy study

To characterize the synthesized PGeAni composite,the FTIR analysis were carried out (**Figure 1**). IR Absorption data of PGeAni composite was tabulated (**Table1**) with their assignments. **Figure 2** represents the possible structure of PGeAni proposed through FTIR spectroscopy.

SEM investigation

The SEM images of the polymer composites **Figure 3** show that they are composed of agglomerated short rodlike rectangular images. In the presence of polyethyleneglycol, PANI poly ethoxy aniline preferentially grows on the surface due to selective adsorption of poly aniline molecules with anilinium cations on the substrate through formation of hydrogen bonds [11]. This leads to core-shell composite structures. It is worth noting that the monodisperse composite along PANI fragment indicates high quality of the composite in core-shell structure.

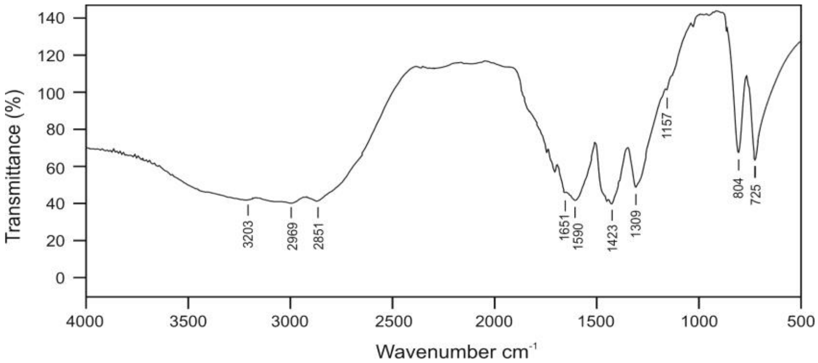

Figure1 FTIR Spectra of Poly (ethyleneglycol –ethoxy aniline) composite.

Table 1 IR Absorption data of PGeAni composite.

Absorption band (cm^{-1})	**Assignment**
3203	C-H aromatic stretch and secondary aromatic amine
2969	Methylene CH_2-CH_2 assymetric/symmetric vibrations
2851	Methylene C-Hstretch
1651	Aromatic N-H bending
1590	Stretching of C=N quinonoid ring structure
1423	Stretching of C=C benzenoid ring structure
1309	aromatic C – N stretch
1309	ortho substitution
1157	C-O stretching of PG
804	para substituted aromatic out of plane bending
725	Methylene rocking vibration-long chain linear aliphatic structure

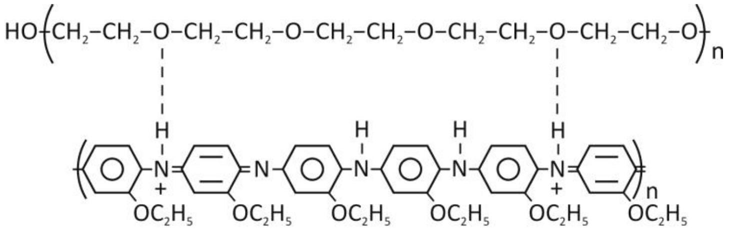

Figure 2 Structure of Poly (ethyleneglycol –ethoxy aniline) composite.

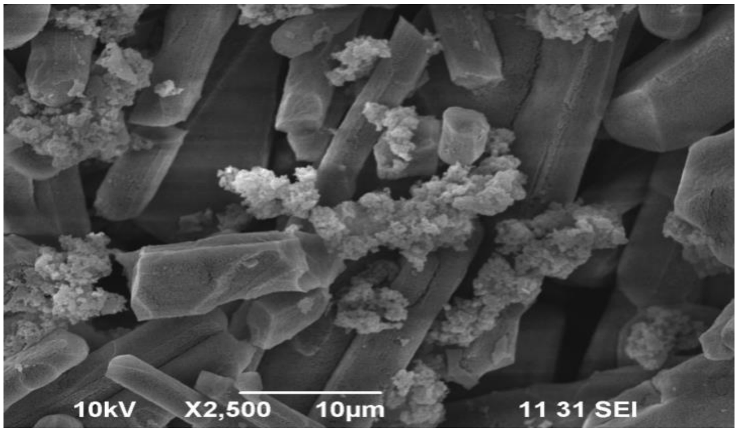

Figure 3 Scanning electron microscopic image of PGeAni.

