

Facile Preparation of AT-PEG Polymer and Its Corrosion Inhibition Performance

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Aniline tetramer grafted polyethylene glycol methyl ether (AT-PEG) was obtained from aniline tetramer (AT), polyethylene glycol (PEG) and toluene-2,4-diisocyanate (TDI). Then the structure of AT-PEG was characterized by fourier infrared spectroscopy (FT-IR) and nuclear magnetic resonance (¹H NMR). The corrosion inhibition performance of AT-PEG for Q235 carbon steel in 1.0 M HCl solution has been investigated using static weight loss, electrochemical impedance spectroscopy (EIS) and polarization curves, respectively. The results proved that the corrosion inhibition efficiency increased with the increase of AT-PEG, and the corrosion inhibition efficiency of hydrochloric acid solution reached its maximum of 92.50% in the concentration of 100 mg/L. Here, the results of static weight loss, electrochemical impedance spectroscopy (EIS) and polarization curves were in good agreement with each other.

Keywords: Aniline tetramer; Carbon steel; Inhibitor; Static weight loss; Electrochemistry; Hydrochloric acid solution

1. INTRODUCTION

The hydrochloric acid solutions (generally, it is the HCl solution with the concentration from 0.1 M to 1.0 M) are widely used for cleaning rusts on the surface of carbon steel or other metals in different industrial sectors, and also widely applied for oil well acidizing and industry acid pickling. However, the hydrochloric acid solutions are also highly corrosive to any metals [1-5]. Corrosion is the most concern in the durability of structures and materials, so it is time to find an effective method on corrosion control for metal. According to the relevant research, the use of a corrosion inhibitor is one

of the most practical and economical methods for protecting carbon steel from corrosion [6-10]. A number of polymer compounds investigated as corrosion inhibitors for magnesium, aluminum, copper and carbon steel have been reported, such as lignin, polyaniline are usually used as inhibitors for carbon steel in various salt and acid medium for corrosion prevention. Ding et, al. obtained a bio-based polymer LAI from the green resource sodium lignosulphonate, which could act as a inhibitor for metal, showing perfect anticorrosion performance in epoxy coatings [11].

Polyaniline has become one of the best candidates for anticorrosion coatings, due to it possessing the strong resistance to pitting corrosion and scratch resistance. But the special rigid conjugated chains structure of polyaniline lead to its poor solubility in conventional solvents. As a result, its application in the field of metal anticorrosion is limited greatly. Aniline oligomer has high environmental stability, good solubility, low price, and outstanding electrochemical activity, and thus, it possesses the advantages to be anticorrosion material for metal in the future. Zhao et, al. synthesized a aniline trimer by direct mixed oxidation, the corrosion inhibition performance of aniline trimer was investigated by static weight loss test, electrochemical impedance spectroscopy, and polarization curves in 1.0 M HCl solution, and when the concentration of aniline trimer was 100 mg/L, the corrosion inhibition efficiency reached its maximum of 99%, indicating that the aniline trimer can significantly reduce the corrosion rate of carbon steel in acid solution [12].

Aniline tetramer (AT) as an aniline oligomer, not only has the similar optical, electrical and chemical properties with polyaniline, but also the molecular structure of AT is more simple and the solubility is better than polyaniline, so it is easier to study the application of AT in various fields. On the other side, due to the advantages of good chemical stability, non-toxic, and harmless of polyethylene glycol (PEG), so the preparation of the graft copolymer from aniline tetramer and PEG has become one of the hot research spots.

The present investigation is confined to the study of inhibiting action of active inhibitor aniline oligomer on the corrosion behavior of Q235 carbon steel. In this article, a new type of active inhibitor AT-PEG was obtained by graft polymerization from aniline tetramer and polyethylene glycol. The chemical structure of AT-PEG was elucidated and confirmed using FT-IR and ^1H NMR spectroscopic techniques. And it was the first time to investigate the corrosion inhibition performance of AT-PEG on carbon steel in 1.0 M HCl solution by electrochemical impedance spectroscopy (EIS) and Tafel plot curves methods.

2. EXPERIMENTAL

2.1 Materials

4-aminodiphenylamine, polyethylene glycol methyl ether 1000 (mPEG1000), ammonium peroxydisulfate (APS), toluene-2,4-diisocyanate (TDI), ethanol, and acetone were purchased from Aladdin Industrial Corporation, and were used without further purification. Deionized water was used throughout the experiment. The Q235 carbon steel electrode was provided by OSS integral institute Co., Ltd, selected for anticorrosion test, and the Q235 carbon steel with the following composition (wt %): 0.16 % C, 0.30 % Si, 0.53 % Mn, 0.45 % P, 0.055 % S, 0.015 % Ni, and the remainder is Fe. All other reagents were purchased from Aladdin and used as received and without other disposition.

