The Inhibition Effect of Polyethylenimine (PEI) on Pitting Corrosion of 304 Austenitic Stainless Steel in 3.5% NaCl Solution

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Abstract

One of the problems in the case of stainless steels is their low corrosion resistance against pitting corrosion in chloride containing environments, thereby leading to severe damage to industries. In this research, the pitting corrosion of 304 austenitic stainless steel was studied in 3.5% NaCl solution at room temperature (25˚C) by performing electrochemical measurements (containing cyclic polarization and electrochemical impedance spectroscopy) and immersion measurements. Moreover, the effect of adding different concentrations of PEI inhibitor with two mean molar masses (2000 and 60,000 g/mol) on pitting corrosion was investigated. Finally, the adsorption behavior of this inhibitor on the alloy surface was investigated by ATR-FT.IR and AFM methods. It was observed that both inhibitors prevented uniform and pitting corrosion successfully, but PEI (60,000 g/mol) had better inhibition efficiency than PEI (2000 g/mol).

Keywords: Pitting corrosion, Polyethyleneimine (PEI), Inhibitor, NaCl solution, Austenitic stainless steel

1. Introduction

Corrosion resistance of stainless steels is highly remarkable, but in some situations and environments, they are prone to certain types of corrosion, especially localized corrosion. This localized corrosion occurs mostly in solutions containing high concentrations of chlorides like sea water. If this localized corrosion is developed to a large extent, this attack can lead to severe damage or even failure of the components. As important examples, tanks are prone to leakage of fluids or gases as a result of corrosion damage. Significant reduction in the strength of a structure is another example of damage induced by corrosion and the subsequent failure. So, in such environments, the use of corrosion inhibitors can be very useful in order to protect the components from corrosion. In this way, an appropriate inhibitor is adsorbed on the surface, forming a corrosion resistant layer. The most common inhibitors are organic inhibitors. One of the most important advantages of inhibitors is that adding the inhibitor to the system does not lead to any disruption in an industrial process. An important rule in organic corrosion inhibitors is that they are just useful for corrosion resistance when they are added in small amounts. But at higher concentrations, additional testing for the effect of the environment is necessary [1, 2]. According to multiple adsorption sites in polymeric compounds, they have stronger adsorption than their monomer analogues on a metallic surface [3]. Thus, polymers are expected to have an appropriate inhibition behavior. Among polymers, those which have a longer hydrocarbon chain have less amount of solubility. So, in order to increase the amount of solubility, the presence of hydrophilic functional groups is necessary. Jianguo et al. [4] have shown that high molar mass PEI (50,000 g/mol) is a very effective corrosion inhibitor for low carbon steel in H_3PO_4. With the comparison of the PEI and polyvinylpyrrolidone (PVP) in 3M H_3PO_4, it was shown that when the concentration of PEI was about half of the concentration of PVP, PEI was as effective as PVP. Gao et al. [5] investigated the corrosion inhibition behavior of low carbon steel by quaternized PEI (QPEI) in 0.5 M H_2SO_4. The use of QPEI was to increase the corrosion resistance as a result of inhibition behavior. The quaternerizing agent in QPEI was Benzyl chloride and a PEI molecule with a ratio of 1:2:1 on primary, secondary and tertiary amine, respectively. It was expected that the adsorption of the synthesized molecule would be the result of physisorption and chemisorption and thus, the formation of protective layer could be because of the combination of two kinds of adsorption [5]. In this research, it was claimed that physisorption could proceed through a positively charged nitrogen atom and a negatively charged metal surface, while in chemisorptions, p-electrons of the benzene ring

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could act as donors for 3d orbitals of the iron, thereby leading to p-d complexes. Although this kind of corrosion mechanism was not proved and there was no evidence proving surface analysis, the experimental results showed remarkable inhibition efficiency (92%) at a concentration as low as 5 mg/L after 72 hours of immersion [5].

Beaglehole et al. [6] studied the adsorption and also, the inhibition behavior PEI (50,000 g/mol) on 304 stainless steel and on gold in sodium perchlorate solution using ellipsometry as a technique for the analysis of the adsorption process. A small change in the adsorbed quantity just occurred as the potential was altered and once the molecule was adsorbed, it remained adsorbed over the entire range of passive potentials. In the case of gold, they found out that when the potential was changed, PEI rotated, forming different conformations. Schweinsberg et al. [7] studied the inhibition behavior of PEI and found that PEI polymer could act as a mixed-type inhibitor for the corrosion protection of copper in H_2SO_4 electrolyte. In this research, the adsorption was almost because of nitrogen atoms, and this was validated by SERS. But PEI with the mean molar mass of 70,000 g/mol was not a very effective inhibitor for the protection of mild steel corrosion in neutral or slightly alkaline solutions containing Ca^{2+} and Cl^- ions [8]. By using PEI as the anchoring layer, in this situation, PEI was effective for layer-by-layer deposition of various polyelectrolytes [9, 10]. Besides this, it was found that PEI with heparin could be used as a coating on NiTi alloys, one of the important and widely used biomaterials. Dong et al. [11] have also shown that PEI/heparin multilayer film have corrosion resistance properties and also, blood compatibility. Besides this, PEI can also make an increase in silica dissolution, thereby preventing from scale silica formation [12–14], which is widely used for process water applications.

