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Scale inhibition performance and mechanism of sulfamic/amino acids modified polyaspartic acid against calcium sulfate

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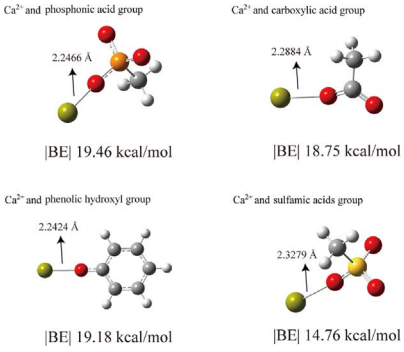
GRAPHICAL ABSTRACT



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ABSTRACT

Modified polyaspartic acid (PASP) scale inhibitors, Tyr-SA-PASP and Trp-SA-PASP, were prepared through grafting copolymerization on PASP with sulfamic/amino acids, and then applied for the inhibition of calcium sulfate from cooling water. Scale inhibition performance evaluation demonstrated Tyr-SA-PASP and Trp-SA-PASP were two cost-effective scale inhibitors for the inhibition of calcium sulfate: Compared to PASP and two commercial scale inhibitors (PAPEMP and JH-907), both modified PASP scale inhibitors exhibited higher inhibition performance, due to coordination between the deprotonation of carboxylic acid and phenolic hydroxyl groups of Tyr-SA-PASP and carboxylic acid groups of Trp-SA-PASP and Ca^{2+}. Scale inhibition mechanism was investigated from microscopic viewpoints: coordination was the intrinsic driving force; Modified PASP scale inhibitors significantly damaged the crystalline structure of calcium sulfate scale, which resulted from coordination between functional groups on modified PASP scale inhibitors and Ca^{2+}; The scale inhibition ability of modified PASP scale inhibitors came from the prevention of the growth of crystal planes ({040}, {041} and {113}). The current study provided a strategy for the design of scale inhibitors from the viewpoint of chemical structures.

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1. Introduction

Water is the most widely applied cooling fluid to remove unwanted heat from heat transfer surfaces [1]. Cooling water contains scale-forming ions, such as Ca^{2+}, Mg^{2+}, CO_3^{2-}, SO_4^{2-} and HCO_3^{-} [2]. In particular, the growth of calcium scale in many industrial processes causes a number of serious problems, such as overheating, loss of system efficiency, unscheduled shutdown time, and ultimately heat exchanger failure [3]. One commonly available calcium scale is calcium sulfate. The scale-deposit mineral is often found in water treatment plants and thermal desalination process [4,5].

Acids can be used as descaling agents. However, because of their aggressiveness, extensive efforts have been made to reduce the rate of dissolution of metals of pipe walls [6]. One effective approach of scale control is the addition of chemical scale inhibitors, which can retard or prevent scale formation [7], through affecting nucleation and crystallization rates of calcium sulfate and inducing morphological changes of crystals [8]. Although amounts of effective scale inhibitors have been investigated [9], some of them, like phosphorus scale inhibitors, are possible to engender secondary pollution and ecological imbalance of water bodies [10]. By contrast, research in scale prevention is oriented to the development of the so-called green products with high inhibition efficiency but low pollution risk [11], such as pteroyl-L-glutamic acid (PGLU) [12], poly (maleic anhydride-*alt*-acrylic acid) [13], sodium gluconate [14], acrylic acid-allyloxy poly (ethylene glycol) polyglycerol carboxylate copolymer [15] and so on. Among them, polyaspartic acid (PASP) is one environmental-friendly and multifunctional polymeric material that possesses the merits of biodegradation, chelation, and dispersion [16]. Although PASP exhibits welcome anti-scaling performance at low temperatures, its poor performance in high-temperature environments markedly limits its application range [17]. Recently, chemical modification has been proven to be an efficient way for improving the anti-scaling efficiency of PASP [18]. For example, carboxylic acid and sulfonic acid groups (providing coordination and dispersing effects, respectively) have represented desired performance in industrial practice for scale control [19]. Despite the fact that some studies enhance the anti-scaling performance of PASP to some degree, problems still exist, such as low biodegradability of products and high toxicity of petrochemical products-based modification reagents, which go against the concept of “green” scale inhibitor [20,21].