Weight loss measurements

The weight loss obtained for the MS coupons immersed in the different concentrations of PGeAni composite inhibitor solutions for ½, 3, 6, 12 and 24 hr are plotted against IE and shown in the **Figure 4**.The percentage inhibition efficiency (IE %) calculated from the weight loss results by the following equation.

$$\text{IE} = \frac{Wo - W}{Wo} X\, 100 \qquad (1)$$

where W_0 and W are the weight loss without inhibitor and with inhibitor respectively.

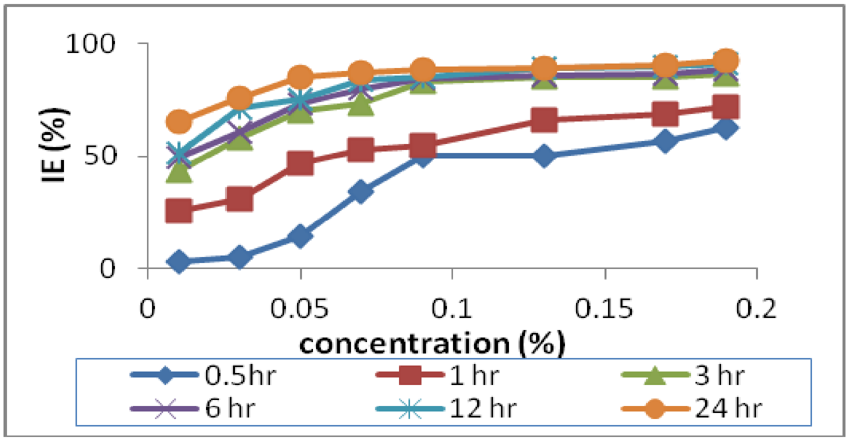

Figure 4 Variation of IE of PGeAni with concentration.

The coupons immersed in PGeAni composite inhibitor solutions showed minimum weight loss. They reduced the corrosion rate to a significant extent and thereby showing higher inhibition efficiencies. It can be seen that the inhibition efficiency increases with increase in concentration of PGeAni composite which suggests that inhibition is a result of adsorption of inhibitor on the metal surface and PGeAni composite acts as an adsorption inhibitor [12]. The highest inhibition efficiency of 92.7 has obtained at highest immersion time 24 hr and the highest concentration 0.19% of PGeAni as shown in **Table 2**. The reason for the high inhibition efficiencies of these studied PGeAni composite towards MS may be due to the presence of nitrogen, oxygen, ethyl, benzenoid and quinonoid groups in the composite.

Effect of temperature on the performance of PGeAni inhibitor

To study the effect of temperature on the inhibition efficiency, weight loss measurements of MS specimens were carried out at 303, 313, 323,333,343K with 0.01 to 0.19% solution. Inhibition efficiencies were found to decrease with increase in temperature is clearly indicated in the **Figure 5.** The decrease in inhibition efficiency with increasing temperature may be due to desorption of some adsorbed molecule from the MS surface at higher temperatures. This shows a weak adsorption interaction between MS surface and the inhibitor [13], [14] and [15]

Adsorption isotherm

The extent of corrosion inhibition depends on the surface conditions and mode of adsorption of inhibitors [16]. Langmuir isotherm is found to provide best description of the adsorption behaviour of the investigated PGeAni composite as evident from straight line plot obtained when *log* $\theta/(1-\theta)$ is plotted against log *C* as shown in **Figure 6** and calculated using the equation

$$\frac{\theta}{1-\theta} = KC \quad or \quad \frac{C}{\theta} = \frac{1}{K} + C \qquad (2)$$

where *K* and *C* are the equilibrium constant of the adsorption process and the concentration of the inhibitor and the θ value is the surface coverage respectively. The data results show that all the linear correlation coefficients (R^2 >0.999) with slopes very close to unity, which indicates that the adsorption of inhibitor on the metal surface obeyed Langmuir adsorption isotherm [17].