The general structure formula of PEI is $-(CH_2-CH_2-NH)_n-$. The PEI used in this work had a mean molar mass of 2000 and 60,000 g/mol. Figure 1 shows the branched-linked polymer structure. PEI is soluble in water, methanol, ethanol, n-propanol, isopropanol and only partially soluble in ethyl acetate, toluene and xylene.
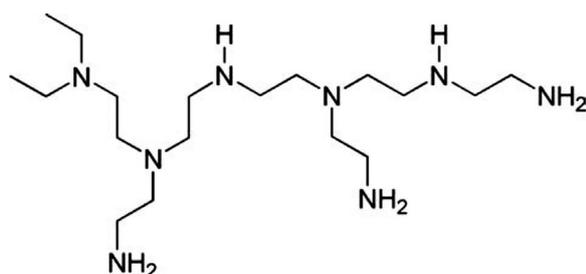

Fig. 1. Branched structure of polyethyleneimine.

As an important characteristic of PEI, the nitrogen atoms in PEI molecules are strong electron donors and thus, they represent active centers for organic adsorption. The process of adsorption in the polymer can take place through n electrons of the organics and vacant d-orbitals of the metal surface atoms by donor-acceptor interactions. There is also another idea proposed for the binding process [8]. According to this idea, when PEI is used in an acidic solution, it is positively charged due to the protonation of –N–, –NH– or $–NH_2$ groups. Therefore, in acidic solutions, PEI is considered as a cationic polymer which is bound to the negatively charged metal surface. According to the basis of adsorption process, when the corrosion potential is more negative than the pzc potential or, as in our study, when the solution contains chloride ions, the metal surface charge is negative. As chloride ions have a strong tendency to be adsorbed to the metallic surface, this leads to the formation of oriented dipoles, making the metal surface charge negative [15].

The purpose of this work was to provide a comparative study of different sizes of PEI (2000 and 60,000 g/mol) as corrosion inhibitors and to find their effect on 304 austenitic stainless steel at room temperature (25 °C) by using different techniques. In order to evaluate the corrosion rate, an aqueous 3.5% NaCl solution was used as corrosive solution.

2. Experimental
2.1. Specimen and solution preparation

As discussed above, the material used for corrosion testing was 304 austenitic stainless steel. It was applied as steel plate with dimensions of approximately 30 × 20 × 1 mm^3 for immersion testing and 10 × 10 × 1 mm^3 for electrochemical measurement. The chemical composition of the steel is given in Table 1.

Table 1. Chemical composition of 304 stainless steel used

Element	C	Mn	Si	Cr	Ni	P	S
Wt%	0.08	2.00	0.75	18.00	8.00	0.045	0.30

The specimens were polished mechanically to a mirror finish with Al_2O_3 powder (0.3 and 0.05μ). Then the specimens were rinsed with distilled water and degreased in acetone and dried in a hot air stream; finally in order to prevent the specimens from re-oxidation, they were put in a desiccator. Polyethyleneimine with the mean molar mass of 2000 and 60,000 g/mol was prepared as a 50% (w) mixture in water. The inhibitor was dissolved in 3.5% (w) aqueous NaCl solution and thus, the desired solutions had the concentrations of 250, 1000 and 2500 ppm. The inhibitors were supplied by Aldrich.

2.2. Electrochemical measurements

Electrochemical measurements were performed in a three-electrode corrosion cell with the volume of 250 mL and 304 stainless steel was used as the working electrode (WE). Experiments were performed at room temperature. The area of the working electrode which was exposed to the desired solution was 1 cm². Platinum and Saturated Calomel electrode were used as counter and reference electrode (RE), respectively. Therefore, all potentials in this research are stated versus saturated calomel electrode (SCE). In order to minimize the IR drop, the RE and WE were as low as possible.

