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Synthesis and Application of Poly Ionic Liquid-Based on 2-Acrylamido-2-methyl Propane Sulfonic Acid as Corrosion Protective Film of Steel

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The present work aims to prepare new ionic liquid polymers based on protonation of diethylethanol amine (DEEA) with polymerizable monomers such as 2-acrylamido-2-methyl propane sulfonic acid (AMPS) and acrylic acid (AA). The polymerizable monomer was polymerized without solvent to prepare viscous poly ionic liquid as AMPS/AA-QA. The chemical structure and thermal characteristics of AMPS/AA-QA were investigated by NMR, DSC and TGA. The wetting characteristics of AMPS/AA-QA were measured at the steel surface by measuring the contact angles. This work describes the successful performance of AMPS/AA-QA as eco-friendly corrosion inhibitors for steel in acidic chloride solution. Corrosion inhibition of steel was carried out by electrochemical techniques. The experimental results reveal that AMPS/AA-QA is efficient mixed type corrosion inhibitors. Inhibition efficiency of 93.7% is reached with 25ppm of AMPS/AA-QA. The Nyquist plots composed of one capacitive loop and its diameter increases with increasing AMPS/AA-QA concentrations. The adsorption of AMPS/AA-QA on steel surface obeys Langmuir isotherm.

Keywords: Poly ionic liquid polymers; Steel, Acid corrosion, Polarization, EIS

1. INTRODUCTION

There is rapidly growing interest in production of ionic liquid (ILs) monomers and polymers due to their promising properties and applications in several industrial fields such as enhanced oil recovery, emulsifier, demulsifiers, catalysis and separation process [1-5]. Many applications of poly (ionic liquid) polymers are related not only for their good performances but also to their high thermal stability, conductivity, chemical stability, non-toxicity, non-volatility and last but not least, their eco-friendly characteristics and feasibility for production on a large scale. The high ability of poly (ionic liquid) polymers to adsorb at interfaces to form thin layer films at very low concentrations accelerates the growing application of ionic liquid in the petroleum fields [6-9]. The combination between electrostatic interactions of charged materials with charged metal substrate (physical adsorption) and charge sharing transfer from charged molecules to the metal substrate (chemical adsorption) is the main advantage to apply ionic liquids as corrosion inhibitors for steel substrate [10-15]. The amphiphilic ILs that have hydrophobic tail and hydrophilic head attracted great attention as anticorrosive materials in aggressive acid conditions due to their greater ability to improve both surface wetting performance and adsorption characteristics [15]. Therefore, the preparation of ILs polymers having the amphiphilic characteristics is a main target of this work.

Synthesis of IL polymers can be preceded by preparation of polymers followed by salt formation or by polymerization of polymerizable organic salts [16-17]. Moreover, these polymerized organic salts can be exchanged with other cations to prepare new IL polymers [18]. Recently, these materials attracted great attentions due to superior wetting characteristics with different metal substrates and it has been reported that the wetting characteristics depend on the size of cationic and ionic components [19]. It was reported that the functionalization of imidazolium ion with polymerizable groups such as vinyl, acroyloyl and styryl will affect the rigidity, thermal stability and wetting characteristics of the prepare IL polymers [18, 20-21]. There are several drawbacks for application of organic inhibitors that will be controlled by using IL polymers such as toxicity, volatility, degradations and cost of materials. The present work aims to prepare new ionic liquid polymers based on quaternization of diethylethanol amine (DEEA) with 2-acrylamido-2-methylpropane sulfonic acid (AMPS) and acrylic acid (AA) by sulfonic and carboxylic groups, respectively. The tertiary amine (DEEA) is quaternized with AMPS and AA to solvate and polymerizes the monomers without solvent. The prepared IL polymer is used to inhibit the corrosion of steel at lower concentrations in aggressive medium of 1M HCl aqueous solution. The wetting and formation of thin layer films by applying IL solutions are investigated via measurements of corrosion inhibition efficiencies using different electrochemical techniques.

2. EXPERIMENTAL

2.1. Materials

Diethyl ethanolamine (DEEA), acrylic acid (AA) and 2-acrylamido-2-methylpropane sulfonic acid (AMPS) were purchased from Sigma Aldrich Chemicals Co. 2,2-Azobisisobutyronitrile, AIBN, is radical initiator purified and recrystallized from methanol solution and produced by Merck. The radical copolymerization of AMPS and AA was carried out at equal monomer ratios in water as solvent as reported in previous work [22].

Corrosion tests have been carried out on electrodes cut from sheets of steel with chemical composition (wt%) described in detail in our previous studies [23].

2.2. Preparation of AMPS/AA-QA IL

A mixture of equal molar ratios (1: 1 mol%) of AMPS and AA (6 mmol of each monomer) was stirred with 12 mmol of DEEA under nitrogen atmosphere at 10 °C in flask. The mixing was carried out for 5 hrs to complete dissolution of AMPS in AA and DEEA solutions. Transparent solution was obtained with yield of 99 % indicates the formation of quaternized DEEA organic salt with AA and AMPS monomers. ABIN initiator (0.08 mmol) was added to the reaction mixture under nitrogen bubbling and the mixture was heated to 70 °C for 24 hrs. The viscosity of mixture was increased and transparent light yellow mixture was precipitated from acetone into cold diethyl ether (dry ice/acetone bath) and collected after filtration. The viscous oil was dried under vacuum at 40 °C to remove any residual volatile materials to obtain AMPS/AA-QA polymer with high yield (98.7 %).

2.3. Characterization

The chemical structure of the prepared AMPS/AA-QA monomer and polymer was confirmed by using ^{1}H- and ^{13}C-HMR spectroscopy (Bruker AC-300 spectrometer) and d6-DMSO used as solvent and tetramethylsilane as internal solvent.