Table 2 Weight loss data, Polarization and Impedance parameters for mild steel in 1 M HCl with different concentrations of PGeAni.

		Concentration w/v (%)						
		blank	**0.01**	**0.03**	**0.05**	**0.07**	**0.13**	**0.19**
Weight loss data	Weight loss(g)	0.34262	0.1182	0.08315	0.05009	0.04406	0.03608	0.02501
	IE (%)		65.5	75.73	85.38	87.14	89.47	92.7
	θ		0.655	0.7573	0.8538	0.8714	0.8947	0.927
Polarization parameters	Ecorr (mV/sec)	-515	-498	-494	-494	-490	-487	-487
	Icorr (mA/cm2x10^{-4})		48.46	32.74	25.99	19.94	18.94	15.7
	ba (mV/dec)	186	150	145	121	136	136	136
	bc (mV/dec)	163	138	131	117	113	112	128
	IE (%)	-	34.82	55.97	65.04	73.18	74.52	78.88
Impedance Parameters	Rct (Ω/cm^2)	18.53	83.39	88.66	99.84	108.19	118.17	149.13
	Cdl (μ F/cm^2)	3.83	0.95	0.9	0.8	0.74	0.67	0.53
	IE (%)	-	77.78	79.1	81.44	82.87	84.32	87.57

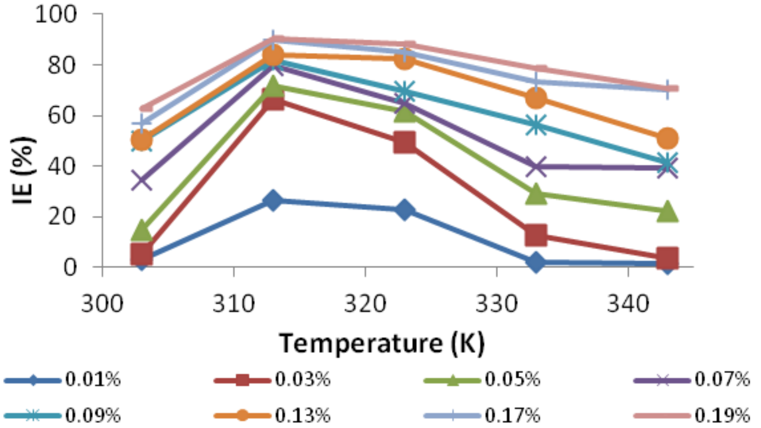

Figure 5 Variation of inhibition efficiency with temperature at various PGeAni concentrations.

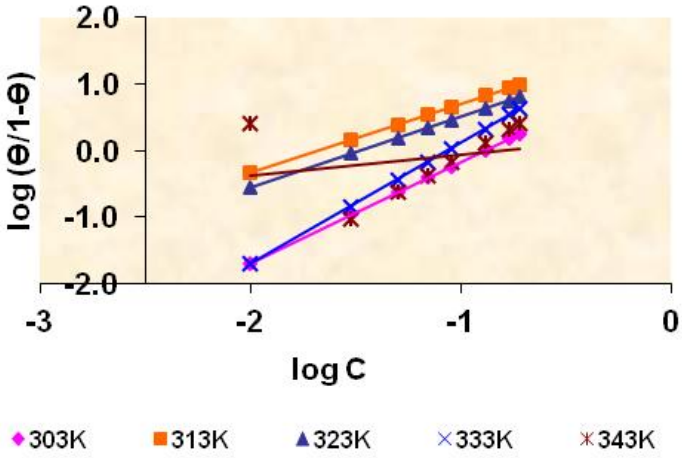

Figure 6 Langmuir isotherm of PGeAni on the mild steel in 1M HCl

Thermodynamic and kinetic parameters of PGeAni on mild steel surface

Thermodynamic parameters are important to study the inhibitive mechanism. The values of free energy of adsorption (ΔG) were calculated using the standard equation