These electrochemical techniques were performed: cyclic polarization (CP) and electrochemical impedance spectroscopy (EIS). Before electrochemical measurements, the specimens were immersed in the solution for 1 hour and therefore, the stabilization process was done. Cyclic polarization started at -200 mV vs. E_{corr} and potential scan rate were switched at 10^{-3} A/cm² current density and not related to a specific potential. The potential was switched after this and continued in cathodic direction to 0 V vs. E_{corr}. The potential scan rate in CP measurements was 0.5 mV/s. CP measurements were performed using an EG&G potentiostat/galvanostat model 263A controlled by a PowerSuite program.

EIS measurements were performed at the corrosion potential in the potentiostatic mode, by applying a 10 mV amplitude sinusoidal wave perturbation to the corroding system. The frequency values usually ranged from 100 kHz to 10 mHz. EIS measurements were performed using an EG&G potentiostat/galvanostat model 263A controlled by a PowerSuite program. The spectra were recorded with an Electrochemical Interface SOLARTRON Mod. 1287 and a Frequency Response Analyser SOLARTRON Mod. 1260.

2.3. Immersion tests

In order to validate the electrochemical measurements results and also evaluate the inhibition effect more accurately, immersion tests were performed for 304 stainless steels in 3.5% NaCl solution in the presence of 250, 1000 and 2500 ppm concentration of inhibitor. Immersion tests were performed at room temperature according to the ASTM G31. According to this standard, the volume of solution (vs. mL) should be at least 15 times more than the effective surface of the specimens (vs. cm²) [16]. So, given the fact that the effective surface of the specimens was 12 cm², the volume of the solutions in this test was 250 mL.

After 45 days of immersion, the specimens were rinsed with deionized water; after removing the corrosion products, specimens were rinsed again with deionized water, dried under the stream of air and microscopic observations were performed by optical microscopy.

2.4. Fourier transform infrared spectroscopy analysis (ATR-FT.IR) and AFM topography-phase graphs

Infrared spectra of inhibitor films formed on the surface of the specimens were measured by a VERTEX 70 FT-IR spectrometer with ATR accessory. In order to compare the amount of inhibitor adsorption on the surface in the solution containing two inhibitors, ATR-FTIR measurements were performed. In order to analyze the spectra, IR solution software was used. In order to omit the strong disturbances of IR absorbance due to carbon dioxide and water adsorbed on the surface of the samples, the absorbance backgrounds of carbon dioxide and water were taken out during data recording in all experiments.

AFM measurements were performed in order to investigate the adsorption mechanism of inhibitors (2000 and 60,000 g/mol) on the surface. Also, AFM experiments were performed at room temperature with a commercial AFM (Dualscope/ Rasterscope C26). The force curves were measured in tapping mode using Si_3N_4 tips. The preparation of the specimens for AFM measurements was the same as ATR-FT.IR measurements. Specimens prepared in 3.5% NaCl containing 1000 ppm of inhibitor by the mean molar mass of 2000 and 60,000 g/mol were immersed in test solutions for 1 hour; then they were taken out of the electrolytes and rinsed with distilled water and dried in the air for measurement. In order to compare the results, these measurements were performed for one specimen in a solution without inhibitor.

3. Results and discussion
3.1. Cyclic polarization (CP) measurements

The cyclic polarization (CP) technique is a very suitable way used to observe and study the active and passive behavior of a metal. Besides this, studying the localized forms of corrosion becomes possible. In this area, breakdown potential, E_{bd} or E_{pit}, is defined as the potential in the forward scan at which the current density in the passive range suddenly is increased. Also repassivation potential, E_{rp}, is defined as the potential in the reverse scan at which current is zero [17].

Several measurements were conducted at each concentration for obtaining a representative curve. CP curves of 3.5% NaCl solution with the addition of 0, 250, 1000 and 2500 ppm PEI and two mean molar masses of 2000 and 60,000 g/mol for 304 stainless steels were obtained. So the desired data related to 304 stainless steel at room temperature are presented here in Figure 2.
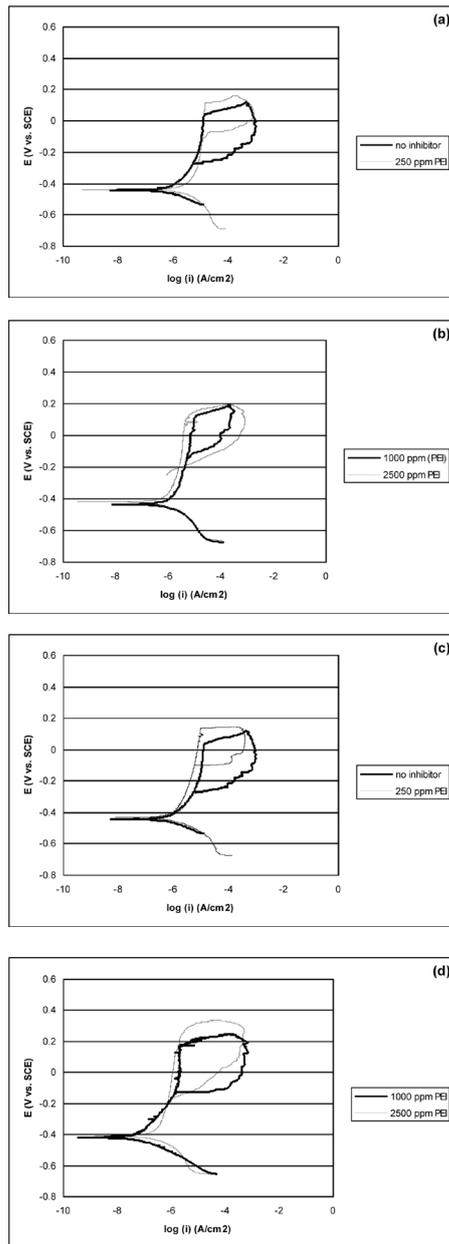
Fig. 2. Cyclic polarization curves for 304 stainless steel at room temperature, a,b) PEI (2000 g/mol), c,d) PEI (60,000 g/mol).