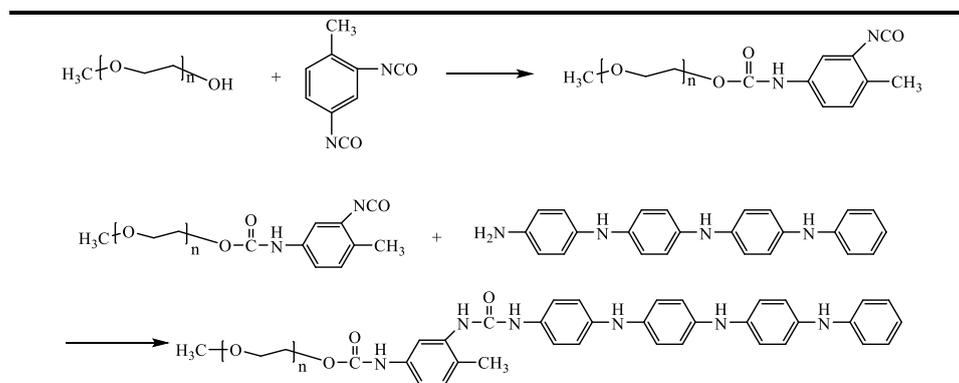
2.2 Synthesis of aniline tetramer (AT)

An amount of 250 mL of acetone, 200 mL of 0.1M HCl, and 30 mmol of 4-aminodiphenylamine were added into three necked round-bottom flask of 500 mL, the mixture was vigorously stirred for 30 minutes until 4-aminodiphenylamine completely dissolved. And then 25 mL of acetone and 25 mL of distilled water mixed with 24 mmol of ammonium peroxydisulfate was dropped into the above solution, and the mixed solution was vigorously stirred under the magnetic stirring in ice water bath for 4 h. The crude product was filtered by sand funnel vacuum, and then the filter cake was washed by 0.1 M HCl, acetone, and ammonia, respectively. Finally, the filter cake was dried in the vacuum oven at 50°C for 48 h. The crude product recrystallised from ethanol to obtain the aniline tetramer (AT).

2.3 Synthesis of AT-PEG

The synthetic route of the aniline tetramer grafted polyethylene glycol methyl ether (AT-PEG) is shown in Table 1.

Table 1. Synthetic route of AT-PEG



10 mmol of polyethylene glycol methyl ether 1000 (mPEG1000) and 10 mmol of TDI were added into 30 mL of dry THF at 35°C for 1 h. And then 30 mL of THF containing 10 mmol of AT was dropped into the above solution at 50°C for 1 h. The solvent was removed by rotary evaporator and the product was dried in the vacuum oven at 40°C for 12 h. The pure product of AT-PEG was obtained in 98.64% yield. The structure of this product was confirmed by Fourier transform infrared spectroscopy (FTIR) and ¹H nuclear magnetic resonance spectrometry (¹H NMR).

2.4 Electrodes preparation

The carbon steel electrodes were moulded by E44 epoxy resin with a surface area of 10 mm×10 mm exposed to acid solution medium for electrochemical measurements. Before do the experiments, the surface of carbon steel electrodes were abraded with a series of sandpapers with different grades

(600-, 800-, 1200-grit) make the surface smooth. Then, the electrodes were washed with alcohol (or acetone) and dried at 60 °C for 15 min. The EIS and potentiodynamic polarization measurements of carbon steel specimens were conducted in 1.0 M HCl solution. The concentration of AT-PEG in the acid solution was in the range of 0~100 mg/L.

2.5 FT-IR and ¹H NMR Tests.

The chemical structure of AT-PEG was confirmed by FT-IR and ¹H NMR spectra. The FT-IR spectrum (KBr) was collected with a Thermo NICOLET 6700 instrument. And the ¹H NMR spectrum was obtained at room temperature on a 400 MHz AVANCE III NMR spectrometer in DMSO-d₆ with tetramethylsilane as internal reference.

