Int. J. Electrochem. Sci., 10 **(2015)** 10389 - 10401

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Poly (ionic liquid) Based on Modified Ionic Polyacrylamide for Inhibition Steel Corrosion in Acid Solution

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Received: 10 September 2015 / *Accepted:* 6 October 2015 / *Published:* 4 November 2015

The green method to protect steel from corrosion becomes target for corrosion science. In this work, synthesis of new poly(ionic liquid) as green inhibitor with lower concentration is used to protect carbon steel from aci corrosion. In this respect, poly(ionic liquid) based on 2-acrylamido-2-methylpropane sulfonic acid, AMPS, was synthesized without solvent in the presence of diethyl ethanolamine (DEEA) as reagent and solvent. The chemical structure of PAMPS-DEA was confirmed by NMR analyses. The wettability of the prepared PAMPS-DEA was confirmed from contact angle measurements. The inhibition activity of poly(AMPS) and PAMPS-DEA for steel in acidic chloride solution was tested using electrochemical techniques. The synthesized Ionic liquids PAMPS-DEA shows an excellent corrosion inhibition performance for steel in 1 M HCl medium at concentration of 5 ppm. The adsorption of IL on steel surface blocked the active centers, which lowered the corrosion rate of steel.

Keywords: Poly (ionic liquid); Steel; Acid corrosion, inhibition, EIS, polarization.

1. INTRODUCTION

Recently amphiphilic ionic liquids (AILs), having a long-chain hydrophobic tail and a polar hydrophilic head, among several materials have been applied as protective coats or corrosion inhibitors to protect metallic substrates from corrosion damages [1-5]. Their low toxicity, good electrical conductivity, high thermal stability, high viscosity and low volatility are the main advantages of these materials to be one of the most favorable green anticorrosion chemicals [6, 7]. The AILs are capable of forming adsorption flexible film at interfaces to reduce both interfacial tension and e the wetting of aggressive media on the steel surfaces which are responsible for corrosion inhibition of metals [6].

They have large tendency to be chemically bonded or physically adsorbed at the surface metal substrates to protect them from corrosive environments [7]. ILs can be applied using several techniques such as electrodeposition, corrosion inhibitors, conversion plating solution and coatings to mitigate materials corrosion [8-10]. It is well known that carbon steel as metal substrate has been widely used in several industrial applications due to its good mechanical properties and cheap prices than other metal substrates [11]. Its chemical composition suffers from absence of Noble metals that increases its ability to damage form surround corrosive environments [12]. On the other hand, there are some of ILs cause damages for metal substrates depending on their kinds [13]. For this reason, it is very important to explore new strategies to overcome this problem. Amphiphilic polymers have several advantages than their monomers to act as corrosion inhibitors [14] due to lower sensitivity to salts, high shear and thermal stability, high resistivity to strong acid and their efficiencies at lower concentrations [9, 15-18]. For these reasons polymeric ionic liquids or poly (ionic liquid)s (PILs) become more favorable than their monomers in the field of anticorrosion.

PILs are a macromolecular architecture of functional materials based on IL monomers connected through a polymeric backbone [18, 19]. The modification of PIL characteristics (density, viscosity, and surface tension) are of great importance for their application [20]. Synthesis and purification PIL attracted further developments due to their valuable applications as green materials in the materials sciences such as metal protection, catalysis, nanomaterials, etc. [18]. PIL with functionalized imidazolium and pyridinium cations gathered from the literature [21-23] can be copolymerized to control segmental motion and chain packing for modifying their industrial applications. The imidazolium and pyridinium cations can be converted to polymerizable monomers by functionalization with vinyl, acrylic or styryl moieties [24-26]. One of the main obstacles to produce imidazolium and pyridinium cations is their high production cost. However, the choosing of new cheaper cations rather than imidazolium or pyridinium can be reduced the production cost [27]. Moreover, more energy efficient techniques are used to reduce the cost [28]. In this respect, the present work extends previous works that succeeded to prepare PILs based on acrylamides followed by quaternization with aliphatic tertiary amine at room temperature [29-30]. The present work aims to promote an ionic liquid character of 2-acrylamido-2-methylpropane sulfonic acid (AMPS) to increase its wettability and adorability at steel surfaces. The quaternization of AMPS with diethyl ethanolamine (DEEA) reported here promotes a wetting actuation of poly(AMPS). The corrosion inhibition activity of the prepared PIL for steel in acidic chloride solution was investigated using electrochemical techniques and contact angle measurements at different concentrations of poly(AMPS) and its IL with DEEA (PAMPS-DEA).

