

Synthesis of Water Soluble Hyperbranched Poly (amine-ester) as Corrosion Inhibitors for Steel

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Encouraged by the excellent performance of dendrimers as scale inhibitors and anticorrosive coatings, we reasoned that dendrimers with properly designed structures might also be used as efficient water soluble corrosion inhibitors. New kind of dendritic polyether water soluble were synthesized using pentaerythritol tetracrylate as a precursor via Michael addition reaction with diethanolamine. The chemical structure of the prepared dendrimer was determined by FTIR, ¹³C and ¹H NMR analyses. The inhibitive effect of HPAE-PEG600 on the corrosion of steel in 1 M HCl solution has been investigated using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The results indicated that HPAE-PEG600 inhibited the corrosion of steel and the extent of inhibition increased with HPAE-PEG600 concentrations. Potentiodynamic polarization data suggests mixed-mode of corrosion inhibition.

Keywords: HPAE-PEG600, FTIR, NMR, Polarization, EIS, Electrochemical, Steel

1. INTRODUCTION

Dendrimers or highly branched molecules are defined as macromolecules containing dimensional structures with a large number of reactive terminal groups [1]. Dendronized polymers are a novel class of branched polymers which carry dendrons at each repeat unit. The amphiphilic dendrimers have attracted considerable interest because their unique properties. The advantages of hyperbranched polymers, easier synthesis, highly solubility, and lower viscosity may be useful in the fields such as coating and modifiers. Dendrimers can be prepared with high regularity and controlled molecular weights, and the macromolecules consist of a polyfunctional central core covalently linked to layers of repeating units (generations) and a number of terminal groups. These materials applied in

different areas such as liquid crystals, preparation of micelles, and molecular encapsulation [2–7]. Oligo(oxyethylene)s (OEGs) and their derivatives are interesting water-soluble components. They were often found to be nontoxic and biocompatible in various applications, and it is therefore not surprising that OEG units were also used in dendrimers [8].

Corrosion inhibitors are widely used materials to overcome the corrosion environment [9]. The application of inhibitors is one of the most practical methods for protection against corrosion in acidic media. There are different types of corrosion inhibitors: (a) inorganic inhibitors, (b) organic inhibitors, (c) surfactant inhibitors and (d) mixed material inhibitors [10]. The organic compounds have different nitrogen, sulphur, and oxygen atoms in their molecules such as ethoxylated fatty acid or amines, and propenethoxylated diol get high efficiencies to adsorb on the metal surface [11-13]. The higher molecular size of organic inhibitors and high electron density on the adsorption centers may be responsible for high corrosion efficiency. Novel anticorrosion ability of different types of water soluble inhibitors in the industry is good options to solve the problems of corrosion on metallic surfaces to prevent the material and economic loss. A hyperbranched poly(ethylene imine) polymer (PEI) was used as organic coatings by reacting with epoxides acting as a cross-linking agent for hybrid film formation while, due to its polymeric nature, has also good film forming ability [14]. It possesses anticorrosive properties and can encapsulate in its interior non-water-soluble organic molecules [14, 15]. A significant advantage to use dendrimers is the ability to functionalize the molecules to improve adhesion, strength, hydrophobicity and chemical resistance. As far as we are aware, the performance of dendrimeric or hyperbranched polymers as oilfield corrosion inhibitors has not been reported previously. In this paper we have to synthesize a hyperbranched poly(amine-ester) via Michael addition reaction. These polymers were then investigated for their ability to prevent corrosion of the steel in aggressive aqueous acidic medium.

2. EXPERIMENTAL

2.1. Materials

Pentaerythritol tetracrylate, 2,2'-dichlorodiethyl ether, diethanolamine, and poly(ethylene glycol) has molecular weight 600 g/mol (PEG600) were purchased from Aldrich Chemical Co. Steel was used as a working electrode (WE) for the electrochemical measurements. The composition of the steel is as follows (wt.%): 0.14% C, 0.57% Mn, 0.21% P, 0.15% S, 0.37% Si, 0.06% V, 0.03% Ni, 0.03% Cr and Fe (balance). The electrode surface was abraded with emery papers up to 2000 grit, rinsed in deionized water then degreased with acetone and finally dried in air.