Thermal stability of the prepared AMPS/AA-QA monomer and polymer determined by using thermogravimetric analysis (TGA; Shimadzu, DTG-60 M). The glass transition temperature was determined using differential scanning calorimetric (DSC; Shimadzu, DSC-60) by heating and cooling under N_2 and liquid nitrogen atmosphere with rate of 25 $cm^3 min^{-1}$ and at a heating rate of 10 $°C\cdot min^{-1}$.

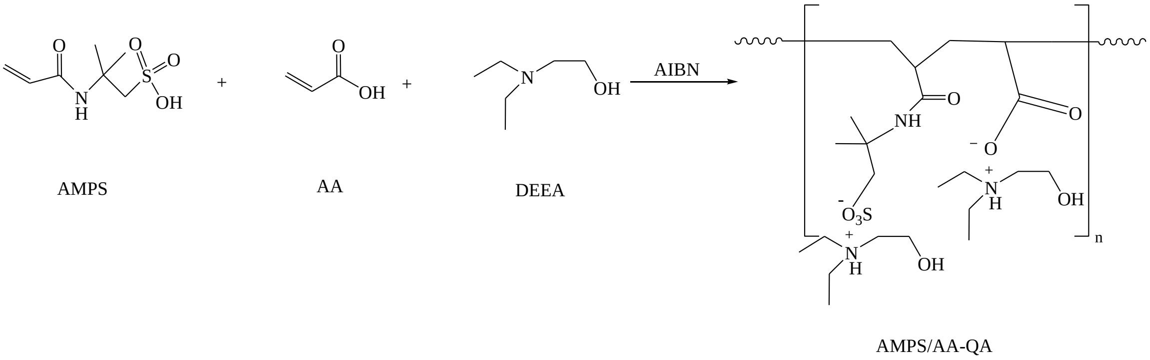
The contact angles of AMPS/AA and AMPS/AA-QA in water and aqueous 1M HCl and steel surface were determined by using sessile drop using drop shape analyzer (DSA-100, Kruss).

2.4. Electrochemical measurements

Electrochemical experiments were carried out using a Solartron 1470E (multichannel system) as and the Solartron 1455A as FRA. The counter electrode and the reference electrode were used as the same described in previous studies [23].

3. RESULTS AND DISCUSSION

The poly ionic liquid-based on AMPS/AA is prepared by quaternization of DEEA with AMPS and AA monomers followed by copolymerization using AIBN as described in the experimental section and represented in the scheme 1. The DEEA was quaternized with AA or AMPS to form polymerizable monomers that can be polymerized without solvent due to their ability to solubilize AMPS solid which has melting temperature at 192 °C. Moreover the presence of ethanol group in DEEA can protect the ammonium cation from coordination with sulfonate or carboxylate groups of AMPS and AA, respectively. In the previous works [22, 24-26], it was reported that the dissociation of sulfonate and carboxylic groups that have pKa 2.3 and 4.2, respectively, decreased at lower pH due to formation of strong hydrogen bond between amides, sulfonate and carboxylate groups. The pH of AMPS and AA mixture increased by adding DEEA, which increases ion dissociations of COOH and SO3H and, consequently, the charges on the polymeric chains increases to easily form ionic liquid monomer[24].



Scheme 1. Synthesis of AMPS/AA-QA IL.

3.1. Characterization of AMPS/AA-QA

The chemical structure of AMPS/AA and AMPS/AA-QA is confirmed by ^{1}H- and ^{13}C- NMR as illustrated in Figures 1 and 2. The ^{1}H-NMR spectrum of AMPS/AA (not presented here for brevity) indicates the complete polymerization of AMPS and AA monomers from the disappearance of peaks of CH_2=CH- at 6.1 and 5.7 ppm and appearance of new peaks at 2.71 and 2.07 ppm of CH_2-CH- polymer skeleton for both AMPS/AA and AMPS/AA-QA (Figure 1). Moreover, the appearance of broad peaks at 8.9 and 7.29 ppm in the spectrum of AMPS/AA-QA (Figure 1) which referred to +NH of DEEA and CONH amide of AMPS indicates the quaternization of DEEA with AA and AMPS. The disappearance of peaks at 12.3 and 3.06 ppm attributed to COOH and SO_3H groups in the spectrum of AMPS/AA-QA, also elucidates the quaternization of DEEA with sulfonic and carboxylic protons. The appearance of peaks at 3.68 and1.1 ppm confirms the OCH_2CH_2- and CH_3 groups of DEEA.

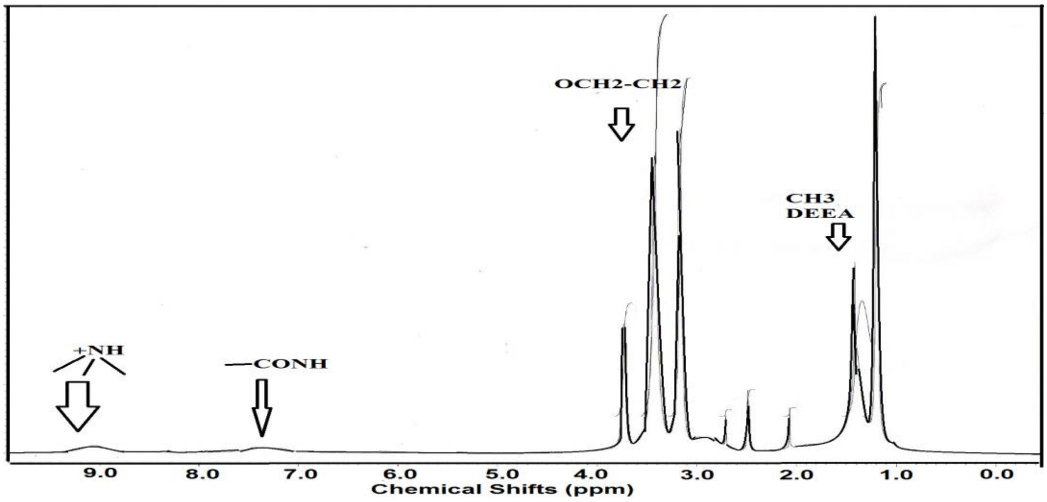


Figure 1. ^{1}H-NMR spectrum of AMPS/AA-QA.