2.6 Static corrosion Tests

The static corrosion behavior of Q235 carbon steels were tested through weight loss experiments. The Q235 carbon steel specimens with the dimensions of 10 mm×10 mm×10 mm were polished by sandpapers, and rinsed with distilled water, degreased by ethanol. The specimens were immersed in 150 mL of inhibitor-free and inhibitor solutions at room temperature for 24 h. After that, the Q235 carbon steel specimens were removed from the corrosion medium, washed by pure water absolute ethanol, dried in the drying closet, and the average weight loss was used to calculate the corrosion inhibition efficiency. The corrosion inhibition efficiency (*CI*), surface coverage (*θ*) and corrosion rates (*CR*) values were calculated by the following equations:

$$CI = \frac{W_0 - W}{W_0} \times 100\% \quad (1)$$

$$\theta = \frac{W_0 - W}{W_0} \quad (2)$$

$$CR = \frac{M_1 - M_2}{St} \quad (3)$$

where the *W*₀ is and *W* are the weight loss (mg) of Q235 carbon steel in the absence and presence of inhibitor after immersion; The *M*₁ is and *M*₂ are the mass of Q235 carbon steel before and after immersion in the corrosion medium, *S* is the total area of an carbon steel sample, and *t* is the immersion time.

2.7 Electrochemical Tests

The electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization curves were acquired in 1.0 M HCl water solution using a classical three-electrode system at room temperature (25 ±1°C). The classical three-electrode system with saturated calomel as the reference electrode (SCE), a platinum plate as the counter electrode, and the carbon steel specimen as working electrode. Typically, the Q235 steel electrode specimens were initially kept at an open circuit potential (OCP) for 0.5 h

peaks at 1593 cm⁻¹ and 1506 cm⁻¹ for benzene absorption peaks further prove that the existence of AT-PEG.

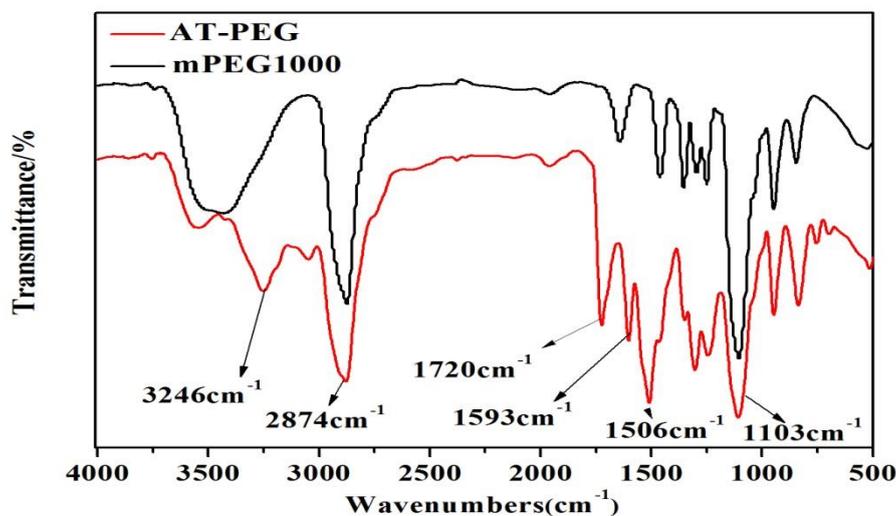
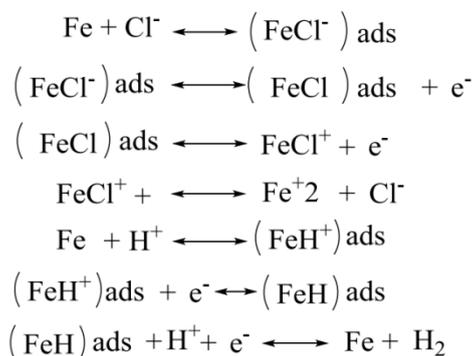


Figure 2. The FT-IR spectra of mPEG1000 and AT-PEG.

3.2 Static weight loss measurements

The corrosion of carbon steel electrodes in acid medium were electrochemical corrosion, and the corrosion rates were carried out in acidic media (1.0 M HCl) by weight loss method. The reaction Ep of carbon steel in hydrochloric acid is shown in scheme 2 [13].



Scheme 2. The reaction Ep of carbon steel in hydrochloric acid

The mass loss of Q235 steel in 1 M HCl solution with and without addition of different inhibitors was determined. The corrosion parameters of corrosion inhibition efficiency (*CI*), surface coverage (θ) and corrosion rates (*CR*) values were calculated based on the static weight loss method and summarized in Table 1. The present results imply that the inhibitor of AT-PEG was able to decreases the corrosion process of Q235 carbon steel at any concentration in 1.0 M HCl solution, and

the corrosion rate decreased as the increased of inhibitor concentration. Besides, the values of corrosion inhibition efficiency (CI) and surface coverage (θ) increased with the increase of inhibitor concentration, and the values of inhibition efficiency reached its maximum of 92.5% with the concentration of 100 mg/L. The result was attributed to the N and O atoms present in the chemical structure of the AT-PEG, which can serve as the adsorption center on the surface of Q235 carbon steel. There is a barrier film on the surface of Q235 carbon steel through the adsorption effect of AT-PEG, it decreases dramatically the carbon steel area from corrosion factors attack, and the surface coverage is relation with increase in the concentration of AT-PEG

Table 1. Effect of Concentration of AT-PEG on Static Corrosion Inhibition Efficiency.