2. EXPERIMENTAL

2.1 Materials

Diethyl ethanolamine (DEEA), and 2-acrylamido-2-methylpropane sulfonic acid (AMPS) were purchased from Sigma Aldrich Chemicals Co. 2,2-Azobisisobutyronitrile, AIBN, produced by Merck was recrystallized from methanol solution to use as radical initiator. The radical polymerization of AMPS was carried out in water as solvent as reported in previous work [31].

Steel was used as working electrode and has a chemical composition described in details in a previous work [32]. Platinum sheet and SCE were used as counter and reference electrode.

2.2. Synthesis procedure

Equal molar ratios of AMPS and DEEA were mixed into a nitrogen purged 50 ml flask at room temperature to dissolve AMPS for 8 hr to produce transparent light amber oil. AIBN (0.6 wt. % related to AMPS monomer) was added to the reaction mixture and the reaction temperature increased up to 70 ^oC for 18 hr. The reaction mixture cooled to room temperature to produce transparent dark amber mixture. The product was dissolved in ethanol with concentration of 20 Wt % and precipitated into 5 folds of acetone and filtrated under vacuum. The wax white product was dried under vacuum to obtain transparent amber oil with % yield polymer 98.2% and melting temperature 42 ^oC. The produced polymer was designated as PAMPS-DEA.

2.3. Characterization

The chemical structure of the PAMPS-DEA was confirmed by ^1H- and $^{13}CNMR$ analyses that recorded on a 400MHz Bruker Avance DRX-400 spectrometer.

Contact angles between steel surfaces and different concentrations of PAMPS-DEA and Poly(AMPS) in aqueous and 1M HCl were measured using drop shape analyzer model DSA-100 at 25 ^oC. The ageing time of contact angle measurements was measured from zero time up to 30 minutes until the contact angles reach the equilibrium. The advancing contact angle was measured using sessile drop technique. The needle of the instrument is located close to the steel surface and the volume of the droplet is gradually increased while recording at the same time the contact angle.

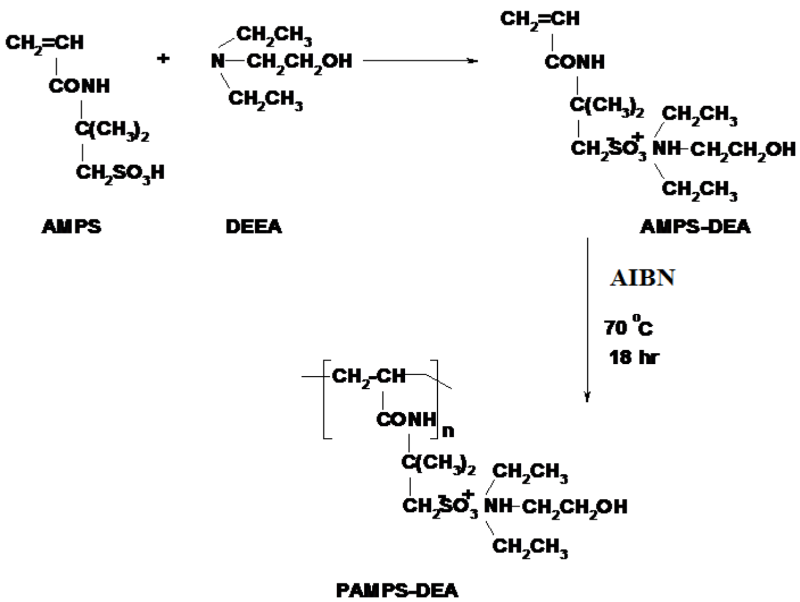
Scanning electron microscope (SEM; Model JEOL-JSM-5400) was used to scan the steel microstructure.

2.4. Electrochemical measurements

All electrochemical experiments were performed using a potentiostat (Solartron 1470E system) with Solartron 1455A as FRA. The potentiodynamic polarization curves were recorded with a scan rate of 1 mV/s. The EIS measurements were carried out in a frequency range from 10 kHz to 10 mHz..

3. RESULTS AND DISCUSSION

Ionic polymers based of AMPS showed excellent characteristics as polyelectrolytes [33-35]. The present work aims to introduce oxyethylene ammonium counter ion into the ionic liquid polymer system to promote the wetting characteristics to form anticorrosion protective layer at the solid surfaces. The proposed chemical structure of the AMPS monomeric and polymeric ionic liquid is represented in Scheme 1.



Scheme 1. Preparation of PIL based on PAMPS-DEA.

