



Polyether copolymer as an environmentally friendly scale and corrosion inhibitor in seawater



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ABSTRACT

A novel environmentally friendly type of corrosion and scale inhibitor acrylic acid-allylpolyethoxy carboxylate copolymer (AL15) was synthesized and characterized by FT-IR and ¹H NMR spectroscopic techniques. The performance of the synthesized copolymer as corrosion inhibitor for mild steel corrosion was evaluated by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The experimental results indicate that AL15 has good corrosion inhibition performance and the inhibition efficiency increased with the increase of AL15 concentration. Scanning electron microscopy (SEM) indicated that the corrosion inhibition is due to the formation of a chemisorbed film on the mild steel. The anti-scale property of AL15 in seawater was studied by static tests and the scale deposits were analyzed by X-ray diffraction (XRD) and SEM, respectively. The results indicated that the scale deposits surface morphology and size were changed significantly in the presence of AL15.

1. Introduction

Desalination is the process of removing dissolved solids, such as salts and minerals from sea water which is the most traditional and feeding source water for desalination facilities and capacities in the world [1]. Two main problems resulting from using water as thermal fluids are corrosion and scale [2]. These problems face most of the metallic industrial production because of the construction materials of various equipment of water systems are mainly mild steels [3].

The use of corrosion and scale inhibitors is one of the most common methods to control corrosion and scale deposition [4–6]. Polymers are widely used as effective corrosion and scale inhibitors [7–12]. They exhibit superior corrosion inhibition because of including long chain carbon linkage and multiple adsorption sites which can block large area of the corroding metal [13]. The adsorbed film on the metal surface acts as a barrier isolating the metal from the aggressive environment.

Most corrosion and scale inhibitors are polymers containing phosphate groups [14], such as phosphate ester as scale inhibitor and phosphonic chitosan as corrosion inhibitor for mild steel in seawater [15]. Although the phosphonate containing inhibitor are highly efficient as a corrosion and scale inhibitor, most of them are nutrients after discharge to sea, which lead to eutrophication. With the increasing environmental awareness, the current trend for corrosion and scale inhibitor usage is toward more environmentally friendly “green”

chemicals that are undoubtedly the trend of development [16,17].

The paper is aimed to overcome the above drawbacks of using toxic scale and corrosion inhibitors especially in desalination water treatment plants. So that, we have synthesized and characterized a novel type of polyether copolymer (AL15). In comparison with traditional corrosion and scale inhibitors, AL15 derived from capped polyether, easily prepared with lower cost, reliable reproducibility and less dosages, have superior corrosion and scale inhibitive performances. In addition, AL15 belongs to an environment friendly corrosion and scale inhibitor, only containing three elements of carbon (C), hydrogen (H), oxygen (O) and is non-phosphorous (P), non-nitrogen (N) and sulfur (S) free, which are potential nutrients for algae.

2. Experimental

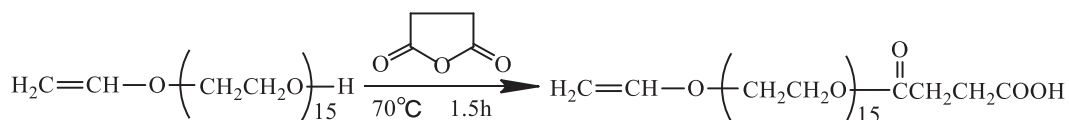
2.1. Materials

AA and APEG (Polyether) is analytically pure grade and was supplied by Zhongdong Chemical Reagent Co. (Nanjing, Jiangsu, China). Distilled water was used for all the studies.

2.2. Synthesis of APEL15

The carboxylic acid functionalization of the surface hydroxyl groups

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Scheme 1. Synthesis of APEL15.

was realized by reaction with succinic anhydride (SA) in acetone [18]. The synthesis procedure of APEL15 is shown in Scheme 1.

2.3. Synthesis of AA-APEL15

A 5-neck round bottom flask, equipped with a thermometer and a magnetic stirrer, was charged with 90 mL distilled water and 0.1 mol APEL15 and heated to 70 °C with stirring under nitrogen atmosphere. After that, 1.5 mol AA in 20 mL distilled water (the mole ratio of APEL15 and AA was 1:10) and the initiator solution (1.5 g ammonium persulfate in 18 mL distilled water) were added separately at constant flow rates over a period of 1.5 h. The reaction was then heated to 80 °C and maintained at this temperature for an additional 2.5 h, ultimately affording an aqueous polymer solution containing approximately 33% solid. AA-APEL15 is called AL15. The Synthesis of AL15 is given in Scheme 2.

2.4. Chemical composition of the tested seawater

The typical characteristics of the used seawater are shown in Table 1 indicating 11 of the constituents of seawater which account for 99.5% of the total solutes, chloride ions are the largest constituent.