Inhibitor(mg/L)	CR (mg cm ⁻² h ⁻¹)	θ	CI (%)
Blank solution	1.764	-	-
25	0.279	0.842	84.2
50	0.212	0.880	88.0
100	0.132	0.925	92.5

3.3 EIS measurements

EIS spectra were usually used to evaluate the anticorrosion properties and water uptake behavior of the carbon steel samples. The impedance data of carbon steel plotted after immersion time of 2 h in 1.0 M HCl solution at room temperature are presented as Nyquist and Bode plots in Fig.3. Accordingly, different corrosion system show different features in the EIS spectra, and the corrosion mechanism of the inhibitor can be determined by analyzing the EIS spectra [14-15].

The EIS spectra obtained for the corrosion of carbon steel electrodes consists of one depressed capacitive loop that corresponds to a charge-transfer process [16-17]. As shown in Fig.3, the impedance spectra possess a single depressed semicircle, indicating the charge transfer between electrodes and solutions, and the transfer process was relevant to the corrosion reaction rates of carbon steels in HCl solution. All the impedance diagrams are not perfect semicircles, which due to the frequency dispersion of the roughness on the electrodes surface. According to the literatures [10], the impedance module at low frequency ($Z_{0.01\text{Hz}}$) represents the ability of corrosion resistance of inhibitor. In the initial stage of immersion, the $Z_{0.01\text{Hz}}$ values of carbon steel electrodes with 25 mg/L, 50 mg/L, and 100 mg/L inhibitor were 150 Ω cm², 200 Ω cm², and 320 Ω cm² respectively. After 1 h of immersion, the $Z_{0.01\text{Hz}}$ values of all the solutions containing inhibitor gradually increased (the values were up to 250 Ω cm², 350 Ω cm², and 350 Ω cm², respectively.) and then remained at the levels. However, the $Z_{0.01\text{Hz}}$ values of carbon steel electrode in the pure HCl solution only were \sim 30 Ω cm² during the whole time of immersion. The $Z_{0.01\text{Hz}}$ values of carbon steel electrodes in solutions with 50 mg/L and 100 mg/L were about 12 times than the pure acid solution.

The EIS results proved that the corrosion inhibition efficiencies of carbon steel electrodes in HCl solutions with different concentrations of AT-PEG were better than the pure HCl solution.