2.2. Synthesis technique

2.2.1. The synthesis of hyperbranched monomer

Hyperbranched monomer based on pentaerythritol amine ester (HPAE) had pentaerythritol as a core and N,N-diethylol-3-amine ethanoate as the branched monomer. It was synthesized by a pseudo-

one-step process. The tetrakis, N,N-diethylol-3-amine pentaerythritol ethanoate synthesized via Michael addition of pentaerythritol tetracrylate (0.1 mol) and diethanolamine (0.4 mol) in methanol solvent, followed by removing solvent through vacuum distillation, obtained faint yellow oily liquid.

2.2.2. Etherification of hyperbranched monomer

A four-necked flask fitted with a condenser was charged with 1 mol of HPAE, 1 mol of PEG600, 1 mol of β,β' dichlorodiethyl ether and 2 mol of sodium hydroxide. The mixture was heated for a period of 5 h at 170°C, under a slow N₂ stream. The progress of the reaction was evaluated by determine the NaCl content that increases gradually to reach a constant value at the end of the reaction. The product was treated with equal volume of saturated NaCl solution and neutralized with diluted HCl. Then the reaction mixture was filtered to get rid of the solid NaCl precipitate.

The prepared ester can be abbreviated as HPAE-PEG600 which referred to the ester of hyperbranched pentaerythritol amine with poly(ethylene glycol 600 (PEG 600)).

2.3. Characterization of the prepared surfactants

FTIR spectra were analyzed with a Nicolet FTIR spectrophotometer using KBr in a wavenumber range of 4000–500 cm⁻¹ with a resolution accuracy of 4 cm⁻¹. All samples were ground and mixed with KBr and then pressed to form pellets.

¹H-NMR spectra of the prepared polymers were recorded on a 400MHz Bruker Avance DRX-400 spectrometer.

2.4. Electrochemical measurements

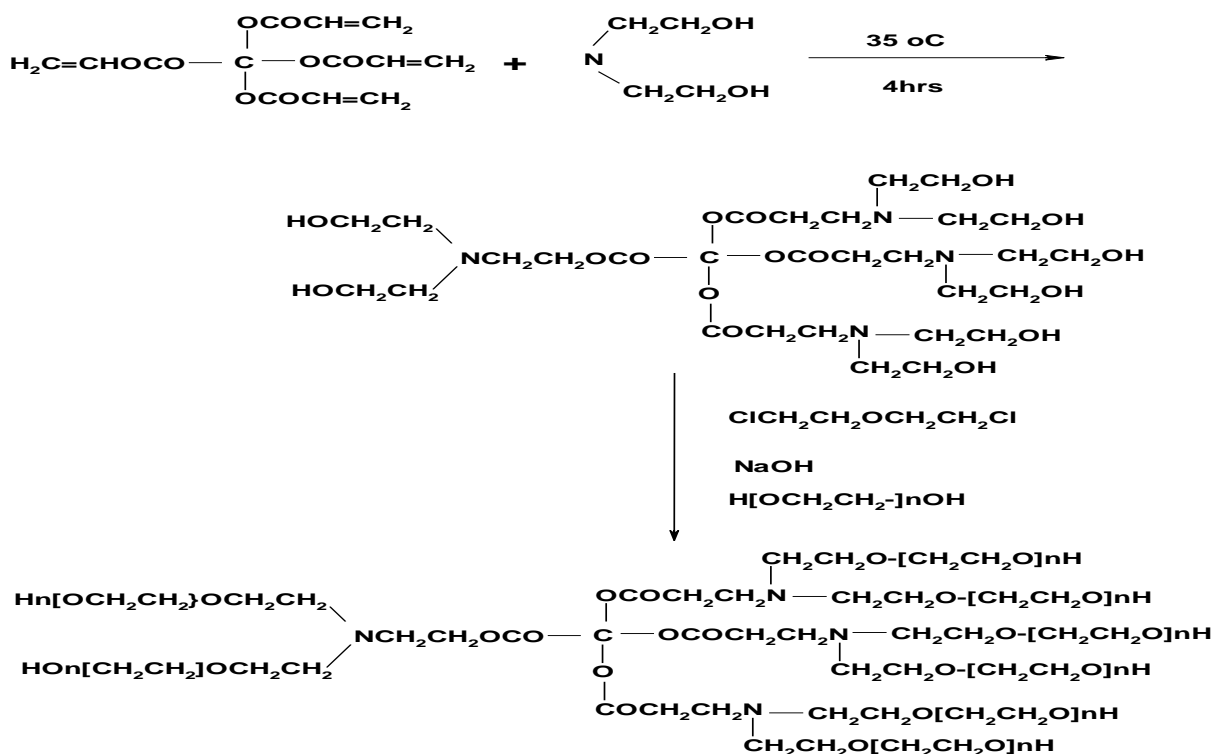
Polarization experiments were carried out in a conventional three-electrode cell. A platinum electrode and a saturated calomel electrode (SCE) were used as auxiliary and reference electrodes respectively. Electrochemical measurements were carried out using a computer-controlled potentiostat (Solartron 1470E system) with Solartron 1455A as frequency response analyzer to perform all polarization and EIS measurements. The polarization curves for steel specimen in 1 M HCl solution with or without various concentrations of the inhibitors were performed after 1 h immersion with a scan rate of 1mV/ s. The impedance measurements were carried out in the frequency range from 10 kHz to 0.01 Hz with a signal amplitude perturbation of 10 mV. Data were collected and analysed using CorrView, Corr- Ware, Zplot and ZView software.