The DEEA is selected in the present work as solvent to solubilize AMPS monomer at room temperature and to prepare polymerizable ionic liquid monomer AMPS-DEA. It is converted to poly(ionic liquid) by radical polymerization the acrylic group of AMPS-DEA monomer. The presence of ethanol group in the chemical structure of DEEA assists its quaternization without coordinating of protonated amine center with the sulfonated anion. This was elucidated from depression the melting point of AMPS from 192 to 42 ^{o}C due to formation of PAMPS-DEA.

3.1. Characterization of PAMPS-DEA

The chemical structure of PAMPS-DEA is elucidated from ^{1}HNMR and ^{13}CNMR as represented in Figures 1 and 2, respectively. In this respect, the polymerization of AMPS – DEA is confirmed from disappearance of acrylic (CH_2=CHCON-) proton peaks at chemical shifts (δ) 6.03 (dd, 1H, J = 17.1 Hz), 5.94 (dd, 1H, J = 17.1 Hz) and 5.49 ppm (dd, 1H, J = 3.06 Hz), it was not represented here for brevity, and appearance of new broad peaks (Figure 1) of polymerized protons –CH_2-CH- at δ 1.2 and 3.2 ppm, respectively. The appearance of broad peaks at δ 9.11 (br s, 1H) and 7.16 (br s, 1H) that attributed to cationic +NH and SO_3H, respectively confirms the quaternization of DEEA with AMPS to form IL. More details of peaks at 3.73 (s, 2 H), 3.57-3.50 (m, 6H), 3.49-3.44 (m, 6H), 3.35-3.30 (m, 6H), 2.68 (s, 1H), and 0.62 (t, J = 4.71 Hz) represented in Figure 1 to confirm the chemical structure of PAMPS-DEA.

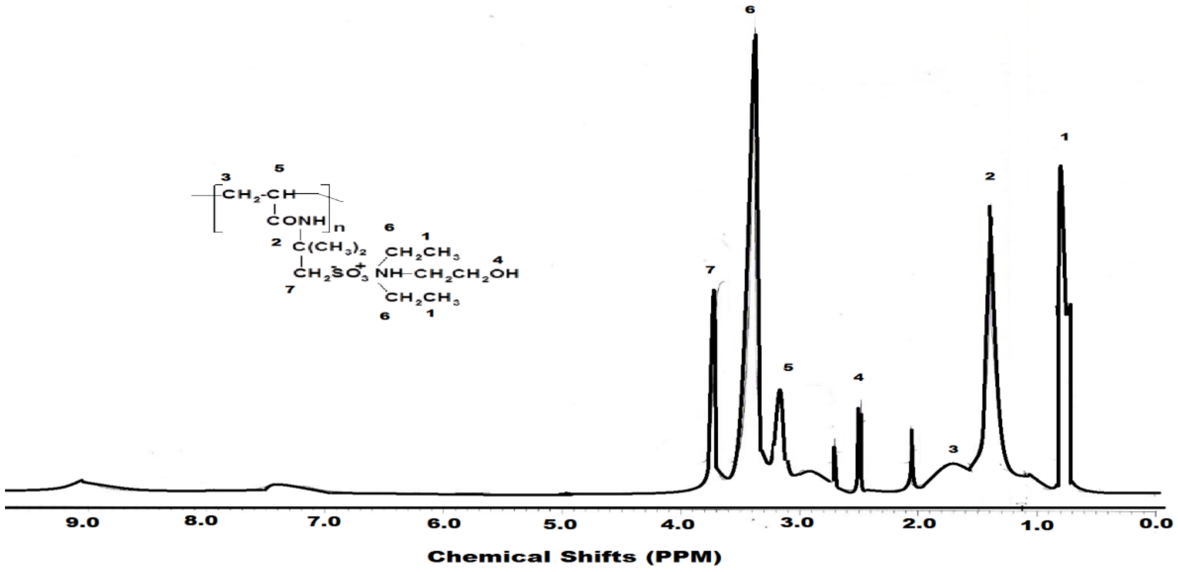


Figure 1. ^{1}HNMR spectrum of PAMPS-DEA.