^{13}C-NMR spectrum of AMPS/AA-QA illustrated in Figure 2 is used to elucidate its chemical structure. The appearance of peak at 163 and 44.5 ppm referred to COO$^-$ and C-SO$_3^-$, respectively indicates the ionization of sulfonic and carboxylic acid groups of AMPS and AA. The peak at 55.3 ppm attributed to $^+$N-C elucidates the quaternization of DEEA and formation of AMPS/AA-QA. The disappearance of C=C peaks at 122-130 ppm confirms the complete polymerization of AMPS and AA monomers.

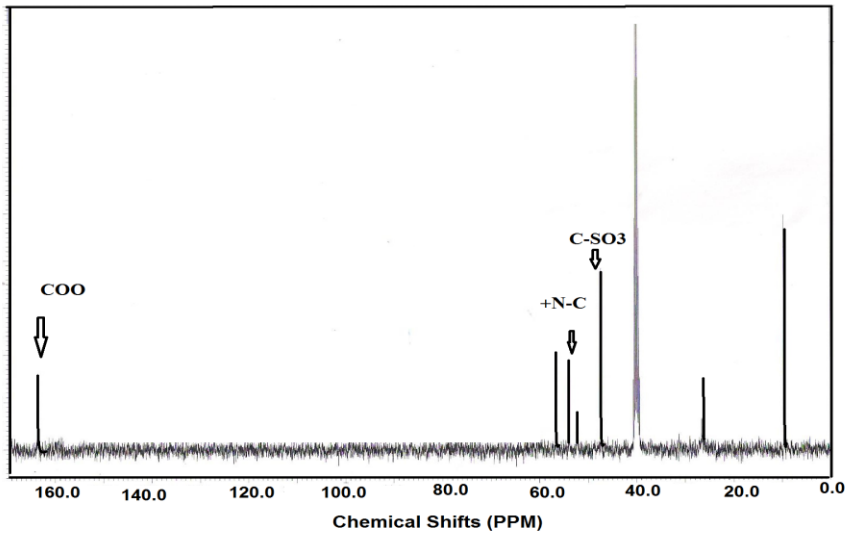


Figure 2. ^{13}C-NMR spectrum of AMPS/AA-QA.

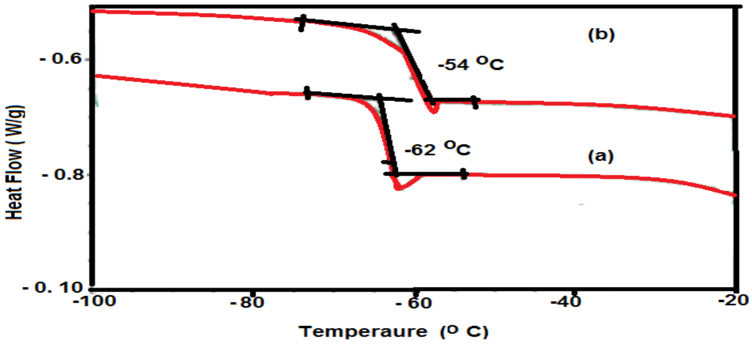


Figure 3. DSC thermograms of AMPS/AA-QA a) monomer and b) polymer.

Differential scanning calorimetry (DSC) thermograms of AMPS/AA-TS polymerizable monomer and polymer were presented in Figure 3 to examine the effect of polymerization and quaternization of AMPS and AA copolymers. It was previously reported that the glass transition temperature (Tg) of AMPS/AA copolymers is 61.9 °C that changed with the copolymer compositions [24]. In the present work the Tg value of AMPS/AA-TS polymerizable monomer and polymer are -62 and -54 °C, respectively. These data indicate that the quaternization and formation of IL molecules increase the molecule flexibility and extend the liquid range of AMPS/AA polymer to liquid at lower temperature. This means that the hydrogen bond formation between polar groups of AMPS and AA is decreased with quaternization [**27**]. Moreover, the produced AMPS/AA-QA is viscous liquid and soluble in water and polar solvents.

Thermogravimetric analysis (TGA) is used to investigate the thermal stability of AMPS/AA and AMPS/AA-QA polymers as illustrated in Figure 4. Thermograms indicate that AMPS/AA was degraded at 185 ^{o}C before AMPS/AA-QA which degraded at 325 ^{o}C. This means that the quaternization prevents decarboxylation of COOH groups of AA that decomposes at temperature above 150 ^{o}C [28]. This data indicates that AMPS/AA-QA as IL has better thermal stability than AMPS/AA. The de-quaternization and degradation of polymer backbone steps started at temperature of 380 ^{o}C up to 500 ^{o}C and accelerate the decomposition of AMPS/AA-QA as described in Figure 4. This confirms that the deprotonation of AMPS/AA and quaternization of DEEA enhanced the thermal stability of AMPS/AA-QA as IL [**29**].

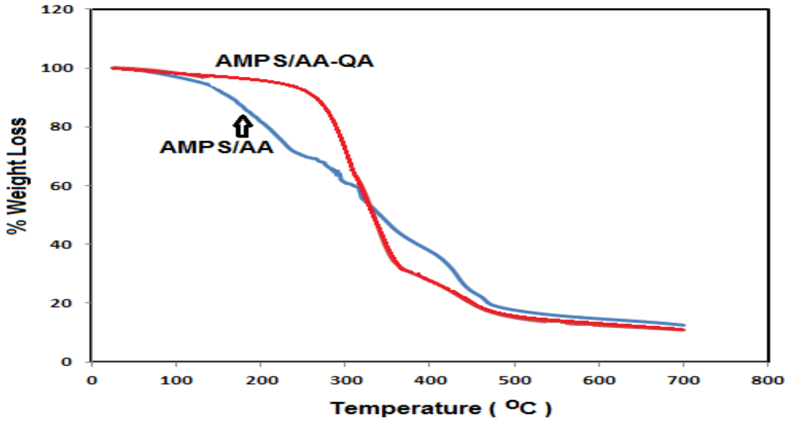


Figure 4. TGA thermograms of AMPS/AA-QA and AMPS/AA polymers.