3. RESULTS AND DISCUSSION

The hyperbranched polymer produced from modification of pentaerythritol triacrylate by reaction with diethanol amine via Michael addition reaction of the vinyl group to the secondary amine

groups. The product HPAE was etherified with PEG 600 in the presence of NaOH as catalyst. The reactions were illustrated in the scheme 1. The modification was used to prepare water soluble hyperbranched polymer. For higher generation dendrimers, solubility characteristics depend predominantly on the properties of their surface groups. As an example, dendrimers with very hydrophobic interiors such as polyethers and polycarbosilanes can be made water soluble by introducing hydrophilic groups into their surface groups. Oppositely, water soluble dendrimers can be made hydrophobic by converting their surface groups into hydrophobic units [16]. For the synthesis of dendrimers constructed by step-by-step sequences, two fundamentally different strategies, the divergent approach (from the inside out) [17-19] and convergent approach (from the outside in) [20], were employed. In this study one must take into account that the structure of water soluble corrosion inhibitors plays an important role in the anticorrosion process. We expected that the more branches the dendritic polymer has, the more effective it is in anticorrosive protection performance.

3.1. Chemical structure of the dendrites



Scheme 1. Preparation of hyper branched HPAE-PEG600 polymer.

The molecular structures of the HPAE and its etherified with PEG 600 (HPAE-PEG600) were confirmed by FTIR, ¹H and ¹³C NMR spectroscopy. In this respect, FTIR spectrum of HPAE-PEG600 was selected and represented in Figure 1. On the other hand, Figures 2 and 3 show the ¹H- and ¹³C - NMR spectra of HPAE-PEG600, respectively. FTIR analysis indicated the disappearance of bands at 3050 and 910 cm⁻¹, which referred to =CH stretching and out of plan bending, respectively, and appearance of new bands at 3500 cm⁻¹ (OH stretching) indicated the addition of DEA to PETA via

Michael addition reaction. Moreover the appearance of bands at 1750 cm^{-1} (ester $\text{C}=\text{O}$), 1050 cm^{-1} ($\text{C}-\text{N}$ stretch), and $2860\text{--}2950\text{ cm}^{-1}$ ($\text{C}-\text{H}$ sat.) indicated the formation of HPAE-PEG600 as represented in the scheme 1.

It can be noticed from ^1H NMR that there are different peaks at 4.4 ($-\text{OCOCH}_2\text{CH}_2-$), 3.6–3.8 ($-\text{OCOCH}_2\text{CH}_2\text{N}-$), 3.4–3.6 ($-\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$), and 3.5 ppm ($-(\text{CH}_2\text{CH}_2\text{O})$) indicated the formation of HPAE-PEG600. The disappearance of peaks above 4.5 ppm which related to $=\text{CHCOO}-$ of triacrylates indicated the addition of DEA to PETA. Careful inspection of peak, figure 2, indicated that the disappearance of OH end group peak.