$$\log C = \log\theta/(1-\theta) - \log B \qquad (3)$$

where $\log B = -1.74 - (-\Delta G/2.303\ RT)$; θ = Surface coverage; C = Concentration; R = Gas Constant; T = Temperature.

Generally, values of ΔG_{ads} around 20 kJ/mol are consistent with physisorption while those around -40 kJ/mol or higher is associated with chemisorptions as a result of sharing or transfer of electrons from inhibitor molecules to the metal surface to form a co-ordinate type of bond (chemisorptions). The observed low and negative values (around 20 kJ/mol) of ΔG_{ads} suggest that the nature of the inhibitor adsorption is mainly physisorption and spontaneous [18].

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

$$\Delta G = \Delta H - T\Delta S \qquad (4)$$

A plot of ΔG_{ads} versus T will be a straight line with intercept ΔH_{ads} and slope ΔS_{ads}. All the obtained values of ΔH_{ads} and ΔS_{ads} for the inhibitor adsorption on the mild steel surface were listed in **Table 3**. The negative values of ΔH_{ads} indicate that the adsorption of inhibitor molecules is an exothermic process [19]. The negative ΔH_{ads} and positive values ΔS_{ads} are characteristic of the occurrence of a replacement process during adsorption of inhibitor molecules on the surface [20].

The increase in apparent activation energy Ea may be interpreted as physical adsorption [21]. Szauer and Brand [22] explained that the increase in activation energy can be attributed to an appreciable decrease in the adsorption of the inhibitor on the mild steel surface with increase in temperature and a corresponding increase in corrosion rates occurs due to the fact that greater area of metal is exposed to the acid environment.

Electrochemical measurements

The results obtained from electrochemical experiments are shown in **Figure 7** and **Figure 8.** The potentiodynamic polarization data are shown in the Tafel plots for MS in 1M HCl with the addition of various concentrations of PGeAni composite (Figure 7). The corrosion kinetic parameters such as corrosion potential (Ecorr), corrosion current density (Icorr), anodic and cathodic Tafel slopes (ba and bc) were derived from these curves and are given in **Table 2**.

Table 3 Thermodynamic and kinetic Parameters for Adsorption of PGeAni on MS surface.

Conc (%) (w/v)	**Ea (kJ/mol)**	**ΔG_{ads} (k J/mol)**				**ΔH_{ads} (kJ /mol)**	**ΔS_{ads} (J/K/mol)**
		313K	**323K**	**333K**	**343K**		
Blank	44.61	-	-	-	-	-	-
0.01	47.08	-19.75	-19.84	-12.71	-13.31	-103.2	0.2645
0.03	52.36	-21.34	-20.14	-15.45	-12.08	-123.8	0.3247
0.05	50.08	-20.63	-20.07	-16.9	-16.39	-70.58	0.1588
0.07	51.92	-20.92	-19.54	-17.29	-17.78	-57.17	0.1167
0.09	54.02	-20.58	-19.44	-18.49	-17.31	-54.26	0.1076
0.13	49.58	-20.10	-20.38	-18.69	-17.38	-51.37	0.0983
0.17	45.54	-20.79	-20.19	-19.29	-18.95	-40.94	0.0644
0.19	46.06	-20.56	-20.62	-19.35	-18.65	-42.73	0.0699