It is previously reported that the organic sulfonic acid such as methane sulfonic acid has surface tension of 50.2 mN/m [30]. In the present work, the surface tension of AMPS/AA-QA is measured using pendant drop method and it is found 55.1 mN/m. This means that there is strong intramolecular interactions between AMPS/AA-QA molecules that inhibit their interaction with water. Moreover, the formation of quaternized ammonium AMPS/AA-QA polymer would increase the intramolecular interactions between of polymer molecules that increase the surface tension of water. It is necessary to study the effect of hydrogen bonding on the dense polymer structure of the AMPS/AA-QA by investigate their wetting characteristics at interfaces such as air or metal substrates from contact angle measurements. In this respect, the relation between contact angles, AMPS/AA and AMPS/AA-QA in aqueous and acid chloride (1M) solutions, and ageing times is illustrated in Figure 5. The effect of AMPS/AA and AMPS/AA-QA concentrations on their contact angles with steel surfaces and their photographs are shown in Figure 6. The data of contact angles (Figure 5) indicate that the AMPS/AA and AMPS/AA-QA are larger values more than water and 1M HCl solutions at different concentrations. Moreover, the contact angles of AMPS/AA-QA solutions with steel are reduced with ageing time. These observations indicate that the increment of viscosity values of AMPS/AA and

AMPS/AA-QA reflects on the increasing of contact angle data. The lowering of contact angle data of AMPS/AA-QA with time is referred to increment of the wetting characteristics and interactions between AMPS/AA-QA solutions more than AMPS/AA which increased the film formation on the steel surface to protect steel from aggressive environments. Accordingly, the reduction in contact angles and surface tension at the solid-liquid interface with time confirms the spreading of the liquid on the charged surface. The difference between AMPS/AA and AMPS/AA-QA, that the latter is charged polymer which behaves as a large anionic polyelectrolyte at interfaces. It is expected that when the steel surface is charged, the AMPS/AA-QA as IL is adsorbed at the surface with its oppositely charged as cationic or ionic. Such behavior increases the wetting characteristics and adsorption of at interfaces more than AMPS/AA polymers. Accordingly, AMPS/AA-QA as IL polymer has greater possibility to maintain its liquid nature as a macromolecule to adsorb at solid liquid interface to wet the steel substrate.

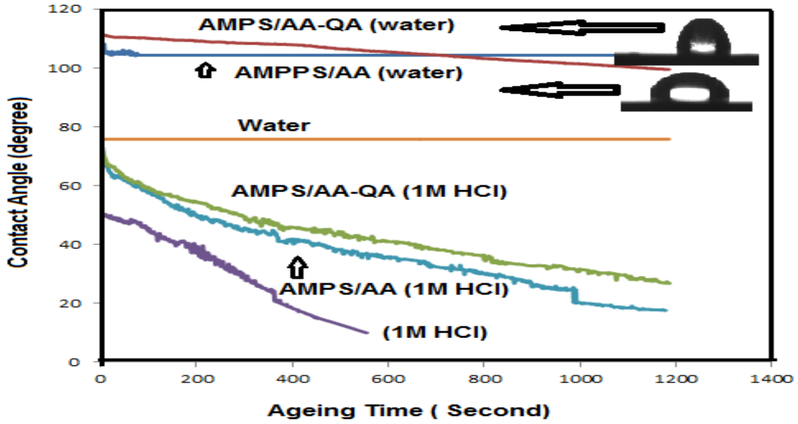


Figure 5. Relation between contact angles data of AMPS/AA and AMPS/AA-QA and ageing time.

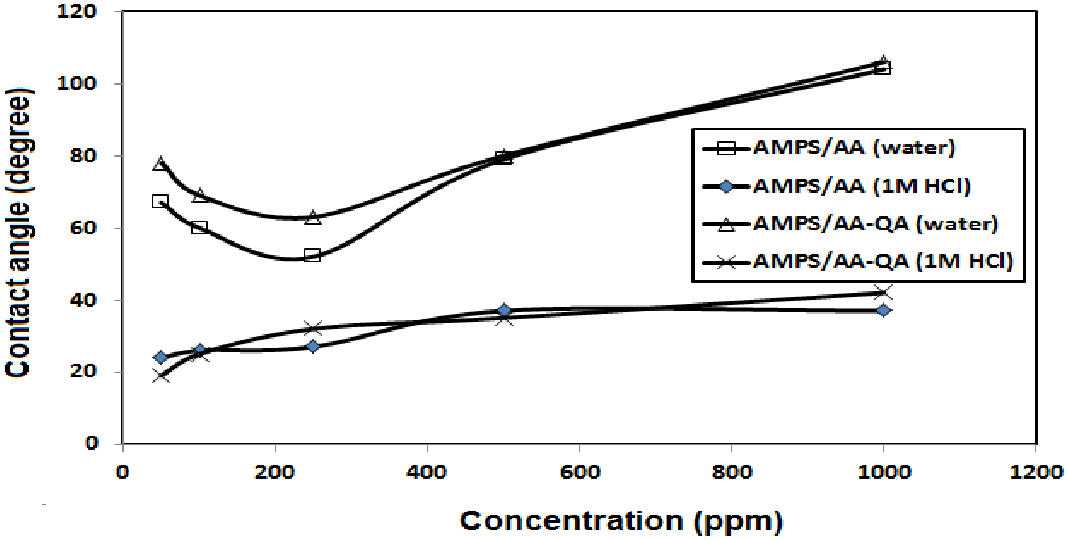


Figure 6. Relation between contact angles data of AMPS/AA and AMPS/AA-QA and their concentrations.