The values of E_{bd} and E_{rp} for 304 stainless steel are also given in Table 2.

The only reducible species in the solution were dissolved oxygen and hydrogen ions.

The treatment of the cathodic part in CP curve was primarily defined by hydrogen evolution and then, at a potential near and below the E_{corr}, the reduction of the dissolved oxygen was controlled by mass transport. From Figure 2, it can be observed that the presence of PEI didn't have a remarkable influence in the cathodic branch of the diagram. Given that E_{corr} is moving toward the anodic direction, it shows that PEI acts as an anodic inhibitor.

According to Figure 2, by increasing PEI concentration, E_{pitt} was increased, thereby showing the increase in pitting corrosion resistance by increasing the PEI concentration. But it was seen that the rate of increase in E_{pitt} was decreased at concentrations over 1000 ppm. In other words, it can be said that adding concentrations more than 1000 ppm of inhibitor doesn't have a significant effect on increasing the pitting corrosion resistance. Thus the optimum concentration for the prevention of pitting corrosion is 1000 ppm for both inhibitors. This shift in E_{pitt} showed that the presence of PEI led to more resistivity against pitting corrosion [18]. In transpassive region, it is known that the protective film is damaged and the initiation of pits can begin at discrete locations on the metal surface. In all these cases, a positive hysteresis was observed, showing that in this manner, the desired solution was too corrosive and the applied potential was too positive to allow the repassivation process to occur. This means that when pitting corrosion starts, inhibitor can no longer prevent it again. At this manner, pits will continue to grow when E_{corr} is greater than E_{rp} [18]. In all measured solutions, the value of E_{corr} was more positive than the value of E_{rp}, thereby validating the statements about positive hysteresis. This also proves the inability to stop the localized attack after its initiation.

3.2. Electrochemical impedance measurements

EIS diagrams for 304 stainless steel are presented in Figure 3.

Table 2. E_{pit}, E_{rp} and i_{pass} values for 304 stainless steel in 3.5% NaCl solution containing two different concentrations of the inhibitor (PEI).

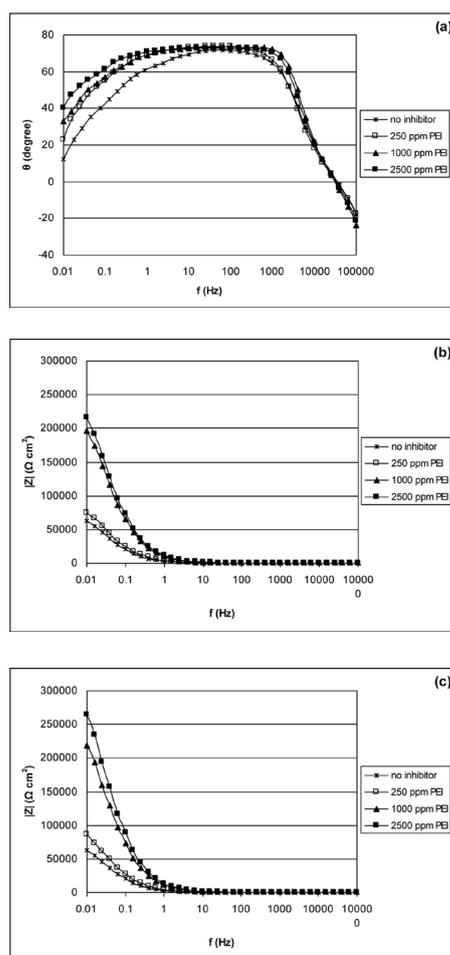|	Inhibitor concentration (ppm)	E_{corr}(V vs. SCE)	E_{pit}(V vs. SCE)	E_{rp}(V vs. SCE)	i_{pass}(V vs. SCE)
3.5% NaCl	-	-0.452	0.034	-0.284	13.51
3.5% NaCl + PEI (2000 g/mol)	250	-0.435	0.106	-0.276	9.68
	1000	-0.416	0.145	-0.281	6.28
	2500	-0.407	0.181	-0.273	4.18
3.5% NaCl + PEI (60000 g/mol)	250	-0.444	0.161	-0.271	8.86
	1000	-0.429	0.272	-0.269	5.57
	2500	-0.411	0.332	-0.276	2.38