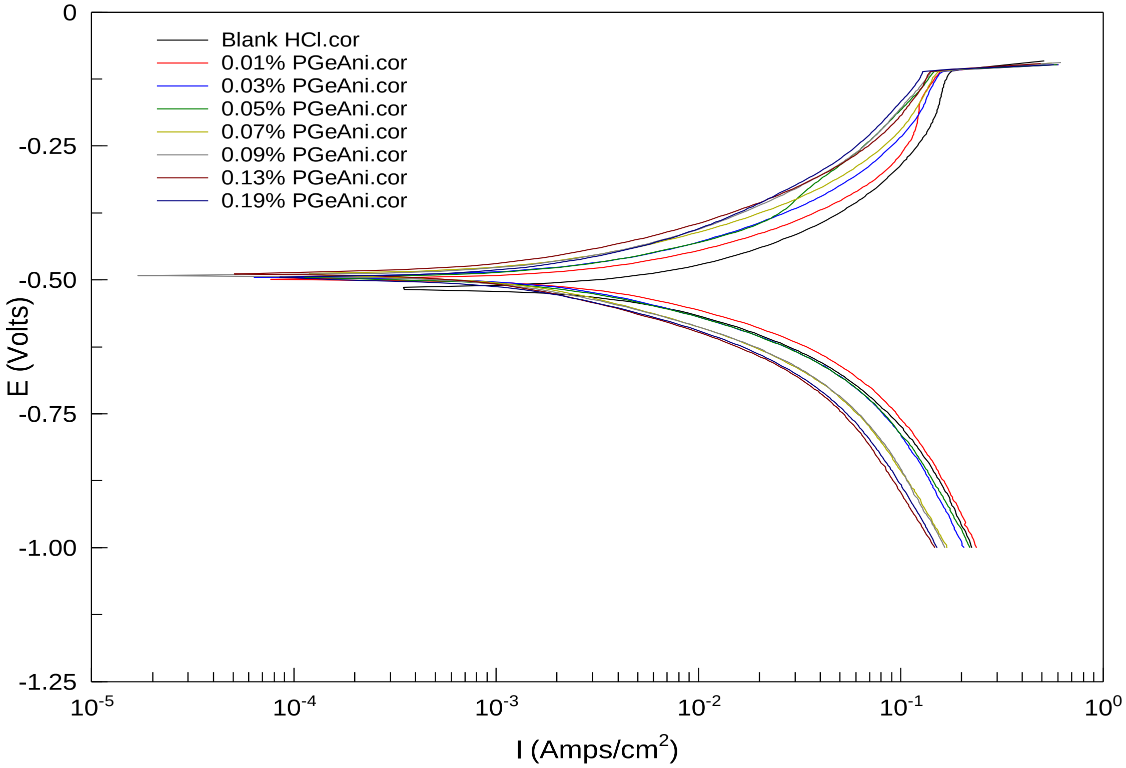

Figure 7 Polarization curves for mild steel in 1 M HCl with different concentrations of PGeAni.

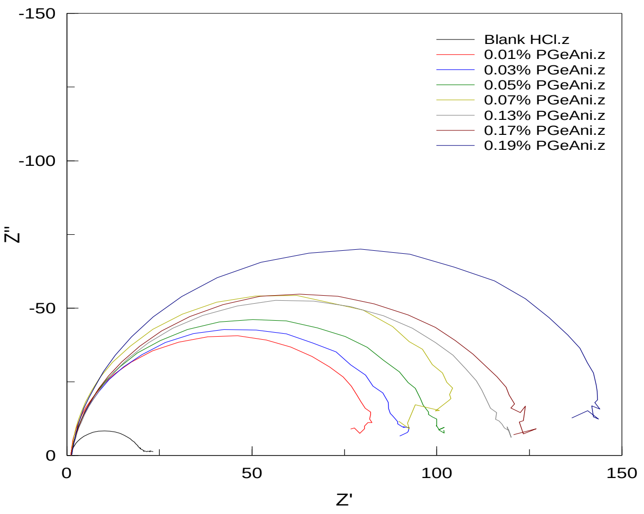

Figure 8 Nyquist plots for mild steel in 1 M HCl with different concentrations of PGeAni.

