



Synthesis of modified polyaspartic acid and evaluation of its scale inhibition and dispersion capacity



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HIGHLIGHTS

- A new scale inhibitor and dispersing agent, modified polyaspartic acid (Ser-PASP), was synthesized.
- Inhibition efficiency is close to 100% against CaCO₃ when the dosage is 4 mg/L.
- It achieves complete inhibition effect on CaSO₄ scale when the dosage is 5 mg/L.
- When Ser-PASP was added, the scale crystals became irregular.

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ABSTRACT

Polyaspartic acid (PASP) is an environmentally friendly scaling inhibitor. In order to enhance the performance of its scale inhibition and dispersion capacity, PASP is commonly modified with side chain functional groups via polysuccinimide (PSI) ring-opened. In this work, environmentally friendly serine was selected as ring-opened agent to prepare modified polyaspartic acid—Ser-PASP. The synthesized polymer was characterized by infrared spectrometry (FTIR) and ¹H NMR. The performance of Ser-PASP on the inhibition of CaCO₃, CaSO₄ and Ca₃(PO₄)₂ and its dispersion ability on Fe₂O₃ were also studied. The results show that the inhibition efficiency of Ser-PASP is close to 100% for CaCO₃ with 4 mg/L inhibitor, and reach up to 100% for Ca₃(PO₄)₂ with 22 mg/L inhibitor. The best dispersion efficiency for ferric oxide is 70.4% when Ser-PASP is 25 mg/L. Ser-PASP and PASP have similar inhibition performance against CaSO₄. The effects on the formation of CaCO₃ and CaSO₄ were investigated by scanning electronic microscopy (SEM) and X-ray powder diffraction (XRD), respectively.

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1. Introduction

In recent years, with the rapid economic development, population growth and water pollution, fresh water crisis is becoming more and more serious [1,2]. In order to solve the water resource crisis, people pay attention to the vast sea and develop seawater desalination technology [3,4]. Desalination of seawater by reverse osmosis (RO) to produce fresh water has been widely used with the construction of large RO plants [5]. But precipitation and scale deposition are one of the major problems in RO desalination plants and other water treatment installations [6,7]. The presence of a scale layer can decrease the efficiency of heat transfer, increase energy consumption, cause pernicious accident, etc. [8–13]. A wide variety of ways have been used to solve this problem, and the most common and effective scale control method is the use of

scale inhibitors [14,15]. With the enhancement of consciousness of environmental protection, the current trend concerning inhibitor use is towards more environmentally friendly “green” chemicals [16,17].

PASP as a representative “green” scale inhibitor has attracted intensive interest since it has nontoxicity and good biodegradability [18,19]. In addition, PASP molecule contains carboxylic group with good chelating ability and dispersability [20]. Nevertheless, as it only contains carboxylic group, the comprehensive scale inhibition performance of PASP is poor, which limits its use [21]. In order to improve the performance, studies on modified PASP have been carried out. Numerous efforts have been made to introduce new functional groups on the side chain of polyaspartic acid, such as hydroxyl group, carboxylic group, sulfonic group, and phosphonyl [22]. For example, Xu et al. got polyaspartic acid–melamine grafted copolymer via polysuccinimide (PSI) ring-opened by melamine [2]. Senthilmurugan et al. have synthesized co-polymers of maleic acid with acrylic acid (MA–AA) and ortho toluidine (MA–OT) and the works were certified that they are efficient CaCO₃ scale inhibitors [23]. Though these studies improve the scale inhibition of PASP, there are also some problems such as those monomers

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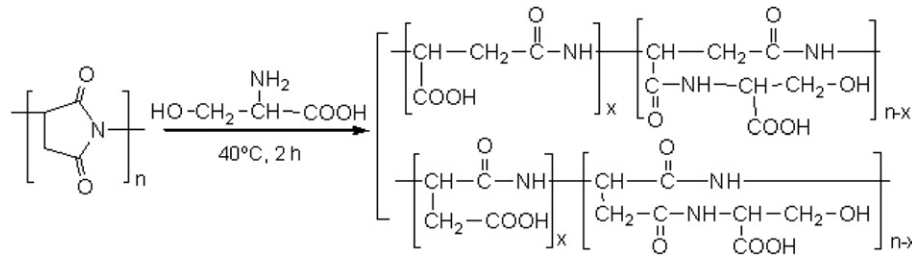


Fig. 1. Synthesis routes of Ser-PASP.

are not easily degradable or degradation products are poisonous, which does not accord with real “green” inhibitor.

In this study, the modified polyaspartic acid was synthesized by using serine and polysuccinimide (PSI) as the starting materials. Serine is an amino acid which contains both hydroxyl and amino groups, and it is biodegradable and environmentally friendly. The intermediate product polysuccinimide (PSI) was synthesized by polymerization with maleic anhydride and ammonia as raw material. Then the side chain of PASP was introduced new functional groups by the method of ring-opened, synthesized PASP and Ser-PASP. The scale inhibition performance of the products was studied by the method of static scale inhibition test, the chemical structure was characterized by FTIR and ^1H NMR, and the scale crystals were investigated by SEM and XRD. Finally, the dispersion capacity for ferric oxide of the synthetic products was also investigated.