The data represented in Figure 6 indicate that the AMPS/AA and AMPS/AA-QA have different characteristics in water and 1M HCl solutions. It was noticed that, the wetting of both AMPS/AA and AMPS/AA-QA increased with decreasing their concentrations as contact angle values are reduced. Moreover, the contact angle data of AMPS/AA-QA are lower in 1M HCl than water and reduced with decreasing its concentrations. This was referred to increase affinity for protonation of nitrogen atom of amide groups of AMPS in 1M HCl when polymer was uncharged as AMPS/AA more than charged as AMPS/AA-QA IL [**31**]. The protonation of nitrogen amide groups of AMPS/AA in 1M HCl decreases its adsorption at steel/water interface and reduces its wettability.

3.2. Potentiodynamic polarization measurements

Cathodic and anodic polarization curves of steel in 1 M HCl solution in the blank solution without and with various concentrations of AMPS/AA and AMPS/AA-QA are shown in Figs. 1 and 2, respectively. The data presented in Figures 7 and 8 indicated that, the addition of AMPS/AA and AMPS/AA-QA to the blank solution suppresses the anodic dissolution of iron as well as the cathodic hydrogen evolution reactions. All the estimated electrochemical corrosion parameters are listed in Table 1 for AMPS/AA and AMPS/AA-QA. It is clear that the addition of AMPS/AA and AMPS/AA-QA lowered the corrosion current (icorr) and the decrease in icorr increases with increasing concentration.

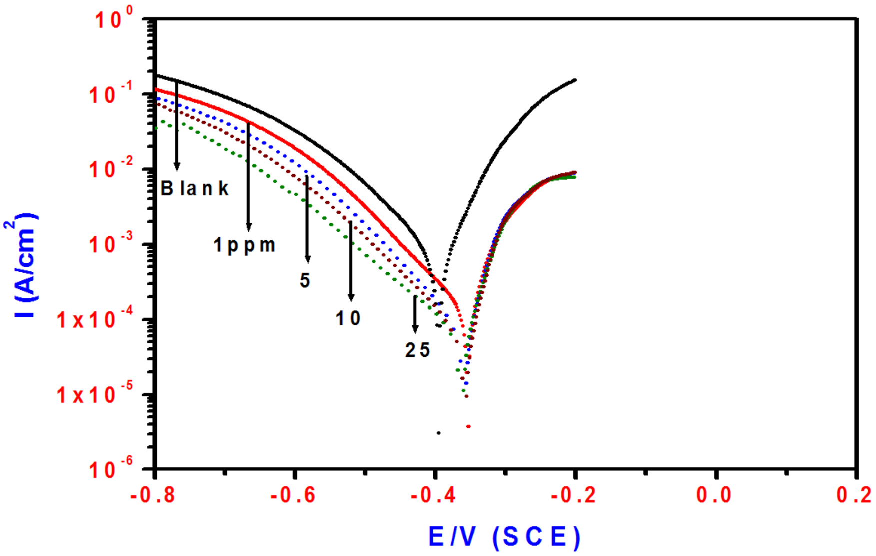


Figure 7. The effect of AMPS/AA concentration on the polarization curves of steel in acidic chloride solutions.

The inhibited solution causes a shift in the corrosion potential (Ecorr) towards more noble potentials compared to the result obtained in blank (uninhibited) solution. Accordingly, these inhibitors can be classified as mixed-type inhibitors. The percentage inhibition efficiency (IE, %) was computed as [32-33]:

$$IE\% = \frac{Icorr(b) - Icorr(i)}{Icorr(b)} \times 100 \qquad (1)$$

Where icorr is the corrosion current density in the inhibited solution and Icorr(b) is the corrosion current density in the uninhibited solution. As the AMPS/AA and AMPS/AA-QA concentration increase the adsorbed area of these inhibitors on steel surface increase, which led to an increase in the protection performance of the inhibitor [34]. It is expected that the higher the inhibitor concentrations the higher the coverage of the steel surface with inhibitor [35-38]. The values of IE% suggest that both materials act as efficient inhibitors on steel corrosion in in acidic chloride solution.

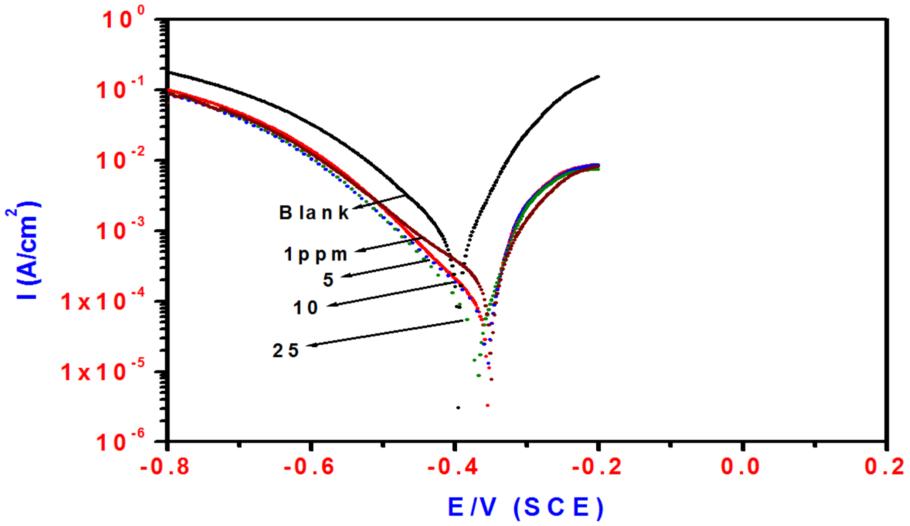


Figure 8. The effect of AMPS/AA-QA concentration on the polarization curves of steel in acidic chloride solution.