The values of inhibition efficiency (IE %) are calculated by the following expression.

$$IE\ (\%) = \frac{Icorr_{(blank)} - Icorr_{(inhibitor)}}{Icorr_{(blank)}}\ X\ 100 \tag{5}$$

Icorr $_{(inhibitor)}$ and Icorr $_{(blank)}$ are the corrosion current density of mild steel with and without PGeAni in 1M HCl

From the **Table 2**, it is observed that the Icorr values gradually decreased with gradual increase in the concentration of inhibitor. The marginal shift in E_{corr} values show that the polymer composite PGeAni is mixed type inhibitor in HCl medium. It is further supported from the fact of anodic and cathodic slope values (b_a and b_c) which suggests that the inhibitor act by simple blocking the mild steel surface. This means that the inhibitor has significant effects both on retarding the cathodic hydrogen evolution reaction and in inhibiting the anodic dissolution of mild steel as discussed by [23].The maximum inhibitor efficiency obtained with highest concentration is 78.88%.

The corrosion inhibition efficiencies observed using polymer are not only due to the presence of π electrons and quarternary nitrogen but can also be attributed to the larger molecular size which ensures greater coverage of the metallic surface [24].

The variation in the impedance behaviour of mild steel in 1M HCl with the addition of various concentration of PGeAni is shown in **Figure 8**. The charge transfer resistance (Rct) and the interfacial double layer capacitance (Cdl) values are derived from these curves are given in Table 2.The inhibition efficiency calculated by charge transfer resistance Rct as follows

$$IE\ (\%) = \frac{Rct_{(inhibitor)} - Rct_{(blank)}}{Rct_{(inhibitor)}}\ X\ 100 \qquad (6)$$

$Rct_{(inhibitor)}$ and $Rct_{(blank)}$ are the charge transfer resistance in presence and absence of PGeAni in HCl. It is found that Rct values increase with increase in the inhibitor concentration which results in maximum IE (87.4%) at high concentration. This indicated that the inhibitive molecules of the PGeAni have been adsorbed on the MS surface and decreased the roughness of the MS surface. The Cdl values decrease from the blank suggested a decrease in dielectric constant between the metal and electrolyte induced by the adsorption of the inhibitor [25].

Mechanism of Inhibition process

Corrosion inhibition of mild steel in hydrochloric acid solution by PGeAni had been explained on the basis of molecular adsorption. In the present work the composite inhibit corrosion by controlling both the anodic and cathodic reactions. In acidic solution the composite exists as protonated species which are adsorbed 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 the anodic dissolution of mild steel [26]. In the polymer composite, polyethylene glycol ethoxy aniline moiety (which includes aromatic rings, azo group and a nitrogen atom), the ethoxy group units contribute to the corrosion inhibition by virtue of electron donating nature of these groups to the metal surface.The high performance of the polymer is attributed to the presence of long π-electrons conjugation, quaternary nitrogen atom and the larger molecular size.

Conclusions

- The PGeAni composite have effectively inhibited corrosion of mild steel in 1 M HCl by forming a protective barrier layer. The inhibition efficiency of the composite increased gradually with increase in its concentration.
- Langmuir isotherm is found to provide best description of the adsorption behaviour of the investigated PGeAni composite
- The calculated values of ΔG_{ads} are negative and spontaneous while those for ΔH_{ads} are negative and ΔS_{ads} are positive.
- The observed increase in the activation energy with increasing inhibitor concentration, in addition to the decrease in inhibition efficiency of the inhibitor with increasing temperature, suggest physical adsorption of the inhibitor on the electrode surface.
- Polarization measurements have shown that the PGeAni composite has acted as a mixed- inhibitor, retarding predominantly anodic dissolution of steel in 1M HCl.
- The results of the weight loss, electrochemical polarization and AC impedance spectroscopy were all in very good agreement to support the above conclusions. So the PGeAni composite is eco-friendly and effective acid corrosion inhibitor.