2. Materials and methods

2.1. Reagents and instruments

Maleic anhydride, serine, calcium chloride, sodium borate and ammonium ferrous sulfate were obtained from Guangfu Fine Chemical Institute Co., Ltd (Tianjin, P.R. China). Ethylenediaminetetraacetic acid disodium salt, sodium hydrate and ethanol were purchased from Tianjin NO.6 Chemical Reagent Factory (Tianjin, P.R. China). Sodium sulfate, sodium hydrogen carbonate and N,N-dimethylformamide (DMF) were supplied by Tianjin Benchmark Chemical Reagent Co., Ltd (Tianjin, P.R. China). All reagents and solvents were reagent grade and directly used without further purification. Distilled water was used throughout the research.

Instruments used in the present research include BRUKER TENSOR 27 Fourier transform infrared spectroscopy (FT-IR), Hitachi U-4100UV-VIS near IR spectrophotometer, Avance III plus 400 MHz Nuclear Magnetic

Resonance, 722 grating spectrophotometer, NanoSEM450LV scanning electron microscopy (SEM), D8 FOCUS X-ray powder diffractometer, FA2004B electronic balance, DH-101 Electro-thermostatic blast oven, Ubbelohde viscosity meter, and DF-101S thermo-static magnetic stirrer.

2.2. Synthesis of polysuccinimide (PSI)

9.8 g (0.1 mol) of maleic anhydride was dissolved in a three-neck flask under heated and 9 mL of ammonia (0.12 mol NH_3) was slowly added into it, and reacted at 75 °C for 1 h with magnetic stirring. Then, the solution was heated under nitrogen to 180 °C for 20, 30, 40, 50, 60 min, respectively.

2.3. Synthesis of polyaspartic acid (PASP)

Certain amounts of PSI and a proper amount of 2 mg·L⁻¹ sodium hydroxide solution were added to a round-bottom flask and heated at 40 °C for 1 h under stirring. The solution was adjusted to reach a pH value of 7.0 with HCl solution and then filtered, washed with absolute alcohol and dried. Finally a reddish-brown solid was attained [24].

2.4. Synthesis of modified polyaspartic acid (Ser-PASP)

Certain amounts of PSI and water were mixed to form a suspension. Then, the sodium hydroxide solution of serine was slowly dropped into the suspension and heated at 40 °C for 2 h under stirring. A small amount of NaOH was added in the mixed solution and the reaction lasted under 40 °C for 1 h. At the end of the reaction, pH was adjusted at 7. Orange yellow viscous solid was obtained after the precipitate being washed with ethanol and dried. Relevant synthetic reaction is expressed in Fig. 1.

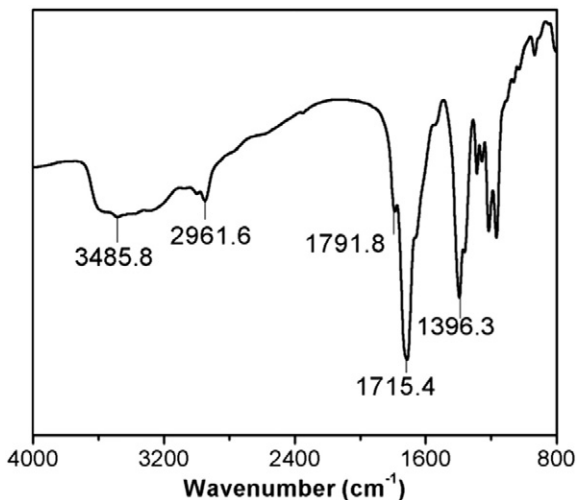


Fig. 2. FTIR spectrum of PSI.

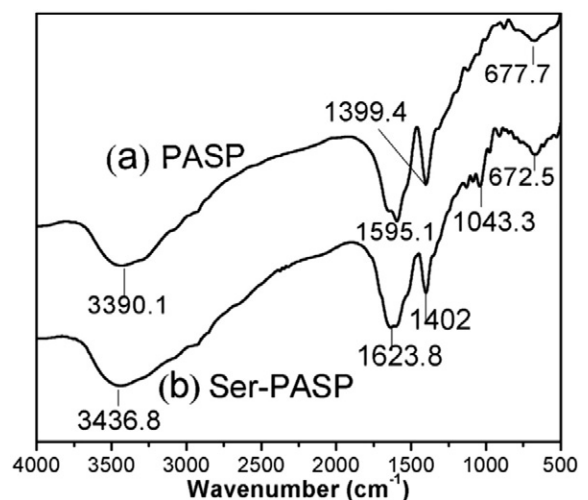


Fig. 3. FTIR spectrum of PASP and Ser-PASP.

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