Fig. 3. EIS diagrams for 304 stainless steel, a) bode-phase diagram for PEI (2000 g/mol), b) bode diagram for PEI (2000 g/mol), c) bode diagram for PEI (60,000 g/mol).

According to bode diagrams, by increasing the inhibitor concentration, the value of |Z| at low frequency range was increased, indicating an increase in corrosion resistance by increasing the inhibitor concentration. Moreover, in Bode-Phase diagram (Fig. 3a), there was a capacitive region with a maximum phase angle at medium frequency range, which was due to a passive layer on the surface of alloy [19]. This passive range in this manner got wider by increasing the inhibitor concentration and shifted to lower frequencies. This showed the formation of a more resistant layer on the surface of stainless steel [18,20]. So the impedance data could be modeled by an equivalent circuit shown in Fig. 4, which also presents the double layer physical model of inhibitor on alloy surface [19-21]. Two constant phase elements (CPE) were replaced with two ideal capacitors in order to calculate the observed deflection [22].
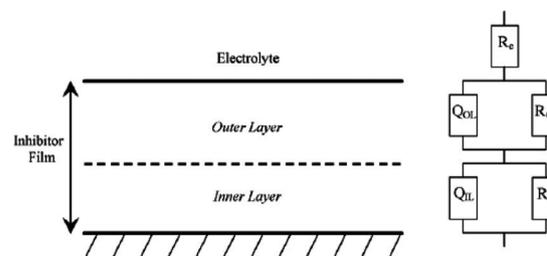

Fig. 4. Equivalent circuit and its physical model in EIS measurements.

Fitness of this equivalent circuit with impedance data was in agreement with protective double layer nature formed on the surface of stainless steel. The inner layer of inhibitor was a very thin and compacted layer covered with an outer thick and porous layer in contact with the desired solution. Impedance data were analyzed by Zview software and equivalent parameters were calculated as presented in table 4. Moreover, the changing behavior of the total resistance of the protective layer versus inhibitor concentration is presented in table 3.

As shown, for 304 stainless steel, the resistance of protective layer was increased by increasing the inhibitor concentration, showing the effective inhibition of PEI was 1000 ppm. But at concentrations higher than 1000 ppm, adding PEI had a little effect on increasing the protective layer resistivity. It can be concluded that the optimum concentration of inhibitor for the prevention of uniform corrosion was 1000 ppm. From data in table 3, it was found that by increasing the PEI concentration, the total capacitance (C_t) was decreased due to the reverse relation between capacitance and layer thickness [19]. It can be concluded that increasing the inhibitor concentration leads to the increase in layer thickness.

Table 3. Obtained results from EIS measurements for 304 stainless steel at room temperature in 3.5% NaCl solution containing two different concentrations of the inhibitor (PEI).

	Inhibitor concentration (ppm)	R_1 (kΩ.cm^2)	C_1 (μF.cm^{-2})	R_2 (kΩ.cm^2)	C_2 (μF.cm^{-2})	R_t (kΩ.cm^2)	C_t (μF.cm^{-2})
3.5% NaCl	-	56.71	32.76	-	-	56.71	32.76
3.5% NaCl + PEI (2000 g/mol)	250	67.70	28.60	1.29	6.12	68.99	5.04
	1000	177.07	17.24	4.69	3.82	181.76	3.13
	2500	194.69	11.03	7.12	2.56	201.81	2.08
3.5% NaCl + PEI (60000 g/mol)	250	72.79	21.02	2.12	5.78	74.91	5.78
	1000	192.11	14.56	6.18	3.70	198.29	3.70
	2500	229.50	9.72	7.78	2.21	237.28	2.21

The higher polarization resistance of the formed layer can also be considered through the comparison of inhibition efficiency of these two inhibitors. Inhibitor efficiency is calculated through equation 1 and its results are presented in Figure 5.