References

[1] SA. Abd El-Maksoud, AS Fouda. Mater Chem Phys., 2005, 93, 84–90.
[2] A. Chetouani, K. Medjahed, KE Benabadji, B. Hammouti, S. Kertit, A. Mansri Prog Org Coat., 2003,46,312–6.
[3] A.K. Satapathy, G. Gunasekaran, S. C. Sahoo, Kumar Amit, P. V. Rodrigues, Corros. Sci., 2009, 51, 2848.

[4] F.C. Giacomelli, C. Giacomelli, M. F. Amadori, V. Schmidt, A. Spinelli: Mater. Chem. Phy., 2004, 83,124.

[5] Pedro de Lima-Neto, Alexsander P. de Araujo, Walney S. Araujo, Adriana N. Correia, Prog. Org. Coat., 2008, 62, 344.

[6] Xiang-Hong Li, Shu-Duan Deng, Hui Fu, J. Appl. Electrochem., 2010, 40, 1641.

[7] Aziz Yagan., Nuran Ozcicek Pekmez., Attila Yildiz., Progress in Organic Coatings., 2006, 57, 314-318.

[8] S.Sathiyanarayanan, C.Jeyaprabha, G.Venkatachari, Materials Chemistry and Physics., 2008,104, 2-3, 422-428.

[9] S. Sathiyanarayanan, S.K. Dhawan, D.C. Trivedi, K. Balakrishnan, Corrosion Science·., 1992, 33, 12,1831-1841.

[10] Rupali Gangopadhayay, Amitabha De, Gowtram, Ghosh, Synth met. 2001, 21-31.

[11] Ligang Gai, Guojun Du, Zhiyuan Zuo, Yanmin Wang, Duo Liu, Hong Liu J. Phys. Chem., 2009,113, 7610–7615.

[12] H.A. Sorkhabi, B. Shaabani, D. Seifzadeh, Electrochem. Acta., 2005, 50, 3446–3452.

[13] A. Aytac, U. Ozmen, M. Kabasakaloglu, Mater. Chem. Phys., 2005, 89,176–181.

[14] O.K. Okorosaye, N.C. Oforka, J. Appl. Sci. Environ. Manage., 2004, 8 (1), 56–61.

[15] V.S. Sastri, Corrosion Inhibition, Principles and Applications, John Wiley & Sons, New York., 1998.

[16] N.C. Subramanyam, S.M. Mayannu, J. Electrochem. Soc. India., 1984, 33, 273.

[17] H. Li, S.D. Deng, G.N. Mu, H. Fu, F.Z. Yang, Corros. Sci., 2008, 50, 420.

[18] S.S. Abd El-Rehim, H.H. Hamd, M.A. Amin, Corros. Sci., 46, 2004, 5.

[19] B.A. Abdel Nabey, E. Khamis, M.S. Ramadan, A. El-Gindy, in: 8th European Symp Corros. Inhibitors, Ann. Univi. Ferrara N.S. Sez., 1995, 10, 299.

[20] A. El-Sayed, J. Appl. Electrochem. 1997, 27, 193.

[21] E.F. El Sherbini, Mater. Chem. Phys. 60, 1999, 286.

[22] T. Szauer, A. Brand, Electrochim. Acta., 1981, 26, 1219.

[23] S.Sathiyanarayanan, C.Marikkannu, N.Palaniswamy, Appli.Surf.Sci., 2005,241, 4775–484S.

[24] S.Sathiyanarayanan, K.Balkrishnan, S.K.Dhawan, D.C.Trivedi,1994, Electrochemica Acta., 39, 6, 831-837.

[25] K. Khaled, N. Hackerman, Electrochemica Acta., 2003,48,2715-23.

[26] M.A. Quaraishi, S. Muralidharan, S.V.K. Iyer, 2000, Anti-corrosion methods and materials., 47, 354-358.

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