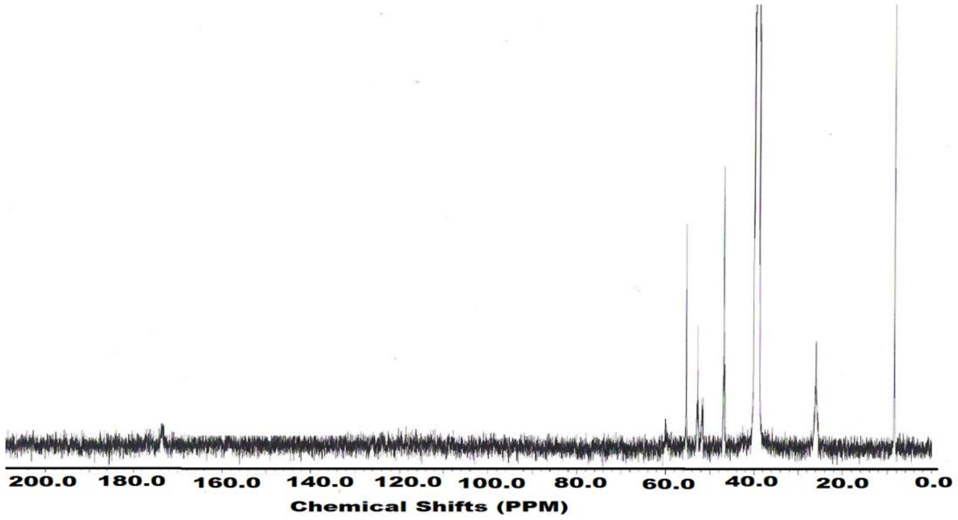


Figure 2. ^{13}CNMR spectrum of PAMPS-DEA.

^{13}C NMR spectrum of PAMPS-DEA (Figure 2) shows peaks at δ 173.58 (CON), 60.06 (C-N^{+}), 58.13 (C-SO3^{-}), 40.3 (C-SO_3^{-}) 26.84 (CH) and 10 ppm (CH_3) that confirm the formation of IL. The polymerization of AMPS-DEA is confirmed by the disappearance of C=C peaks at 122-130 ppm.

The wetting characteristics for different concentrations of poly(AMPS) and PAMPS-DEA in water and 1M HCl solutions from contact angle measurements at the steel surface to investigate their abilities to form thin layer on the steel surfaces. The contact angles data versus ageing time for blank water and 1M HCl solutions and poly(AMPS), PAMPS-DEA solutions at the steel surface are represented in Figure 3.

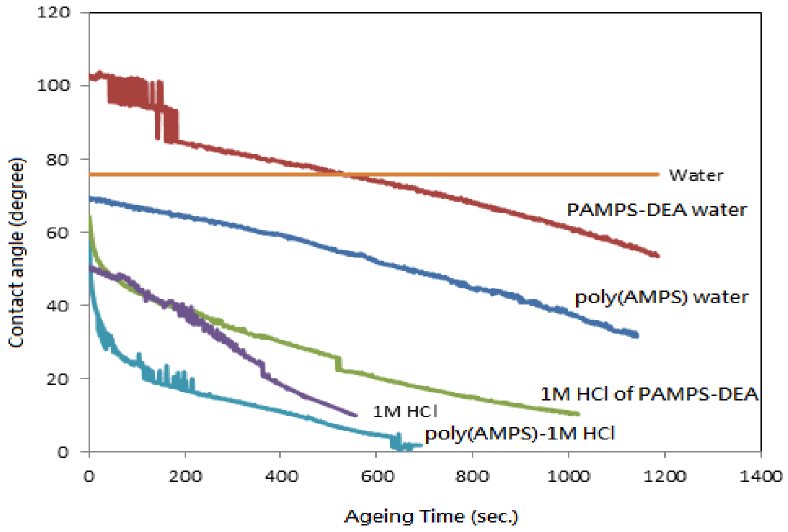


Figure 3. Effect of ageing time on contact angle measurements of the 100 ppm and 5 ppm of poly(AMPS) and PAMPS-DEA on the steel surface at 25 °C.

Their contact angles average values were listed in Table 1. The data confirm that the contact angle of 1M HCl greatly reduced more water as blank solutions that indicate the wettability of 1M HCl increased on the steel surfaces. However, these data indicate increment of HCl attack to steel surface. Careful inspection of data indicates that the contact angle values of polymer solutions lowered than blank. Moreover, the greater reduction of contact angles data for poly(AMPS) solution is more than PAMPS-DEA either in water or 1M HCl solutions. This means that the formation of IL in cationic and ionic form increased the contact angle than a parotic poly(AMPS). This can be referred to increased hydrophobicity by incorporating of DEEA in the chemical structure of PAMPS-DEA. These data indicate that the PAMPS-DEA has strong ability to form hydrophobic layer on the steel surface and reduce diffusion of HCl on the steel surface, consequently, the corrosion rate can be inhibited. Moreover, it is expected that the IL based on PAMPS-DEAA will behave a large anionic polyelectrolyte at interfaces in 1M HCl while amide groups of poly(AMPS) can be easily protonated with 1M HCl more than PAMPS-DEAA [**36**]. This means that poly(AMPS) can attack easily than PAMPS-DEAA to increase the diffusion of HCl to steel surface to reduce the ability of poly(AMPS) to inhibit the corrosion rate of steel at lower concentrations.