Another route to determine the chemical structure of the HPAE-PEG600 was based on ^{13}C NMR data (Figure 3). The disappearance of peak at 120–130 ppm indicated the addition of DEA to PETA via Michael addition reaction. The data of HPAE-PEG600 indicated the appearance of peaks at 20, 26.2, 72, 83 and 172.2 ppm which attributed to $\text{C}-(\text{OCO})_4$, CH_2OH , $\text{CH}_2\text{CH}_2\text{O}$, $\text{CH}_2\text{CH}_2\text{N}$ and COO , respectively. The data indicated that the HPAE-PEG600 product required no further purification as illustrated in Scheme 1.

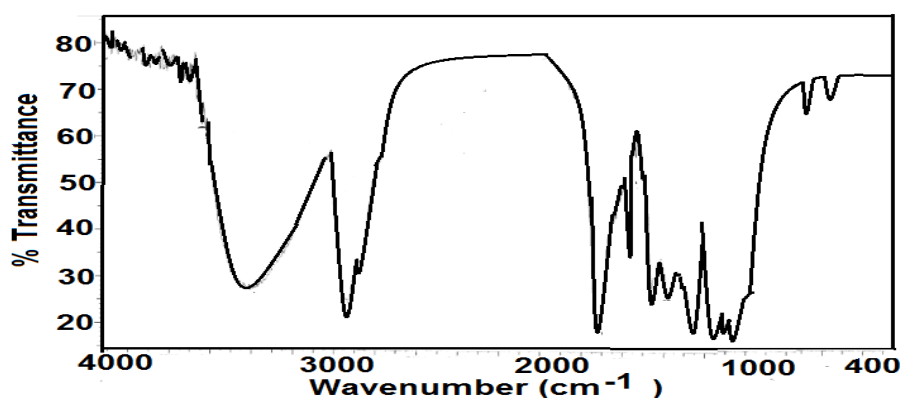


Figure 1. FTIR spectrum of HPAE-PEG600.

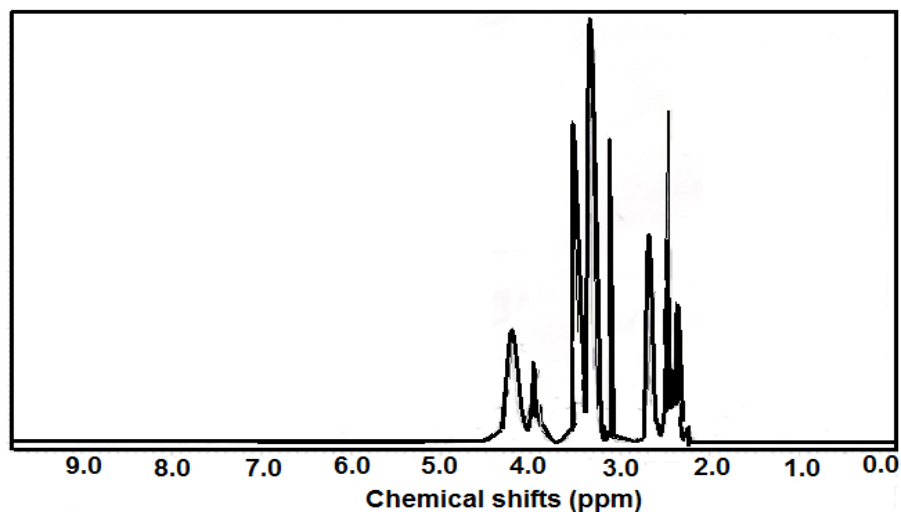


Figure 2. ^1H NMR spectrum of HMPE-PEG600.