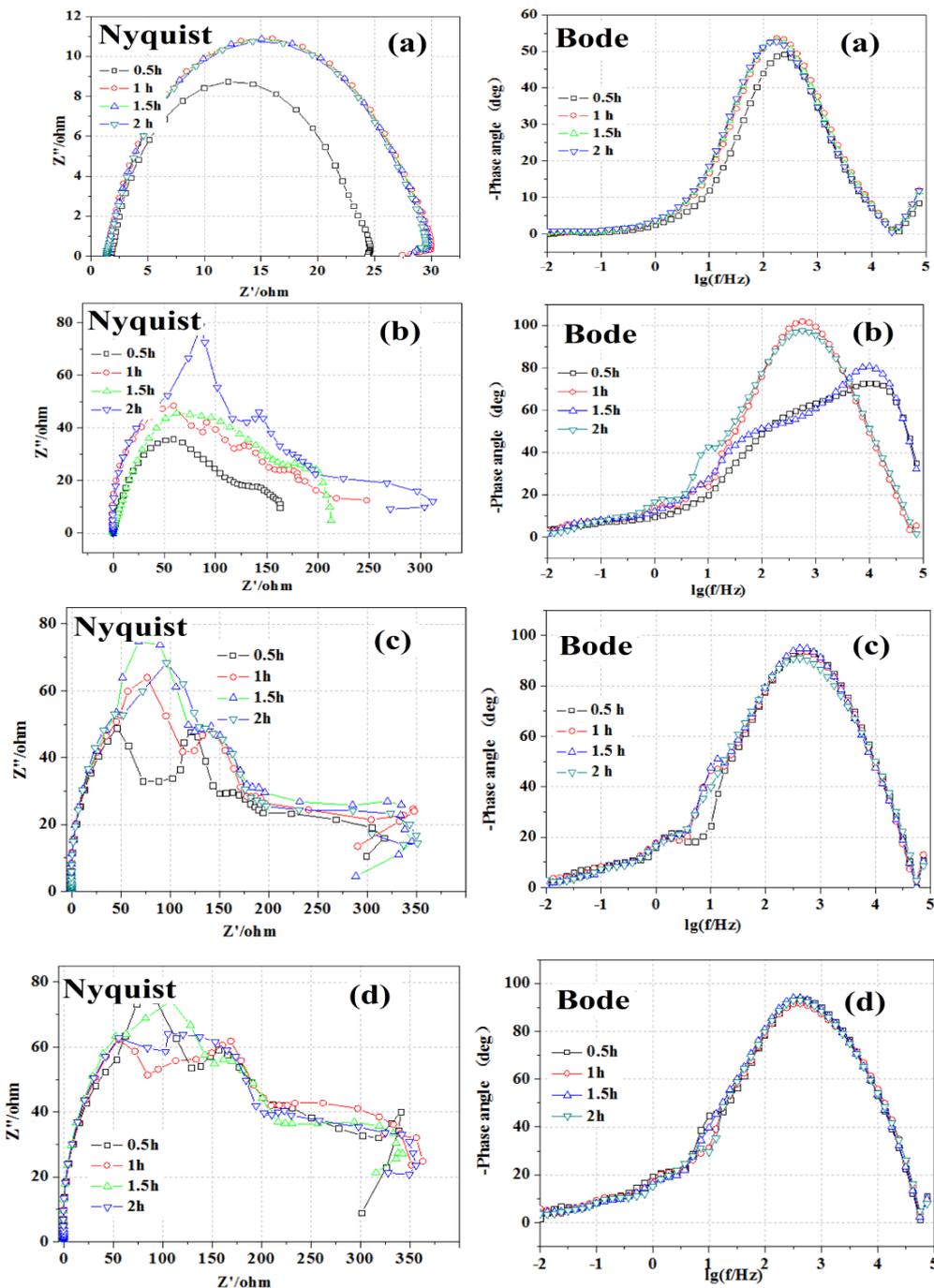


Figure 3. The Nyquist and Bode curves for different concentrations of inhibitor in 1M HCl solution: 0 mg/L (a), 25 mg/L (b), 50 mg/L (c), and 100 mg/L (d).

In practice, there are two ways to describe the EIS spectra of heterogeneous films on metal surfaces or rough porous electrodes in the literature. One is a finite transmission line model, the other is the film equivalent circuit model, is usually used to study the degradation of coated metal. It has been proposed that the EIS spectrum of the metal coated by the organic inhibitor film is very similar to the failed coated metal [18-20]. Here, the EIS data were fitted by the electrical equivalent circuit in

Fig. 4, and the corrosion parameters were listed in Table 2. The R_s represents the solution resistance, which is the resistance between the reference electrode and the working electrode, R_t represents charge transfer resistance, and Q_c represents the double-layer capacitance and Q_c is expressed as $\omega^{-n}/Y_0 \cdot (\cos n\pi/2 + j \sin n\pi/2)$, where n and Y_0 are the exponent and constant, respectively, and ω is the angular frequency in rad s^{-1} .

Table 2. Electrochemical corrosion parameters fitted from the equivalent circuit.

Solution	Time/h	$R_s/(\Omega \cdot \text{cm}^2)$	$Q_{dl}/(\mu\text{F} \cdot \text{cm}^{-2} \cdot \text{Hz}^{1-n})$	n	$R_t/(\Omega \cdot \text{cm}^2)$
0 mg/L	0.5	1.759	337.3	0.8523	22.55
	1.0	1.398	386.2	0.8481	28.06
	1.5	1.412	431.8	0.8424	27.96
	2.0	1.411	475.1	0.8395	27.93
25 mg/L	0.5	3.146	188.5	0.7543	137.8
	1.0	3.525	76	1.0000	164.3
	1.5	3.370	261	0.7289	181.4
	2.0	3.780	81	1.0000	208.9
50 mg/L	0.5	4.230	91.3	1.0000	199.4
	1.0	4.792	93.5	0.9999	236.2
	1.5	4.812	96.5	0.9979	250.6
	2.0	4.023	114.6	0.9724	247.3
100 mg/L	0.5	6.235	78.8	0.9996	254.3
	1.0	6.234	87.6	0.9803	267.5
	1.5	6.458	80.3	0.9998	261.6
	2.0	6.754	81.6	0.9926	267.0

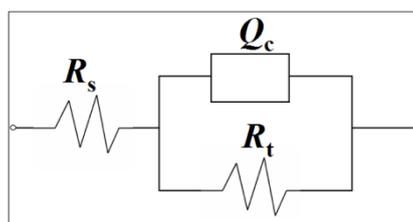


Figure 4. Equivalent electrical circuit used to fit the EIS data.