Table 1. Influence of AMPS/AA and AMPS/AA-QA concentrations on the Inhibition efficiency values of steel in 1M HCl calculated by different Electrochemical methods.

Inhibitor	Polarization Method						EIS Method		
		Ba (mV)	Bc (mV)	E_{corr} (V)	i_{corr} µA/cm^2	IE%	R_p Ohm	Cdl (µF/cm^2)	IE%
	Blank	69	120	-0.395	839	____	1.80	334	____
AMPS/AA	1ppm	98	268	-0.3500	391	53.3	4	270	55.0
	5 ppm	75	111	-0.355	147	82.4	10.5	134	82.8
	10 ppm	68	108	-0.360	89	89.3	17.6	114	89.7
	25 ppm	64	124	-0.364	59	92.9	26.0	106	93
AMPS/AA-QA	1ppm	67	141	-0.3575	99	88.2	17	118	89.4
	5 ppm	67	107	-0.335	89	89.3	17.5	114	89.7
	10 ppm	69	107	-0.369	85	89.8	19	108	90.5
	25 ppm	62	99	-0.356	57	93.2	29	105	93.7

3.2. EIS measurements

EIS experiments were undertaken mainly, as a complementary tool and and powerful technique to determine corrosion rates in a rapid and accurate way The influence of AMPS/AA and AMPS/AA-QA concentrations on the Nyquist plots of steel in acidic chloride solution is shown in Figures 9 and 10, respectively. The diameter of semicircle increases significantly with the additions of AMPS/AA and AMPS/AA-QA into the aggressive solution. The results indicate that both AMPS/AA and AMPS/AA-QA can significantly inhibit the corrosion of steel in acidic chloride solution. In addition, the diameter of Nyquist plots increases with increasing concentration of both inhibitors. The larger diameter of semicircle measured in the presence of AMPS/AA-QA implies that the inhibition effect of AMPS/AA-QA is better than that of AMPS/AA. It is clear from Figures 3 and 4 that the data of EIS exhibit one single capacitive loop, which suggests that the corrosion of steel in chloride containing environment is mostly controlled by charge transfer process [39]. The EIS data were fitted to an equivalent electrical circuit described in detail in the previous studies [1]. It consists of Rct, Cdl and Rs. The values of impedance parameters are quoted in Tables 1 for AMPS/AA and AMPS/AA-QA. Increasing the value of Rct is accompanied by a decrease in the corrosion rate [40]. The observed increase in Rct with the inhibitor concentration confirms the inhibitory action of AMPS/AA and AMPS/AA-QA. It is expected that the values of Rct and Cdl dependent upon the type of and concentration of the inhibitors. The adsorption of inhibitor on the active sites area of steel led to formation of an insulating protective film , which in turn acts as a barrier layer for diffusion of aggressive ions. The increase in Rct values may be attributed to the formation of an inhibited and protective film on steel surface. The water molecules adsorbed on steel surface were replaced by inhibitor molecules, which led to a decrease in local dielectric constant [41-42]. In addition, the decrease in Cdl values can be attributed to an increase in the thickness of the electrical double layer, which depends on the type and concentration of inhibitor. The percentage inhibition efficiency (IE, %) is calculated using the following equation:

$$\mathrm{IE\%} = \frac{\mathrm{Rct(i)} - \mathrm{Rct(b)}}{\mathrm{Rct(i)}} \times 100 \qquad (2)$$

where Rct(i) and Rct(b) are the charge transfer resistances in the inhibited and uninhibited solution, respectively. It is evident that the values of inhibition efficiency IE% increase with the concentration of these inhibitors. Increasing the covered area of the steel with adsorption of inhibitor led to an increase in the protection performance of the inhibitor and consequently increase IE%. The result clearly proves that AMPS/AA and AMPS/AA-QA showed good performance in protection of on steel surface and the inhibitory action may be accounted to the formation of protective and inhibited layer acting as barrier for diffusion of aggressive ions and hinder the attacking the steel surface. The estimated IE% values obtained from the different electrochemical techniques were in good agreement.

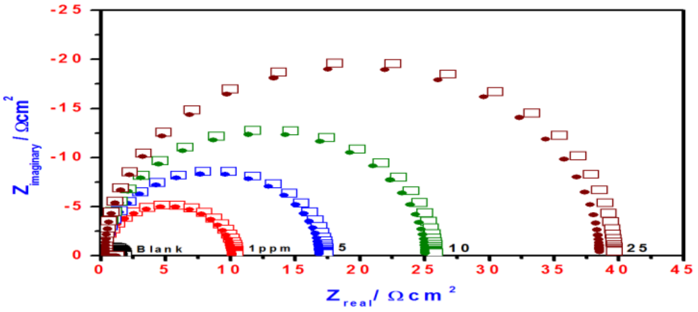


Figure 9. The effect of AMPS/AA concentration on the Nyquist diagram of steel in acidic chloride solutions.