Table 1. Contact angle data for different concentrations of poly(AMPS) and PAMPS-DEA on the steel surface at 25 °C.

Compounds	Medium	Contact angle (degree) at different concentrations (ppm)		
		100	250	500
Poly(AMPS)	water	54	53	52
	1M HCl	12	13	14
PAMPS-DEA	water	73	74	75
	1M HCl	24	25	26

3.2. Potentiodynamic polarization measurements

The potentiodynamic polarization curves of steel electrode in 1 M HCl solution containing different concentrations of poly(AMPS) and PAMPS-DEA are shown in Figures.4 and 5, respectively. It is clear that the additions of poly(AMPS) and PAMPS-DEA lowers the current density of both branches of polarization curves. The results can be explained on the basis of ILS adsorption on active centers of steel, which decreases the anodic and cathodic reactions. All electrochemical parameters were estimated and quoted in Table 1. It is evident that the shift in E_{corr} in both directions is lower than 85 mV indicating that both ILS acted as a mixed type of inhibitors [37, 38]. Moreover, the parallel variation of cathodic and anodic Tafel curves in case of PAMPS-DEA indicates that the mechanism of inhibition in the presence of the investigated inhibitors is activation controlled. In case of poly(AMPS) the steel dissolution mechanism is not affected by the changing the concentrations in the presence of poly(AMPS) [39].

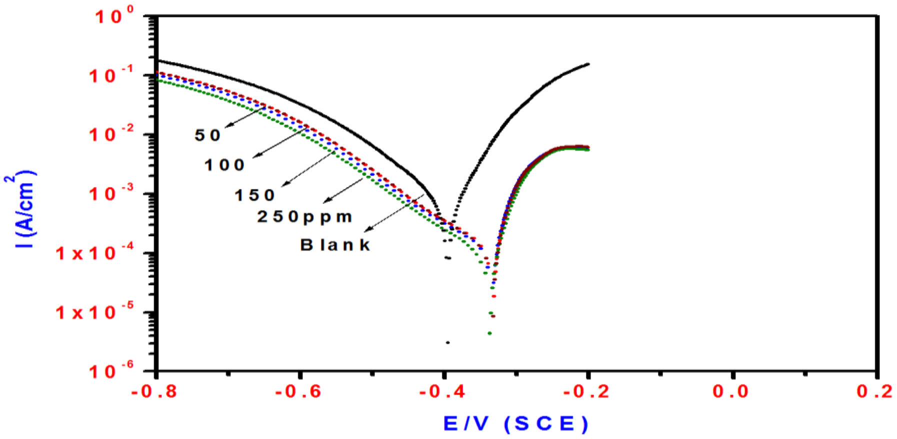


Figure 4. Polarization plots of steel electrode obtained in 1M HCl solution and containing various concentrations of poly(AMPS).

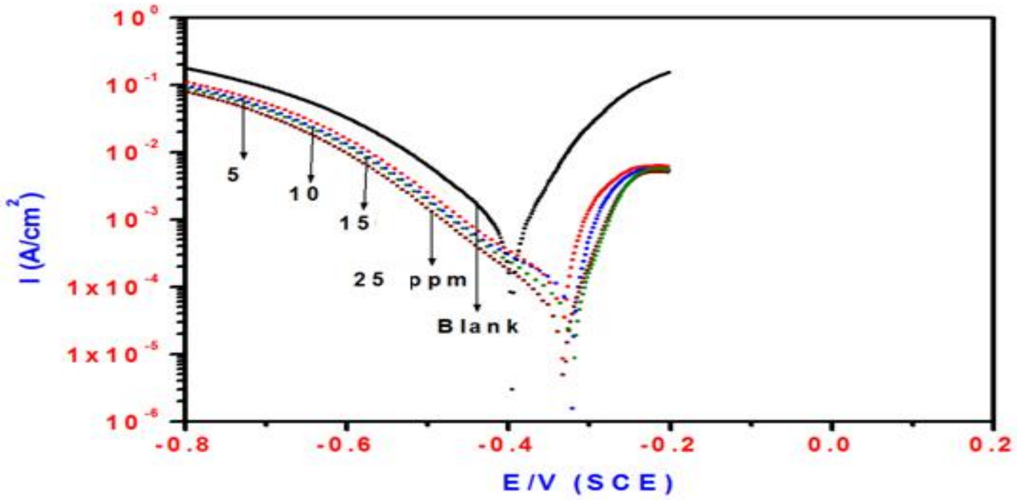


Figure 5. Polarization plots of steel electrode obtained in 1M HCl solution and containing various concentrations of PAMPS-DEA.