In addition to the design and synthesis of green scale inhibitors, scale inhibition mechanism on interactions between Ca^{2+} and functional groups of scale inhibitors, is another important aspect for both fundamental study and application. Traditional means to study scale inhibition mechanism, including UV–vis spectra [6,19], scanning electron microscopy (SEM) [22–24] and X-ray diffraction (XRD) [25–27], focus on characterizations of the macroscopic scales, in order to speculate the microscopic mechanism. However, direct evidences in molecular level to prove the interactions between Ca^{2+} with functional groups are rarely provided. According to authors' and others' recent works, X-ray photoelectron spectroscopy (XPS) and differential UV–vis absorbance give efficient ways to directly characterize the microscopic interaction of solid material formed in water [28–31]. Besides, theoretical calculation, a useful tool for investigating materials in molecular level, has been well established and widely applied in researches on water bodies. Thus, these methods are worthy employing in scale inhibition study, despite that little work has done so.

In this work, new scale inhibitors were synthesized by introducing carboxylic acid and sulfonic acid groups onto the side chains of PASP, in which tyrosine (Tyr) or tryptophan (Trp), two environmental-friendly amino acids, provided carboxylic acid groups, while sulfamic acid offered sulfonic acid groups. Aromatic-rings structures in both amino-acids are also expected to enhance UV–vis absorbance of the products, beneficial for further in-situ mechanism investigation. Performances of the resultant copolymers for inhibition of calcium sulfate were assessed by static tests under different conditions. Finally, microscopic scale inhibition mechanisms were discussed in detail, using SEM, XRD, XPS, differential UV–vis absorbance spectra analyses, and density functional theory (DFT) calculation.

2. Materials and methods

2.1. Materials

Maleic anhydride and urea were purchased from Shanghai Yuanye Bio. Technol. Co. Tyr and Trp were purchased from Aladdin Industrial Co. Two commercial scale inhibitors, PAPEMP and JH-907 (their structure are shown in Fig. 2), were obtained from Shandong PRIO Environmental Protection Technology Co. Ltd. All other chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd. Ultrapure water (18.2 MΩ·cm^{-1}) was used in all the experiments.

2.2. Synthesis and characterizations of sulfamic/amino acids modified PASP

Firstly, polysuccinimide (PSI) was prepared according to the method in Supporting information Fig. S1 and Text S1 [32]. Then, two sorts of sulfamic/amino acids modified PASP, named as Tyr-SA-PASP and Trp-SA-PASP according to the amino acids types, respectively, were synthesized according to Fig. 1a: After certain amounts of PSI were added into water to form a suspension, sodium hydroxide solutions of sulfamic acid and Tyr/Trp were slowly dropped into the suspension and heated at 313 K for 2 h under stirring. Next, the pH of the mixture was adjusted to 7. The solid product was obtained after precipitated, washed with ethanol and vacuum dried.

Characterization methods of the obtained scale inhibitors included IR on a Bruker Tensor-27 IR spectrometer within a wave number range of 400–4000 cm^{-1}, UV–vis spectra on a Hitachi UH-5300 UV–vis spectrophotometer, elemental analysis on a vario EL III elemental analyzer, and thermogravimetric (TG) analysis on a Diamond DMA spectrometer.

2.3. Evaluation of the scale-inhibition performance against calcium sulfate

The scale-inhibition performance of the prepared inhibitors against calcium sulfate was investigated by static scale-inhibition tests according to the Chinese National Standard GB/T 16632-2008 for EDTA titration. Main differences between Chinese National Standard GB/T 16632-2008 and ASTM-D511-2009 standard have been provided in Supporting information Text S2. The solution in calcium sulfate inhibition tests contained $CaCl_2$ (6800 mg/L Ca^{2+}) and Na_2SO_4 (7100 mg/L of SO_4^{2-}), and the concentration of each component was selected according to previous literatures [33] for comparison.

Stock solutions of scale inhibitors (1000 mg/L) were always freshly prepared by dissolving inhibitors in water. During each test, once a designed volume of scale inhibitor stock solution was dropped into $CaCl_2$ solution in a 500 mL volumetric flask, borax buffer solution and Na_2SO_4 solution were immediately added. The mixture solution, with a pH of 7, was diluted to 250 mL, stirred to ensure complete mixing, and then transferred into a beaker and kept at predesigned temperature in water-bath for 10 h. Unless specified, the temperature is 353 K. The borax concentration in the diluted solution was 150 mg/L. Finally, the solution was cooled to room temperature, and remained Ca^{2+} concentration in supernatant was determined using EDTA titration [34]. Blank experiments without scale inhibitor were made as references. Each data was calculated by the average of triplicated measured values. The inhibition efficiency was calculated as

$$\eta = (C_2 - C_1)/(C_0 - C_1) \times 100\% \quad (1)$$

where C_0, C_1 and C_2 are Ca^{2+} concentrations of initial $CaCl_2$ solution, blank sample, and tested sample after 10 h, respectively.