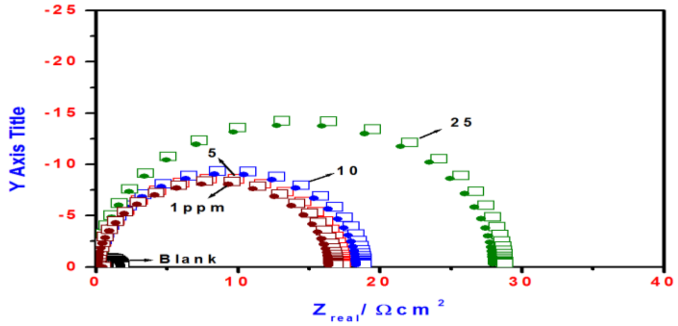


Figure 10. The effect of AMPS/AA-QA concentration on the Nyquist diagram of steel in acidic chloride solutions

3.3. Adsorption isotherm

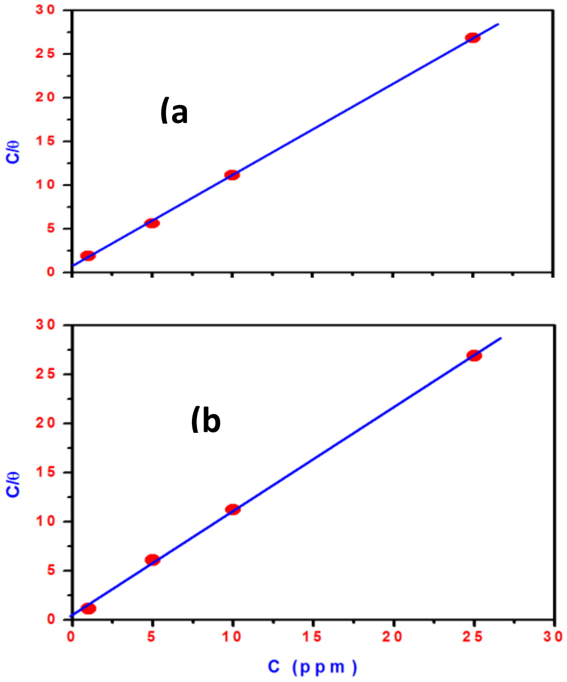


Figure 11. Langmuir's isotherm adsorption model of: (a) AMPS/AA and b) AMPS/AA-QA on steel surface in acidic chloride solution .

The mechanism of corrosion inhibition can be interpreted from studying the adsorption isotherm, which has insights into the interaction between the adsorbed materials and the exposed surface [43]. The experimental data of the surface coverage (θ) was fitted to different adsorption isotherm models. The data fitted well the Langmuir adsorption isotherm, which can be described as:

$$C_{(inh)} / \theta = 1/K_{ads} + C_{(inh)} \qquad (3)$$

Where $C_{(inh)}$ is inhibitor concentration and Kads is the equilibrium constant for the adsorption process. Figures 11 a and b show the linear relationships of C/θ versus C for AMPS/AA and AMPS/AA-QA, respectively.

The correlation coefficient (R= 0.999 in both cases) and slopes are close to 1 (1.03 for AMPS/AA and 1.04 for AMPS/AA-QA) suggesting that the adsorption of inhibitors on steel surface obeyed the Langmuir adsorption isotherm [44]. The standard free energy of adsorption (ΔG°ads) and the adsorption constant (Kads) are related by the following equation[45]:

$$\Delta G°\text{ads} = -RT \ln(55.5K\text{ads}) \qquad (4)$$

It is well established that the type of adsorption dependent upon the calculated values of Δ*G*°ads. If the values around - 20 kJ mol/1 or lower the adsorption process is a physisorption. It is labeled as a chemisorption when the values of Δ*G*°ads around -40 kJ mol/1 or higher through formation a co-ordinate type of bond [46–48]. The calculated values of Δ*G*°ads , were -46.99 , and -46.01 kJ mol/1 for AMPS/AA and AMPS/AA-QA, respectively. Accordingly, the adsorption process of AMPS/AA and AMPS/AA-QA on steel surface is chemical adsorption [49–51].

4. CONCLUSIONS

1. New AMPS/AA-QA as IL has been prepared without solvent by quaternization of DEEA with AMPS and AA monomers.
2. The AMPS/AA-QA as IL showed flexible molecule more than AMPS/AA polymer and showed greater wetting characteristics at the steel surface.
3. AMPS/AA-QA has good protection performance towards the corrosion of steel in acid chloride containing environment and acts as mixed-type inhibitor.
4. EIS plots exhibit individual capacitive loop and the addition of AMPS/AA and AMPS/AA-QA in 1 M HCl solution led to an increases in the charge transfer resistance of the inhibited system.
5. The adsorption of studied inhibitors on the steel surface occurred via adsorption on the active sites of steel surface and the inhibition efficiencies obtained from the different electrochemical techniques were in good agreement.