Table 2. Inhibition efficiency values of steel electrode in 1M HCl containing various concentrations of poly(AMPS) and PAMPS-DEA calculated by polarization and EIS methods

Blank	Polarization Method						EIS Method		
		Ba (mV)	Bc (mV)	E_{corr} (V)	i_{corr} □A/cm^2	IE%	R_{ct} Ohm	Cdl (µF/cm^2)	IE%
	1M HCl	69	120	-0.3955	839	_____	1.80	334	____
Poly(AMPS)	50 ppm	78	197	-0.3345	211	74.8	7.4	136	75.6
	100	77	195	-0.3358	186	77.8	8.3	131	78.3
	150	72	154	-0.3353	158	81.1	9.8	127	81.6
	250	73	171	-0.3383	134	84.0	12	119	85.0
PAMPS-DEA	5 ppm	72	154	-0.3353	158	81.0	9.7	123	81.4
	10	58	134	-0.3219	80	90.4	19	108	90.5
	15	55	145	-0.3201	74	91.1	21.5	106	91.6
	25	54	103	-0.3328	37	95.5	43	101	95.8

The additions of ILS to 1M HCl solution is accompanied by a remarkable drop in the values of I_{corr} and the extent of reduction is highly dependent upon ILS concentrations. The inhibition efficiency (%IE) was computed using the following equation [40]:

$$IE(\%) = 1- (i_{inhibited} / i_{uninhibited}) \times 100 \qquad (1)$$

where $i_{nhibited}$ and $i_{uninhibited}$ are the inhibited and uninhibited corrosion current densities, respectively.

The data presented in Table 2 indicates that all the studied ILS has higher inhibition efficiency than experienced in blank solution and increased with increasing ILS concentrations. I_{corr} decreases in the presence of the studied ILS compared to the blank solution, indicating that these ILS acting via adsorption on the steel surface and suppresses the corrosion process. The Increase in IE% with increasing ILS concentration can be accounted to more inhibitor molecules adsorption on the steel surface covering wider surface and suggesting that the ILS has a protective inhibition performance [41]. It can be concluded that when the IE% values of the inhibitor approaches near 100 the inhibitor has a good protective barrier for diffusion the aggressive ions and suppresses the corrosion process of the steel in the acidic chloride solution.

3.3. EIS measurements

Figures 6 and 7 show the Nyquist plots of the steel in 1 M HCl in containing different concentrations of poly(AMPS) and PAMPS-DEA, respectively.

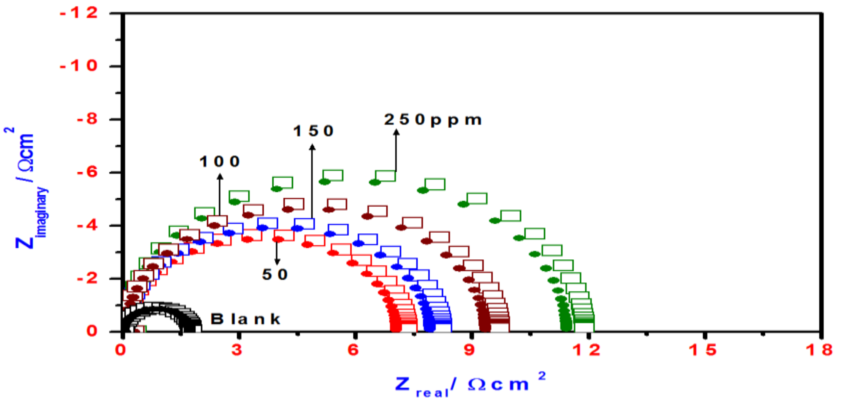


Figure 6. Nyqusit plots of steel electrode obtained in 1M HCl solution and containing various concentrations of poly(AMPS).