For the HCl solution in the presence of inhibitor, the R_s values did not change much during the immersion process, but the R_t were gradually increased, indicating that the corrosion rate of carbon steel electrodes were inhibited. For the pure HCl solution, the values of R_s and R_t were almost

unchanged with the immersion time, but they were far less than the HCl solution in the presence of inhibitor.

The values of R_t increased as the AT-PEG added into the 1.0 M HCl solution, which mainly due to the cover film was formed on the carbon steel surface, and the film reduced the contact areas between the corrosive medium and the carbon steel. From the Fig. 5a, the R_t values of different solutions with 0 mg/L, 25 mg/L, 50 mg/L, and 100 mg/L inhibitor were 27.93 $\Omega \text{ cm}^2$, 208.90 $\Omega \text{ cm}^2$, 254.3 $\Omega \text{ cm}^2$, and 267.03 $\Omega \text{ cm}^2$, respectively. Obviously, the R_t values were increased with the increase of AT-PEG concentration, and reached the mixture in the concentration of 100 mg/L. In addition, the corrosion inhibition efficiencies (η) of solution with inhibitor were calculated by means of the following equation [21-23]:

$$\eta = \frac{R_t - R_t^0}{R_t} \times 100\% \quad (4)$$

here, R_t^0 and R_t are charge transfer resistance for acid solution in the absence and presence of inhibitors, respectively.

It is seen that the η values increases with the increase of corrosion inhibitor concentration, and when the concentration was 100 mg/mL, the η value reached the maximum value of 90.50%. the results revealed that the HCl solution containing 100 mg/L of AT-PEG possessed the best corrosion protection performance for carbon steel.

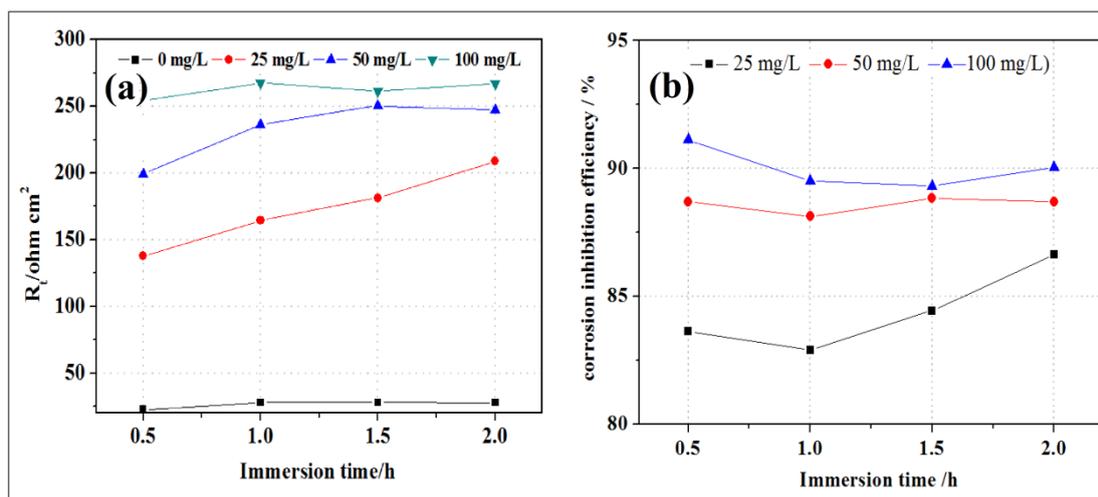


Figure 5. The charge transfer resistance R_t (a) and corrosion inhibition efficiency (b) of inhibitor in 1M HCl solution of after in different immersion time.

3.3 Tafel polarization measurements

In order to further study the corrosion reactions, the polarization measurements (Tafel plots) of Q235 carbon steel specimens were carried out in 1.0 M HCl in the presence of AT-PEG at room temperature, the results were shown in Fig. 6. The Tafel plots were analyzed, and the electrochemical data of corrosion current density (i_{corr}), corrosion potential (E_c vs. SCE), corrosion inhibition efficiency

($T\eta$), cathodic and anodic Tafel slopes (β_c and β_a) were fitted from extrapolation of Tafel lines and the final data were summarized in Table 3. In addition, the corrosion inhibition efficiency was also calculated via the following equation [17-19]:

$$CE = \frac{i_0 - i}{i_0} \times 100\% \quad (5)$$

here, the i_0 and i are corrosion current densities in 1.0 M HCl solution without and with inhibitor, respectively.