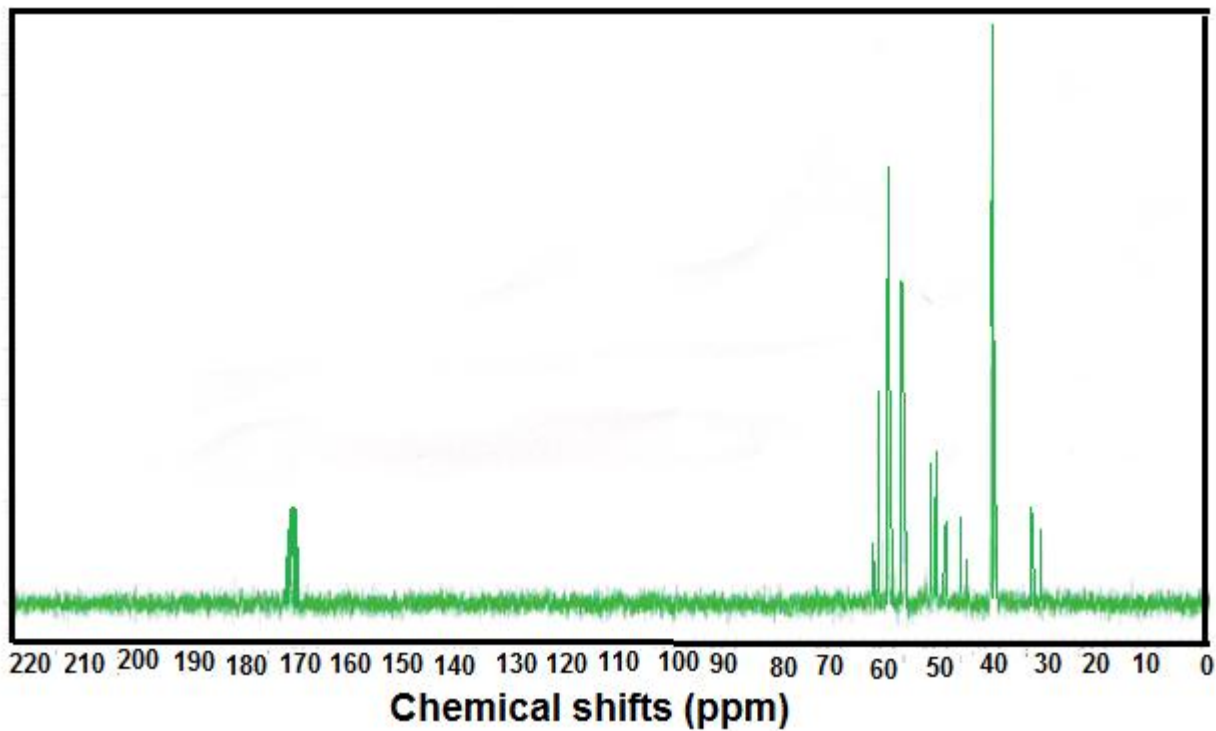


Figure 3. ¹³CNMR spectrum of HMPE-PEG600.

3.2. Potentiodynamic polarization curves

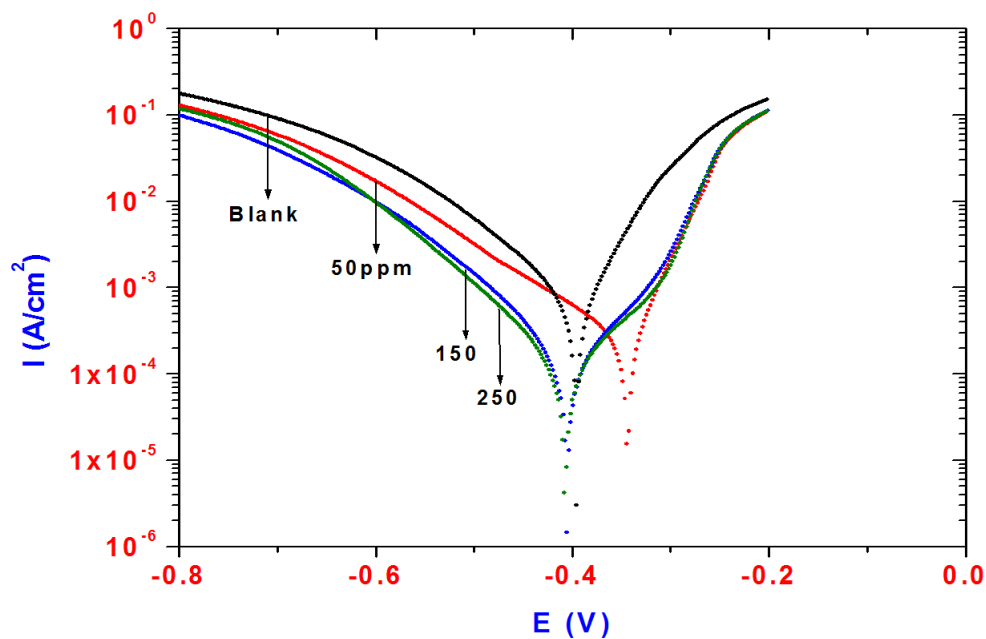


Figure 4. Polarization curves for steel in 1m HCl solution containing different concentrations of HPAE-PEG600.