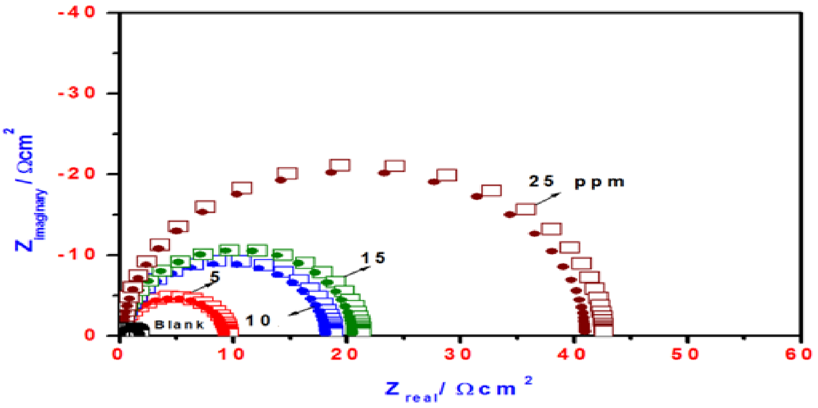


Figure 7. Nyqusit plots of steel electrode obtained in 1M HCl solution and containing various concentrations of PAMPS-DEA.

The Nyquist plots are characterized by one capacitive semicircle showing that the corrosion process was charge transfer controlled and the diameter of the semicircle increases as the inhibitors concentration increased [42]. The higher protection performance of both inhibitors was observed at high concentration of inhibitors can be accounted to an increase in the area covered with poly(AMPS) and PAMPS-DEA molecules on steel surface [43].The equivalent circuit employed for fitting the data consists of *R*s, *R*ct and *C*dl. The estimated parameters gathered from the analysis of Nyquist diagram are given in Table 2. %IE is calculated from R_{ct} using the following relation:

$$\%\boldsymbol{IE} = \frac{\mathbf{Rct\,(2)-Rct\,(1)}}{\mathbf{Rct\,(2)}} \text{ x } 100 \qquad (2)$$

where Rct (1) and Rct (2) are the charge transfer resistances in the absence and in the presence of the inhibitors, respectively. It is evident that *R*ct increased while *C*dl decreased with increasing inhibitor concentration. Further inspection of the data presented in Table 2 shows that the values of IE increased as the concentration of inhibitor increases. The increase in Rct values with ILS concentration implies that both ILS acted via adsorption and a more surface coverage experienced at high concentration resulted in an increase in the charge-transfer resistance (Rct) values [44]. The thickness of the of the adsorbed protective layer increases with ILS concentration, which renders the corrosion inhibition performance of both inhibitors is more effective and ILS has a good protection performance for steel in aggressive chloride solution [45].

3.4. Adsorption isotherm

The electrochemical measurement data were tested by fitting to several adsorption isotherms in order to gain insights of ILS adsorption on steel surfaces in acidic chloride solutions. Figures 8a and b displayed a strong correlation of Langmuir adsorption isotherm between the $C_{(inh)}$ / θ and $C_{(inh)}$ for poly(AMPS) and PAMPS-DEA, respectively. A straight line with an average correlation coefficient of 0.999 for both ILS is obtained . The slopes of the straight lines were computed and found to be 1.1 and for poly(AMPS) and PAMPS-DEA, respectively. This data suggests that the adsorption of both inhibitors on steel surface obeys Langmuir adsorption isotherm [46]. The standard free energy of adsorption (ΔG^{o}ads) for ILS is determined from the values of the adsorption constant, K_{ads} [47, 48]. The estimated ΔG^{o}ads values for poly(AMPS) and PAMPS-DEA are -34.99 and -55.33 kJ / mol, respectively. This suggests that the adsorption of these ILS on steel surfaces is a complex interaction and occurred via physical and chemical adsorption. The spontaneity of adsorption of ILS onto the steel surface in the acidic chloride solution is expected due to the high negative values of ΔG^{o}ads.

