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Synthesis of polyaspartic acid derivative and evaluation of its corrosion and scale inhibition performance in seawater utilization



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HIGHLIGHTS

- A new corrosion and scale inhibitor, polyaspartic acid derivative, was synthesized.
- Polyaspartic acid derivative is non-phosphorus and biodegradable.
- Polyaspartic acid derivative has a super scale inhibition property in seawater.
- Polyaspartic acid derivative has a super corrosion inhibition property in seawater.
- Polyaspartic acid derivative would be suitable for different water quality of seawater.

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ABSTRACT

A polyaspartic acid derivative (PASP-SEA-ASP) was synthesized from polysuccinimide with 2-aminoethanesulfonic acid and aspartic acid. PASP-SEA-ASP achieved a better corrosion inhibition rate for A3 carbon steel in seawater compared with polyaspartic acid (49% cf. 45% at the dosage of 100 mg/L). The development of a composite inhibitor (a mixture of PASP-SEA-ASP, zinc sulfate, 2-hydroxyphosphonoacetic acid (HPAA) and hexadecylldimethyl (2-sulfite) ethyl ammonium on a mass ratio of 15:3:6:1, respectively) led to a significantly enhanced corrosion inhibition effect, achieving an inhibition rate of 97%. The mass ratio of the composite inhibitor could be adjusted to achieve the desired corrosion inhibition rate for seawater with varying characteristics. PASP-SEA-ASP also showed excellent scale inhibition properties for seawater, with a scale inhibition rate of 100% achieved with a dosage of 14 mg/L. This study demonstrated the potential of PASP-SEA-ASP to inhibit both corrosion and scale formation in domestic and industrial utilization of seawater such as cooling systems and thermal desalination processes.

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1. Introduction

The consumption of fresh water by industrial processes has increased significantly with the rapid development of major industries such as iron and steel, power generation, chemical production over the past decades, which has intensified the shortage of fresh-water resources [1]. In addition, population explosion has also contributed to increased fresh water consumption. To alleviate the pressure on water supply, the utilization of seawater for industrial applications such as cooling systems has been increasing in recent years. However, natural seawater contains not only most of the elements present on the earth but also a significant amount of organic compounds and marine

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microorganisms [2,3]. This can result in a range of operational issues for cooling water systems, including corrosion and scale formation [4–6]. Corrosion can result in unpredictable and rapid deterioration of equipment materials and hence result in great economic losses and potentially catastrophic risks [7,8]. Furthermore, the presence of corrosion products can lead to a decrease in heat exchange efficiency [9,10]. Apart from corrosion products, scale formation also impedes heat exchange efficiency. The use of corrosion inhibitors is one of the practical methods for the protection of carbon steel components against corrosion in seawater utilization due to its advantages such as convenience, ease in its application and low cost [11–13]. Another issue associated with seawater utilization such as thermal desalination processes is scaling which can lead to a reduction in heat transfer, resulting in the loss of production capacity due to scheduled and unscheduled shutdowns for scale removal [14-17]. Scale inhibitors are widely used in industry to avoid formation of scale and to reduce the rate of dissolution of metals [18,19].

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Polyaspartic acid (PASP) is a non-phosphorus based biodegradable polyamino acid, which has been used as an environment-friendly scale and corrosion inhibitor for fresh-water applications [20,21]. However, its corrosion and scale inhibition performance was not prominent when used for seawater [22]. Several methods have since been developed to improve the corrosion and scale inhibition of PASP [23,24]. The most promising method appeared to be the introduction of functional groups having scale inhibition effect (e.g., carboxylic acid, phosphonic acid and sulfonic acid) to the side chain of PASP through the ring-opening reaction by amine-group catalysis [20,21,25]. A polyaspartic acid derivative (PASP-ASP) has been synthesized by introducing the carboxylic acid to the side chain of PASP, and investigated for its antiscaling performance in fresh water applications [26,27]. Nevertheless, there is generally a lack of information from the literature relating to the anti-corrosion and anti-scaling performance of polyaspartic acid derivatives in a seawater environment.