Figure 4 shows the potentiodynamic polarization curves for steel in 1.0 M HCl solutions in the absence and presence of different concentrations of HPAE-PEG600. It can be seen from Fig. 2 that both anodic and cathodic reactions of corrosion process of steel electrode were inhibited after adding HPAE-PEG600 into the acidic solution. It is evident that, as the inhibitor is added to the corrosive medium both anodic dissolution of iron and cathodic reactions were retarded. The presence of HPAE-PEG600 in the acidic solution results in a shift of current density to lower one in comparison to that in blank solution. These results indicate that HPAE-PEG600 acts as a mixed-type inhibitor. In other words, the addition of inhibitor to 1 M HCl solutions reduces the anodic dissolution of steel and also retards the cathodic reaction. The adsorbed protective film of inhibitor on steel surface impedes by blocking the active sites of the steel. In this way actual surface area available for anodic and cathodic reactions is decreased. Electrochemical parameters such as anodic (B_a) and cathodic Tafel slopes (B_c), corrosion potential (E_{corr}), corrosion current density (i_{corr}), acquired from extrapolation of polarization curves are given in Table 1.

Table 1. Inhibition efficiency values for steel in 1M HCl with different concentrations of inhibitor calculated by Polarization and EIS methods.

| | Polarization Method | | | | | EIS Method | | |
|--------|---------------------|------------|-----------------------|---|--------|---------------------|---|--------|
| | B_a (mV) | B_c (mV) | E_{corr} (V) | i_{corr} ($\mu\text{A}/\text{cm}^2$) | $IE\%$ | R_{ct} Ohm | C_{dl} ($\mu\text{F}/\text{cm}^2$) | $IE\%$ |
| Blank | 69.00 | 120.00 | -0.3955 | 839 | ----- | 1.80 | 334 | ----- |
| 50 ppm | 51.50 | 166.44 | -0.3437 | 320 | 61.00 | 5.90 | 181 | 69.49 |
| 150 | 79.36 | 90.34 | -0.4050 | 120 | 85.69 | 6.90 | 173 | 73.91 |
| 250 | 88.72 | 92.91 | -0.47721 | 111 | 86.67 | 10.40 | 138 | 82.17 |

It is clear from Table 1 that the values of corrosion current density (i_{corr}) noticeably decreases in presence of inhibitor, which suggests that rate of electrochemical reaction was retarded due to formation of a protective film of inhibitor on steel surface and this protective film created a barrier between metal and corrosive medium. The inhibition efficiency was calculated using the following equation:

$$IE\% = 1 - i_{\text{corr}(1)} / i_{\text{corr}(2)} \times 100$$

where $i_{\text{corr}(1)}$ and $i_{\text{corr}(2)}$ are the corrosion current densities of steel in the presence and absence of inhibitor, respectively. It can be seen from the calculated results (Table 1) that HPAE-PEG600 inhibits the corrosion of steel to an appreciable extent and that the extent of inhibition is dependent on the inhibitor concentration. These results revealed that the corrosion current density (i_{corr}) decreased remarkably with the increasing inhibitor concentrations, leading to the increase of inhibition efficiency. Therefore, it could be concluded that the anodic dissolution of steel and the cathodic reactions were both inhibited by the inhibitor through merely blocking the reaction sites on the surface.

3.3. Electrochemical impedance spectrum (EIS)

Figure 5 shows the Nyquist plots of steel in the absence and presence of HPAE-PEG600. The plot is composed of a semicircle, which increased notably with inhibitor concentration. This result indicates that the charge-transfer process predominantly controls the corrosion inhibition of steel. The diameter of the impedance plot significantly increases, suggesting that the corrosion protection increases with the addition of inhibitor.