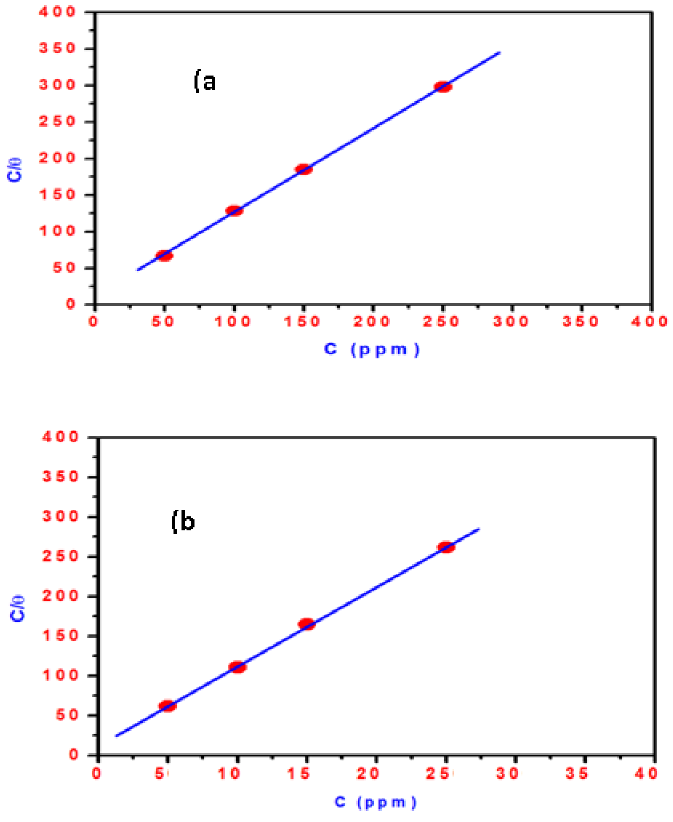


Figure. 8. Langmuir adsorption plot of steel in 0.1 M HCl solution containing different concentrations of a) poly(AMPS) and b) PAMPS-DEA.

SEM can be used to investigate the morphology of the protective layer of PAMPS-DEA on the steel surface as illustrated in Figure 9. The SEM micrograph of blank material of carbon steel before immersion in 1M HCl, Figure 9a, shows a uniform finishing that indicates the good sample preparation. Figure 9b shows a damages as dense film of corrosion products on the steel surfaces after exposure to 1 M HCl (24 hr). Figure 9c shows the cleaner metallic surface after the electrochemical test in the presence of 25 ppm of PAMPS-DEA. Moreover deposits are observed on steel surface which suggests that PAMPS-DEA does mitigate steel corrosion rate with complete all over the steel surface. This results confirm the chemical adsorption of PAMPS-DEA on the steel surface.

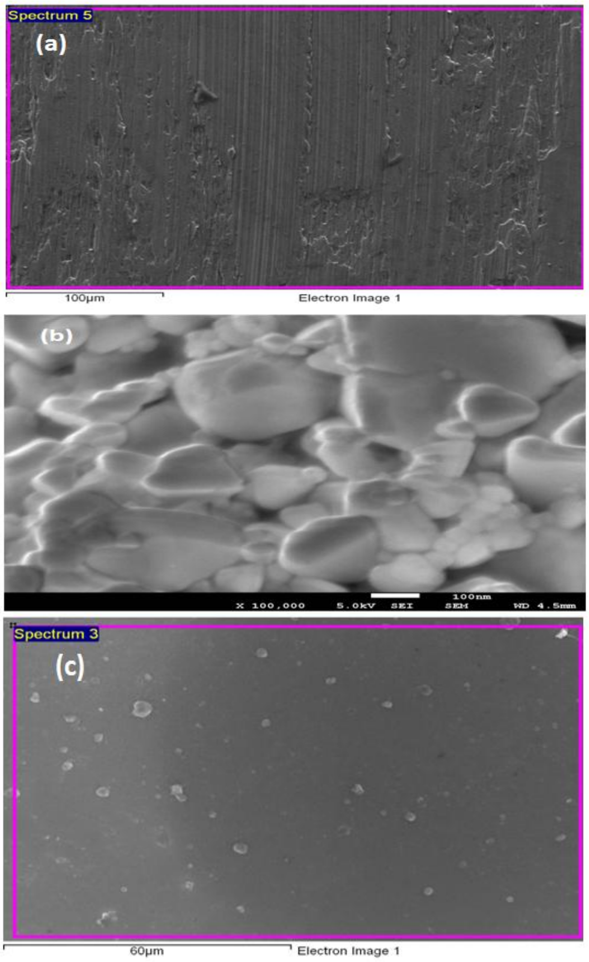


Figure 9. SEM micrograph of steel a) polished b) immersed in 1 M HCl (24 hr) and c) after electrochemical measurement treated with 15 ppm of PAMPS-DEA.

ACKNOWLEDGEMENT

The project was financially supported by King Saud University, Vice Deanship of Research Chairs.

4. CONCLUSIONS

- New poly (ionic liquid) based on PAMPS-DEA was prepared in cationic and ionic form. The wettability of PAMPS-DEA decreased than protic poly(AMPS).

- PAMPS-DEA has a strong corrosion protection performance for steel in acidic chloride solution.
- The additions of PAMPS-DEA to 1M HCl solution is accompanied by a remarkable drop in the values of I_{corr} and enlargement of charge transfer resistance at very low concentration.
- Polarization data indicated that PAMPS-DEA behaved as a mixed type inhibitor and acted via adsorption on steel surface by hindering and retarding the active centers from the corrosion reaction and obey Langmuir adsorption isotherm.

ACKNOWLEDGEMENT

The project was financially supported by King Saud University, Vice Deanship of Research Chairs.

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