The carboxylic acid group has better scale and corrosion inhibition performance, whereas the sulfonic acid group has better dispersing performance [28]. Consequently, the simultaneous introduction of these groups into the molecular structure of PASP was considered a potential approach to improve both the corrosion and scale inhibition performance of carbon steels in seawater utilization. A previous study of the scale inhibition performance of the polyaspartic acid derivative (PASP-SEA-ASP) in fresh water environment showed that it had good scale inhibition performance with the scale inhibition rate exceeding 80% in the static experiments at the dosage of 2 mg/L and the solution temperature of 40 °C. There was almost no scale formed on the heat exchanger surface and the fouling thermal resistance decreased substantially with the presence of the PASP-SEA-ASP in the cooling water. The yield percentage obtained from this study was 82% [29]. The ratio of the carboxylic acid group to the sulfonic acid group in the synthesis of the PASP-SEA-ASP may be changed to maximize its scale inhibition effect for other applications such as seawater. The applications in sea water which would have more serious corrosion and scale formation problems as opposed to fresh water. The aim of this study was to synthesize a polyaspartic acid derivative (PASP-SEA-ASP) from polysuccinimide (PSI) with 2-aminoethanesulfonic acid (SEA) and aspartic acid (ASP) and to evaluate its corrosion and scale inhibition effect in seawater. The corrosion inhibition efficiency of the PASP-SEA-ASP as a single inhibitor and in composite form (a mixture with other conventional inhibitors), and its scale inhibition efficiency were determined by weight loss and static scale inhibition tests, respectively.

2. Experimental

2.1. Synthesis of PASP and PASP-SEA-ASP

2.1.1. Synthesis of PASP

Polysuccinimide was synthesized by pyro-condensation of L-aspartic acid monomer at 240 °C for 4 h in an electric thermostatic drying oven. Sodium hydroxide solution (15%) was added to the suspension of the polysuccinimide, the mixture was then stirred for 4 h at 12 °C; pH was kept at 8–9. Double the volume of absolute alcohol was added to the mixture, and the produced precipitate was then washed for 3 times with deionized water and dried at 80 °C for 48 h to obtain PASP solid. The relevant synthesis reactions are expressed in Figs. 1 and 2.

Fig. 1. Synthesis route of polysuccinimide.

Fig. 2. Synthesis route of PASP.

2.1.2. Synthesis of PASP-SEA-ASP

Aspartic acid and 2-aminoethanesulfonic acid were dissolved in sodium hydroxide solutions (15%), respectively, which were then added to the suspension of polysuccinimide. The mixture was stirred for 24 h at 25 °C; pH was maintained at 8–9. The pH of the mixture was adjusted to 5.2 with HCl solution to remove unreacted 2-aminoethanesulfonic acid from the mixture through filtration, and then the pH was adjusted to 2.8 to remove unreacted aspartic acid from the mixture through filtration. Double the volume of absolute alcohol was added to the filtrate, and the produced precipitate was then washed for 3 times with deionized water and dried at 80 °C for 48 h to obtain the target copolymer solid. The relevant synthesis reaction is expressed in Fig. 3.

2.2. Preparation of PASP-SEA-ASP composite

In order to enhance the corrosion inhibition performance for seawater utilization, PASP-SEA-ASP composite was prepared by mixing the synthesized PASP-SEA-ASP with solutions of zinc sulfate, 2-hydroxyphosphonoacetic acid (HPAA) and hexadecylldimethyl (2-sulfite) ethyl ammonium in a beaker at various mass ratios for determining the optimum composition.

2.3. Methods for examining the efficiency of corrosion and scale inhibition

2.3.1. Weight loss method for corrosion inhibition efficiency

The corrosion inhibition performance of PASP-SEA-ASP was determined according to Chinese National Standard method (GB/T 18175-2000) [30]. The main steps were as follows: 1600 mL of seawater (Bohai Sea, China) was added to a beaker containing 100 mg/L of different seawater treatment chemicals respectively, including PASP, PASP-SEA-ASP and PASP-SEA-ASP composite, in order to evaluate their corrosion inhibition effects. The beaker was put into a water bath to maintain the temperature of 40 °C. The carbon steel test coupons with dimensions of 50 mm \times 25 mm \times 2 mm were sectioned from plate. Standard metallographic preparation (grinding and polishing) using SiC paper and diamond paste was adopted to provide a polished surface finish. The carbon steel test coupons with a surface area of 28 cm² were then hung in the solution and rotated at 75 rpm for 72 h. The corrosion rate of the carbon steel test coupon was calculated from Eq. (1). The typical characteristics of Bohai Seawater are shown in Table 1 and the composition of the carbon steel test coupons is shown in Table 2.

$$X = \frac{8760 \times 10 \times (W_0 - W)}{A \times D \times T} \tag{1}$$

where W is the mass of corrosive carbon steel test coupon after test (g); W_0 is the mass of carbon steel test coupon before test (g); A is surface area of carbon steel test coupon (28 cm²); D is the density of carbon steel test coupon (7.85 g/cm³); T is test time (72 h); 8760 is a constant which represents the hours in a year (365 × 24 h); 10 is the conversion factor from cm to mm (mm/cm); X is the annual corrosion rate of carbon steel test coupon (mm/y).

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