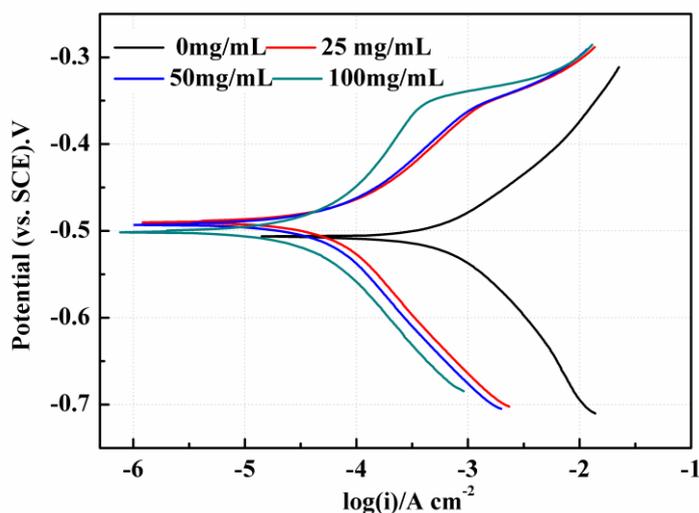


Figure 6. Polarization curves of inhibitor in 1M HCl solution: 0 mg/L (a), 25 mg/L (b), 50 mg/L (c), and 100 mg/L (d).

According to the data in the Table 3, the values of $T\eta$ and i_{corr} increased with the increase of AT-PEG concentration, and the value of E_c decreased with the concentration. The $T\eta$ values of different HCl solutions with AT-PEG were 83.10% (25 mg/L), 86.90% (50 mg/L), and 90.50% (100 mg/L), respectively. The results shown that the concentration with 100 mg/L of corrosion inhibitor in HCl solution possesses the best protective effect on carbon steel. This behavior can be explained as follows: the inhibitor adsorbed on the metal surface, the increase in concentration led to increased adsorption of the inhibitor, so that more metal surface and acidic media isolation, reducing the metal dissolution rate and improve the inhibition efficiency. So, the addition of AT-PEG causes the calculated i_{corr} values to shift towards more negative values, and the E_c values to shift towards more positive values.

As the result, there was a good agreement in the corrosion inhibition efficiency obtained by the EIS and Tafel polarization measurements.

Table 4. Corrosion parameters of carbon steel electrodes in 1M HCl solution with different concentration inhibitor after 2h.

AT-PEG (mg/L)	b_a (V/dec)	b_c (V/dec)	E_{corr} (vs SCE/mV)	I_{corr} ($\mu\text{A}\cdot\text{cm}^{-2}$)	$T\eta$ (%)
0	0.07	-0.11	-0.48	420	-
25	0.10	-0.13	-0.48	71	83.10
50	0.11	-0.12	-0.50	55	86.90
100	0.15	-0.13	-0.51	40	90.50

3.4 Morphological Measurements

The of surface morphologies of Q235 carbon steel samples without and with 100 mg/mL of AT-PEG in 1.0 M hydrochloric acid solution after 24 h immersion were investigated by scanning electron microscope (SEM) and the result were shown in Fig. 7. It is clear from the picture that the severely corroded surface morphology can be observed on the surface of the Q235 carbon steel in 1 M hydrochloric acid solution without any inhibitor. However, a thin and uniform film can be clear seen on the surface of Q235 carbon steel sample in the presence of 100 mg/mL AT-PEG, and very few corrosion products are observed on the surface of the Q235 carbon steel. This result indicates that AT-PEG can insulate the surface from the acidic medium by the adsorption on the carbon steel surface.