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References

1. J. Yuan, C. Giordano and M. Antonietti, *Chem. Mater.,* 22 (2010) 5003.
2. J. P. Paraknowitsch, J. Zhang, D. Su, A. Thomas, and M. Antonietti, *Adv. Mater.,* 22 (2010) 87.
3. R. S. Varma and V. V. Namboodiri, *Pure Appl. Chem.,* 73 (2001)1309.
4. P. Wasserscheid and T. Welton, *Ionic Liquids in Synthesis*, Wiley-VCH Verlag GmbH Co., Weinheim (2002).
5. S. Liu, C. Xie, S. Yu and F. Liu, *Catal. Commun.,* 9 (2008) 2030
6. R. C. B. Lemos, E.B. da Silva, A. dos Santos, R. C. L. Guimarães, B. M. S. Ferreira, R. A. Guarnieri, C. Dariva, E. Franceschi, A. F. Santos and M. Fortuny, *Energy Fuels*, 24 (2010) 4439.
7. G.K. Yue, X.M. Lu, Y.L. Zhu, X.P. Zhang and S.J. Zhang, *Chem. Eng. J.,* 147 (2009) 79.
8. M. Bin Dahbag, A. AlQuraishi and M. Benzagouta, *J Petrol Explor Prod Technol.,* DOI 10.1007/s13202-014-0147-5 (2014).
9. M.S. Benzagouta, I.M. AlNashef, W. Karnanda, and K. Al-Khidir, *Korean J. Chem. Eng.*, 30 (2013) 2108.
10. X. Zhou, H. Yang and F. Wang, *Electrochimica Acta,* 56 (2011) 4268.
11. L.C. Murulana, A.K. Singh, S.K. Shukla, M.M. Kabanda and E.E. Ebenso, *Ind. Eng. Chem. Res.,* 51 (2012) 13284.
12. M. Hasib-ur-Rahman, F. Larachi, *Ind. Eng. Chem. Res.*, 52 (2013) 17682.
13. I. Lozano, E. Mazario, C.O. Olivares-Xometl, N.V. Likhanova and P. Herrasti, *Mater. Chem. Phys.,* 147 (2014) 191.
14. Q.B. Zhang and Y.X. Hua, *Electrochimica Acta*, 54 (2009) 1881.
15. N. V. Likhanova, M. A. Dominguez-Aguilar, O. Olivares-Xometl, N. Nava-Entzana , E. Arce and H. Dorantes, *Corros. Sci*,. 52 (2010) 2088.
16. J. Zhang, S. Zhang, J. Han, Y. Hub and R. Yan, *Chem. Eng. J.,* 271 (2015) 269.
17. H. L. Ricks-Laskoski and A. W. Snow, *J. Am. Chem. Soc.*, 128 (2006)12402.
18. M. Yoshizawa, W Ogihara and H. Ohno, *Polym. AdV. Technol.*, 13 (2002) 589.
19. S. Millefiorini, A. H.Tkaczyk, R. Sedev, J Efthimiadis and J. Ralston, *J. Am. Chem. Soc.*, 128(2006) 3098.
20. S. Washiro, M. Yoshizawa, H. Nakajima and H. Ohno, *Polymer*, 45 (2004) 1577.
21. H. Tang, J. Tang, S. Ding, M. Radosz, and Y. Shen, *J. Polym. Sci., Part A: Polym. Chem.,* 43 (2005)1432.
22. A. M. Atta , Z. H. Abd El Wahab , Z. A. El Shafey, W. I. Zidan and Z. F. Akl, *J. Dispersion Sci. Technol.,* 31 (2010) 1415.
23. G.A . EL-Mahdy, A.M. Atta, H.A. Al-Lohedan and A.O. Ezzat, *Int. J. Electrochem.Sci.,* 4 (2014)7925.
24. A.M. Atta and K.-F. Arndt, *Polym. Adv. Technol.,* 16 (2005) 442.
25. A.M. Atta and K-F Arndt, *Polym. Int.,* 52 (2003) 389.
26. M. K. Kärnä , M. K. Lahtinen and J. U. Valkonen, *J. Chem. Eng. Data,* 58 (2013) 1893.
27. S. Brahmachari, S. Debnath, S. Dutta, P. Kumar Das, *Beilstein J. Org. Chem*. 6 (2010) 859–868.
28. A. Pourjavadi, M. Kurdtabar and H. Ghasemzadeh, *Polym. J.,* 40 (2008) 94.
29. D. Navarro-Rodriguez, Y. Frere and P. Gramain, *J. Polym. Sci., Part A: Polym. Chem.,* 30 (1992) 2587.
30. J.A. Dean (Ed.), “Lange's Handbook of Chemistry”, 15th Ed., McGraw-Hill, 1999.
31. N. Greesh, P. C. Hartmann, V. Cloete, R. D. Sanderson, J. Coll. Interf. Sci., 319 (2008) 2–11.
32. E. McCafferty, *Corros. Sci.,* 47 (2005) 3202.
33. Q. Qu, L. Li, W. Bai, S. Jiang and Z. Ding, *Corros. Sci.,* 51 (2009) 2423.
34. X. Li, S. Deng and X. Xie, *Corros. Sci.,* 81 (2014) 162.
35. A. Tizpar and Z. Ghasemi, *Appl. Surf. Sci.,* 252 (2006) 8630.

36. K.R. Fuchs-Godec and V. Dolecek, *Colloids Surf., A* 244 (2004) 73.
37. R.A. Prabhu, T.V. Venkatesha, A.V. Shanbhag, G.M. Kulkarni and R.G. Kalkhambkar, *Corros. Sci.*, 50 (2008) 3356.
38. R.R. Annand, R.M. Hurd and N. Hackerman, *Electrochem. Soc.*, 112 (1965) 138.
39. Q.B. Zhang and Y.X. Hua, *Electrochim. Acta*, 54 (2009) 1881.
40. R. Rosliza, W.B. W. Nik and H.B. Senin, *Mater. Chem. Phys.*, 107 (2008) 281.
41. S.K. Singh, S.P. Tambe, G. Gunasekaran, V.S. Raja and D. Kumar, *Corros. Sci.*, 51 (2009) 595.
42. P. Mourya, S. Banerjee and M.M. Singh, *Corros. Sci.*, 85 (2014) 352.
43. K.C. Emregul and M. Hayvali, *Corros. Sci.*, 48 (2006) 797.
44. M. Behpour, S. M. Ghoreishi, N. Soltani, M. Salavati-Niasari, M. Hamadanian and A. Gandomi, *Corros. Sci.*, 50 (2008) 2172.
45. R. Solmaz, E. Altunbas and G. Kardas, *Mater. Chem. Phys.*, 125 (2011) 796.
46. I. Ahamad, R. Prasad and M.A. Quraishi, *Corros. Sci.*, 52 (2010) 933.
47. E.A. Noor and A.H. Al-Moubaraki, *Mater. Chem. Phys.*, 110 (2008) 145
48. M. Ozcan, R. Solmaz, G. Kardas and I. Dehri, *Colloids Surf., A* 325 (2008) 57.
49. Q. Deng, H-W Shi, N-N Ding, B-Q Chen, X-P He, G Liu, Y. Tang, Y-T Long and G-R Chen, *Corros. Sci.*, 57 (2012) 220.
50. J.M. Bastidas, P. Pinilla, E. Cano, J.L. Polo and S. Miguel, *Corros. Sci.*, 45 (2003) 427.
51. L. Cai, F. Qing, R. Shi, Y. Tang, Y-T Long, Y. X-P He, G.L. Jin, G-R Chen and K. Chen, *Ind. Eng. Chem. Res.*, 53 (2014) 64.