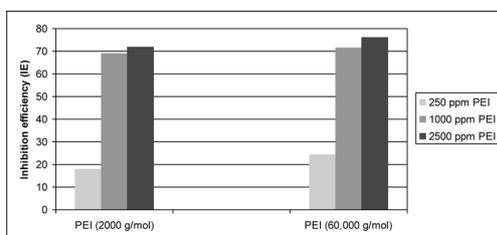$$E = \frac{R_p(inhibited) - R_p(uninhibited)}{R_p(inhibited)} \times 100 \qquad (1)$$

Fig. 5. Inhibition efficiency of PEI (2000 and 60,000 g/mol) for 304 stainless steel obtained from EIS measurements.

As can be seen in Fig. 5, inhibition efficiency of PEI (60,000 g/mol) was more than PEI (2000 g/mol).

3.3. Immersion measurements

In order to evaluate the effect of PEI inhibitor on the pitting corrosion of 304 stainless steel, microscopic observations were performed from the surface of immersed specimens by optical microscopy. This investigation was performed to compare the number of pits formed on the alloy surface and those performed after the removal of corrosion products from alloy surface. These microscopic graphs are presented in Figure 6.

According to this figure, by increasing the inhibitor concentration, the number and also, the size of pits were decreased. It was also shown that at the concentration of 2500 ppm of inhibitor, the pitting corrosion was inhibited very successfully.
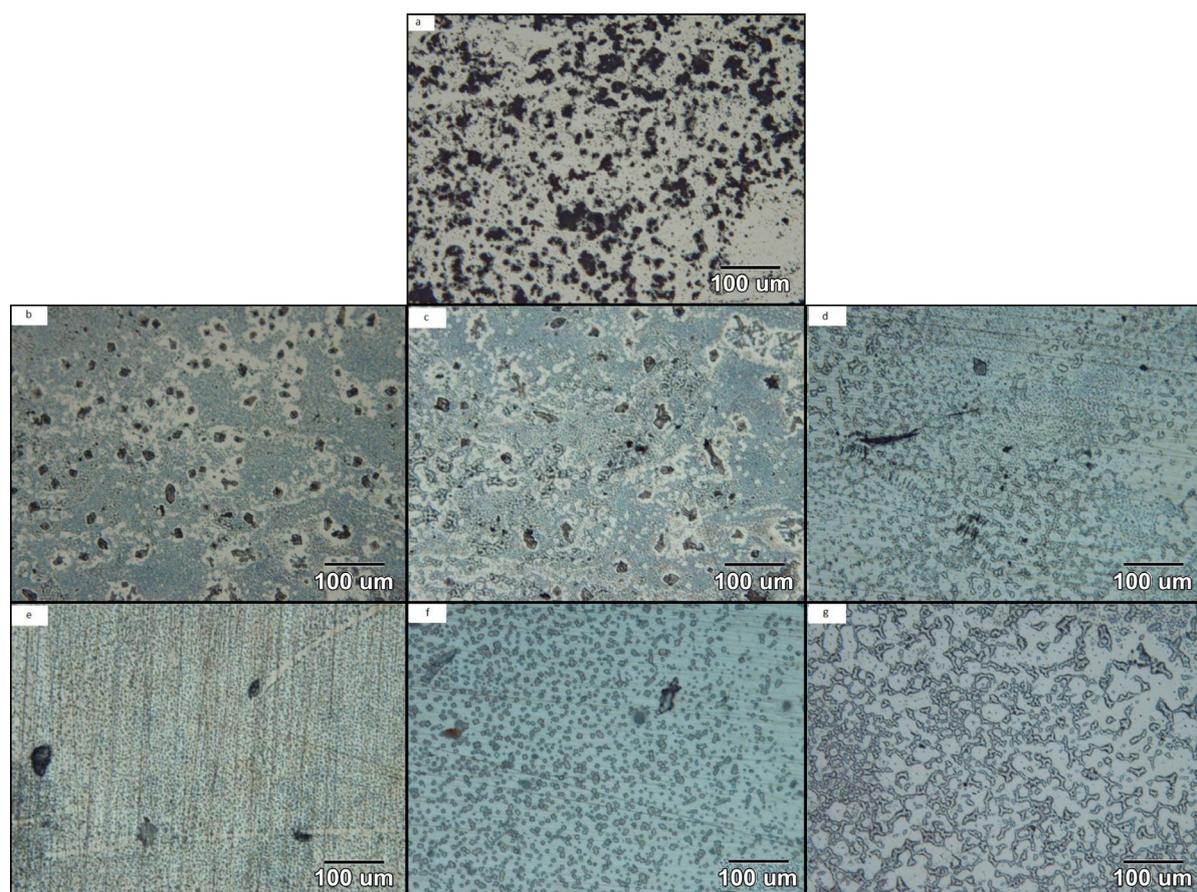
Fig. 6. Optical microscopy diagrams obtained from 304 stainless steel surface in solutions containing 3.5% NaCl, a) without inhibitor, b) 250 ppm PEI(2000 g/mol), c) 250 ppm PEI(60,000 g/mol), d) 1000 ppm PEI(2000 g/mol), e) 1000 ppm PEI(60,000 g/mol), f) 2500 ppm PEI(2000 g/mol), g) 2500 ppm PEI(60,000 g/mol).