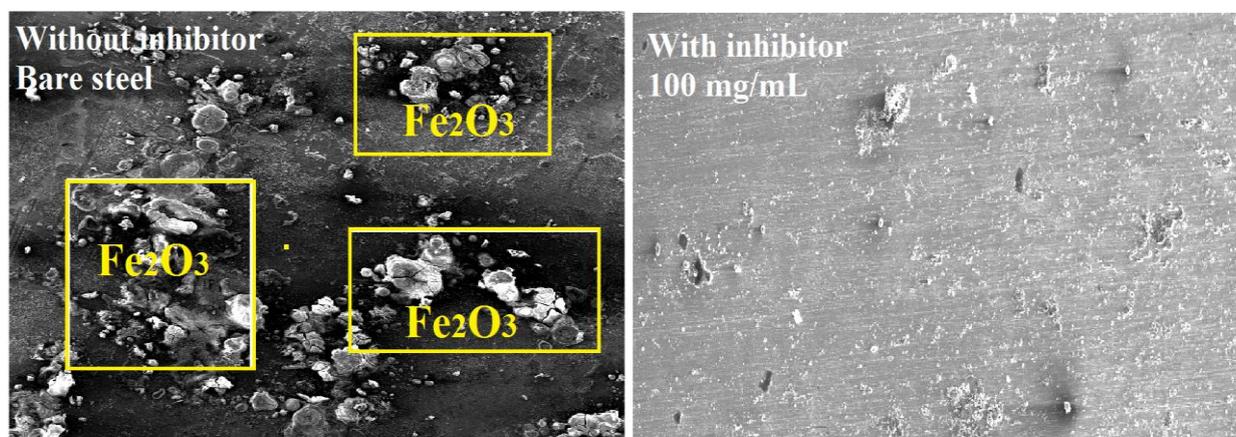


Figure 7. The SEM image of Q235 carbon steel surfaces without any inhibitor and with 100mg/ml inhibitor after immersion in HCl solution for 24h.

3.5 Postulated mechanism of inhibition

Generally, an inhibitor is not only can absorb on the metal surface to forming insoluble complexes, chelates, or a oxide film, but also prevent further dissolution of steel by blocking either the anodic or cathodic reaction. An excellent inhibitor depends mainly on its structure with the heteroatom (P, S, N, O), and these heteroatom are active centers for the process of inhibitor adsorption, which give higher electron density on the metal surfaces. According to Ahmed the inhibition efficiency of heteroatom are the sequence $O < N < S < P$, and the use of N and O atoms have been studied in some details to reduce corrosion attack on metal [24-25].

The AT-PEG is composed of two kinds of polar groups, which are N and O atoms with large electro negativity, and two kinds of nonpolar groups C and H atoms. In HCl solution, the N atoms of polar groups act as ligand with Fe to form chelate adsorption formation and absorbed on metal surface, thus changing the structure of electric double layer metal, improve the activation energy of metal ionization, and non polar groups are aligned on the metal surface and form a layer of hydrophobic membrane covering the metal surface, which protected metal from corrosion [26-27].

The inhibition efficiency of AT-PEG also can be explained as follow: when the inhibitor was added to the water, the amino groups (hydrophilic group) were adsorbed on the metal surface, and the alkyl groups (lipophilic group) were outward (corrosive environment). The organic amine covered on metal surface to form a layer of adsorption film, the alkyl groups in the adsorption film to prevent water, chloride and oxygen and other corrosive substances and metal contact, which played a role in preventing metal corrosion. Since the amino groups can be firmly adsorbed on the metal surface, it is possible to prevent the water flow rate from destroying the adsorbed film. The organic amine of AT-PEG can form a protective film on the metal surface through the existing corrosion products or dirt surfaces on the metal surface, which can be used not only for cleaner systems, but also for systems that have been in operation for some time and have some corrosion and dirt. The organic amine of AT-PEG penetrate through the corrosion products and attach to the metal surface, so that the dirt and corrosion products can be combined with each other relaxation, and the metal surface adhesion decreased, so that they gradually fall off and washed away by water. Therefore, AT-PEG possesses excellent corrosion resistance and resistance to chlorine in HCl solution [28-31].

4. CONCLUSIONS

In this work, the polymer AT-PEG was synthesized and characterized using ^1H NMR and FT-IR spectra. The electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization measurements were used to study the corrosion inhibition of mild steel in 1.0 M HCl solutions with different concentration of AT-PEG. The AT-PEG exhibited excellent inhibition performance as an effective corrosion inhibitor. In general, the acidic corrosion of mild steel was reduced by addition of an appropriate inhibitor concentration. The inhibition efficiencies obtained from the static weight loss method were comparable with those obtained from EIS data and polarization measurements, the inhibited solution had higher values than the uninhibited solution. And the SEM micrographs demonstrated that the AT-PEG form a cover film on the steel surface and exhibited a maximum inhibition efficiency of 92.50% with 100 mg/L AT-PEG.

It is noted that there were a little difference in the inhibition efficiency obtained from the static weight loss measurements and EIS, Tafel polarization measurements. This phenomenon can be attributed to the follow reasons: the static weight loss experiments give average corrosion rates, but the electrochemical experiments are instantaneous corrosion rates.

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