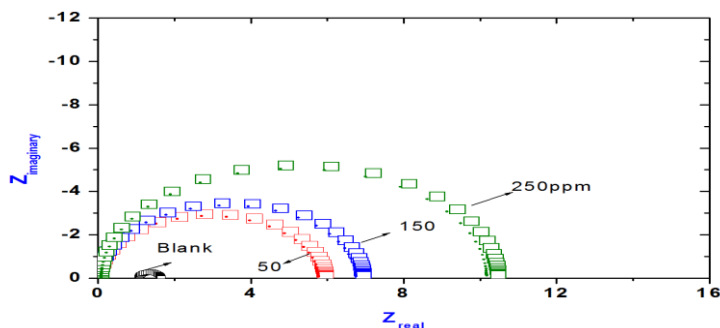


Figure 5. Nyquist plot for steel in 1m HCl solution containing different concentrations of HPAE-PEG600.

EIS spectra were analyzed using the equivalent circuit shown in Figure 6, which comprises of R_s as a solution resistance, R_{ct} as charge transfer resistance and C_{dl} presents the double-layer capacitance on the electrode surface. The fitting Nyquist plots deduced from the experimentally and fitted data show that the fitting results are in good agreements with the experimental data. The impedance parameters derived from these figures are given in Table 1. The fitting results showed that the R_{ct} values increased and the C_{dl} values decreased with inhibitor concentration. It can be concluded that the larger the diameter of the semicircle is the more densely the formed film. A large R_{ct} is associated with a slower corroding system, due to decrease in the active surface necessary for the corrosion reaction.

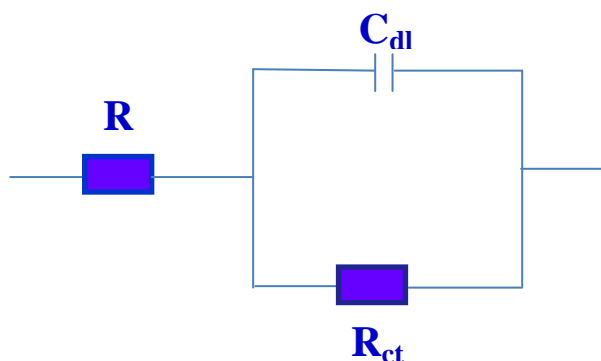


Figure 6. Equivalent circuit employed for fitting experimental data.

The decrease in C_{dl} values in the presence of HPAE-PEG600 inhibitors has been ascribed to a decrease in the dielectric constant and/or an increase in the double electric layer thickness, due to inhibitor adsorption on the steel/electrolyte interface [21-22]. The adsorption of inhibitor on the steel surface decreases its electrical capacity by displacing water molecules and other ions which are adsorbed on its surface. The decrease in capacity in inhibited system may be attributed to the formation of a protective layer on the electrode surface [23]. The inhibition efficiency (η) calculated by the Eq. (7) using the charge transfer resistance as:

$$\eta\% = 1 - \frac{R_{ct(1)}}{R_{ct(2)}} \times 100$$

where $R_{ct(1)}$ and $R_{ct(2)}$ are the charge transfer resistances in the HCl solution in the absence and in the presence of the inhibitors, respectively. The values of $\eta\%$ increase with inhibitor concentrations as shown from Table 1. This is attributed to the increase of surface coverage of inhibitive film on steel surface with the concentration of the inhibitors. The results can be attributed also to more and rapid adsorption of HPAE-PEG600 leads to a formation of a protective layer, which protected the reactive steel surface from the aggressive acid environment. This implies that the extent of adsorption on the steel/solution interface increases with HPAE-PEG600 concentration. This result showed the same trend as those obtained from potentiodynamic polarization measurements.

4. CONCLUSIONS

- The hyperbranched polymer produced from modification of pentaerythritol triacrylate by reaction with diethanol amine via Michael addition reaction of the vinyl group to the secondary amine groups. The product HPAE was etherified with PEG 600 in the presence of NaOH as catalyst.
- The data of analyses indicated that the HPAE-PEG600 product prepared with high purity and required no further purification
- HPAE-PEG600 acted as a good inhibitor for steel in severe acidic medium and behaved as a mixed type of inhibitor.
- Polarization curves and EIS measurements showed that inhibition efficiency increased with inhibitor concentration

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