3.4. Fourier transform infrared spectroscopy analysis (ATR-FT.IR) and AFM topography-phase graphs ATR-FT.IR measurements are widely used for the determination the adsorption amount of inhibitor on the surface [23]. In this method, the peak intensities indicate the adsorption amount of species on the surface [24]. In this research, the adsorption amount of PEI with two mean molar masses (2000 and 60,000 g/mol) were compared. Figure 7 Shows the FT.IR spectra of PEI polymer.

The FT.IR spectra of 304 stainless steel surface after 1 hour immersion in 3.5% NaCl solution containing 1000 ppm of PEI with different mean molar masses are also presented in Figure 8.

As shown in Fig. 8, adsorption in the wave numbers of 1568.2, 1475.44, 1313.43 cm^{-1} indicated the presence of N-H bond in primary, secondary and tertiary amines, respectively. Moreover, adsorption at the wave number of 1112.85 cm^{-1} showed the presence of C-N bond [25]. According to the FT-IR spectra of the formed inhibitor layer on alloy surface, it was found that each of four peaks in spectra was observed but with a higher number of the waves. This showed the adsorption of both kinds of PEI on the surface of stainless steel.

It can also be stated that according to the spectra of the formed layer in the presence of PEI with the mean molar mass of 2000 and 60,000 g/mol, spectra related to PEI (60,000 g/mol) showed a stronger adsorption. This revealed that the thickness of the layer formed in the presence of PEI (60,000 g/mol) was more than that of the other mean molar mass [24,26]. This validated the results obtained from electrochemical and immersion measurements, because the stronger adsorption of an inhibitor and the increase inthe thickness of the inhibitor layer can demonstrate a more effective inhibition effect.

As shown before, electrochemical and immersion measurements indicated the better inhibition behavior for PEI (60,000 g/mol) than PEI (2000 g/mol) and in this section, ATR-FT.IR measurements also revealed this issue.

Figure 9 shows the atomic force microscopy (AFM) graphs of 304 stainless steel surface after 1 hour immersion in solution without and also, with 1000 ppm of PEI.

The relative porous passive layer shoed in topographic graphs is the secondary layer explained in EIS measurements. It is in contact with the solution. But it should be noted that under this porous layer, there is a compact layer covering the overall surface of steel. This can also be understood from AFM phase graphs because it showed that by adding PEI to solution, phase changes would be observed all over the surface; thus it can be said that the inhibitor layer exists all over the stainless steel surface, thus preventing the contact between steel and solution [24]. The results obtained from AFM measurements were completely in agreement with those obtained from EIS measurements, thereby validating the double layer manner of surface adsorption mechanism of PEI.
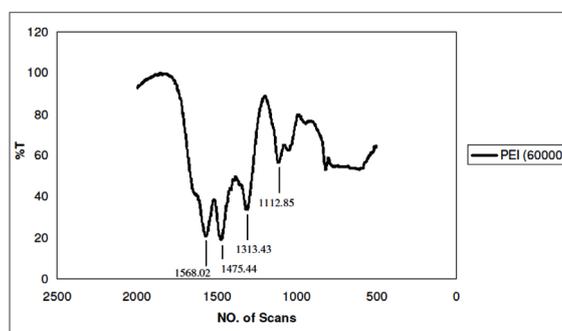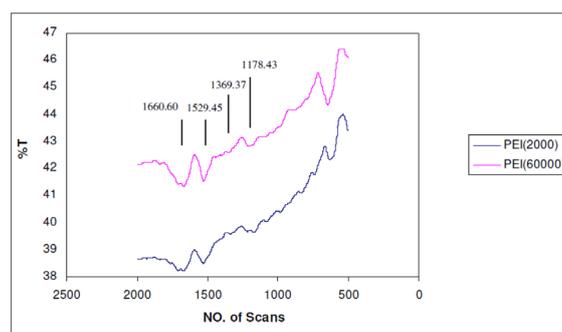

Fig. 7. FT-IR spectra of PEI (60,000 g/mol).