2.5. Methods for evaluation the corrosion and scale inhibition of AL15

2.5.1. Static tests for scale inhibition

Static tests for scale were conducted according to the Chinese National Standard method [19]. The tests were maintained for 10 h at a certain temperature with a certain amount of AL15. The remaining Ca^{2+} was determined by EDTA titration after cooling to room temperature. The scale inhibition efficiency was calculated as follows:

$$\text{inhibition (\%)} = \frac{[\text{Ca}^{2+}]_{\text{final}} - [\text{Ca}^{2+}]_{\text{blank}}}{[\text{Ca}^{2+}]_{\text{initial}} - [\text{Ca}^{2+}]_{\text{blank}}} \times 100\%$$

where $[\text{Ca}^{2+}]_{\text{final}}$ is concentration of Ca^{2+} ions in the filtrate in the presence of inhibitor after seawater solutions heated for 10.0 h at 60 °C, $[\text{Ca}^{2+}]_{\text{blank}}$ is concentration of Ca^{2+} ions in the filtrate in the absence of inhibitor after seawater solutions were heated for 10.0 h at 60 °C, and $[\text{Ca}^{2+}]_{\text{initial}}$ is concentration of Ca^{2+} ions at the beginning of the experiment.

2.5.2. Electrochemical studies for corrosion inhibition

Corrosion tests were carried out using mild steel samples with a composition (wt%) of: C, 0.055; Mn, 0.52; P, 0.018; S, 0.005; Si, 0.052; Al, 0.044; Cr, 0.021; Cu, 0.006; Nb, 0.001; Ti, 0.001; and rest Fe in the tested seawater. CHI660B electrochemical analyzer was used for electrochemical measurements. The polarization measurements a conventional three-electrode cell containing mild steel specimen (of exposed area of 1 cm²), a platinum wire and a saturated calomel were used as working, auxiliary and reference electrodes, respectively. The working

electrode and the reference electrode were connected via a salt bridge. In order to minimize the ohmic voltage error, the salt bridge was as close as possible to the electrode surface. The working electrode was polished mechanically, washed with acetone, distilled water and dried before measurement. The potentiodynamic polarization measurements conduct from scans ± 200 mV relative to the open circuit potential (OCP) at scan rate of 0.50 mV/s.

2.6. Infrared spectroscopy

Fourier-transform infrared (FT-IR) spectra were taken on a Bruker FT-IR analyzer (VECTOR-22, Bruker Co.) by using the KBr-pellet method (compressed powder). The wave number of the IR peaks of functional groups was determined in the range of 4000–400 cm⁻¹.

2.7. Surface analysis

2.7.1. Surface analysis for corrosion inhibition

The test coupons were immersed in 150 mL of seawater with AL15 at 60 °C and washed with distilled water and then dried in air at room temperature. The morphology information was obtained using scanning electron microscope (SEM, S-3400N, HITECH).

2.7.2. Characterization of scale deposits

The change of crystal morphology and size of CaCO_3 and CaSO_4 were examined through a scanning electron microscope (SEMS-3400N HITECH) and X-ray diffraction (Rigaku D/max 2400).

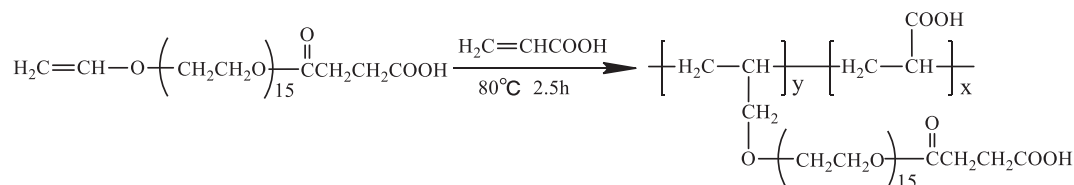
3. Results and discussion

3.1. Characterization of APEL15 and AL15

The FT-IR spectra of APEL15, APEL15, and AA-APEL15 are exhibited in Fig. 1. The 1736 cm⁻¹ strong intensity absorption peak ($-\text{C}=\text{O}$) in curve b reveals clearly that APEL15 has been synthesized successfully. The fact that the ($-\text{C}=\text{C}-$) stretching vibration at 1646 cm⁻¹ appears in curve b but disappears completely in curve c reveals that free radical polymerization between APEL15 and AA has happened.

APEL15 ((CD₃)₂SO, δ ppm): 2.25–2.55 ($-\text{CH}_2\text{CH}_2-$, protons in $-\text{COCH}_2\text{CH}_2\text{COOH}$), 2.50 (solvent residual peak of (CD₃)₂SO), 3.00–3.80 ($-\text{OCH}_2\text{CH}_2-$, ether groups), 3.80–4.10 and 5.00–6.00 ($\text{CH}_2=\text{CH}-\text{CH}_2-$, propenyl protons) [Fig. 2(b)]. The δ 4.40–4.60 ppm ($-\text{OH}$) active hydrogen in (a) disappeared completely and ($-\text{CH}_2\text{CH}_2-$) protons in $-\text{COCH}_2\text{CH}_2\text{COOH}$ appears obviously in 82.25–2.55 ppm in (b). It proves that $-\text{OH}$ in APEL15 has been entirely replaced by $-\text{COCH}_2\text{CH}_2\text{COOH}$.

AL15 ((CD₃)₂SO, δ ppm): 2.50 (solvent residual peak of (CD₃)₂SO), 3.00–3.80 ($-\text{OCH}_2\text{CH}_2-$, ether groups) (Fig. 2(c)). δ 3.80–6.00 ppm in (b) double bond absorption peaks completely disappeared in (c). This



Scheme 2. Synthesis of AL15.

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