Fig. 8. ATR-FT.IR spectra of stainless steel specimens surface immersed in solutions containing the inhibitor.
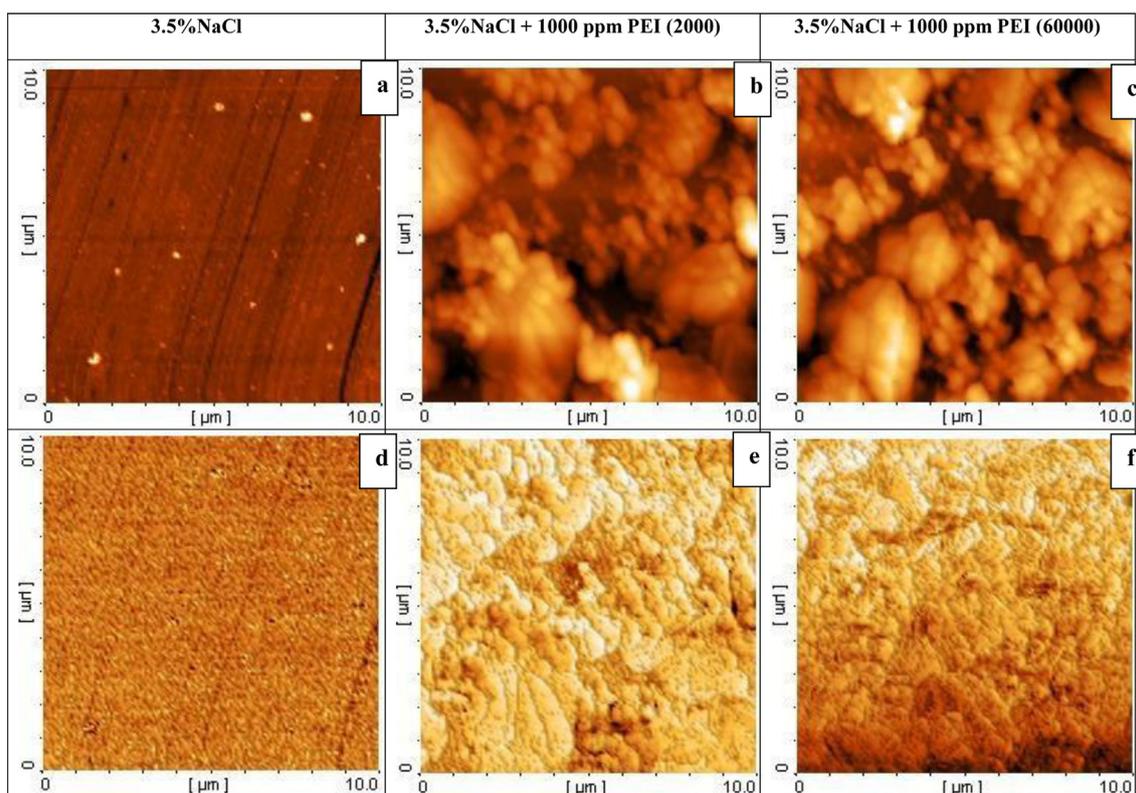
Fig. 9. Diagrams of the surface layer for 304 stainless steel by AFM: a,b,c,) topographic diagrams and d,e,f) phase diagrams.

4. Conclusions

According to the performed measurements, the following conclusions can be drawn:

1. Both PEI inhibitors with 2000 and 60,000 g/mol mean molar masses had a remarkable effect on the prevention of uniform and pitting corrosion of 304 austenitic stainless steel in 3.5% NaCl solution. This was due to the results obtained from measurements. For example, in EIS measurements, the inhibition efficiency for PEI (2000 g/mol) and PEI (60,000 g/mol) was 87% and 91% respectively, which were considered high efficiencies. Moreover, these inhibitors increased E_{pit} by 93% and 201% respectively.

2. According to electrochemical measurements (CP and EIS) and also immersion measurements, it was observed that PEI with 60,000 g/mol mean molar mass had a better inhibition behavior than PEI with 2000 g/mol mean molar mass against both uniform and pitting corrosion.

3. EIS measurements showed that with increasing the inhibitor concentration, the thickness of passive surface layer was increased, leading to the increase in the corrosion resistance of the substrate alloy.

4. Immersion tests validated the results from electrochemical measurements. It was observed that by increasing the inhibitor concentration, the number of pits per unit area was decreased. Moreover, it was observed that the amount of pitting corrosion in the presence of PEI(60,000 g/mol) was less than that in the presence of PEI (2000 g/mol). These results were also obtained in electrochemical measurements.

5. ATR-FT.IR and AFM measurements also showed the better adsorption of PEI (60,000 g/mol) than PEI (2000 g/mol). These results were also in agreement with those obtained from electrochemical and immersion measurements.

6. According to EIS and AFM measurements, it was observed that the inhibition mechanism of PEI was surface adsorption in the form of a double layer (the upper passive porous layer and the inner compact layer).

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