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Evaluation of a polyether-based polycarboxylate as precipitation inhibitor for calcium carbonate and calcium sulfate

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ABSTRACT

A potential polymeric scale inhibitor, acrylic acid–succinic anhydride–methallyl methoxy polyethylene glycol (AA–HPEL), was synthesized by radical polymerization. The inhibition ability of new antiscalant to calcium carbonate and calcium sulfate are better than current commercial inhibitors which are listed in this paper. The static inhibition rate on calcium carbonate and calcium sulfate can reach up to 93.6% and 100% at dosage levels of 8 and 5 mg/L, respectively. Influences of the solution property (temperature, ions concentration and pH value) on inhibition efficiency were also researched. Scanning electron microscopy and X-ray diffraction analyses were used to investigate the impact of the scale inhibitor on the calcium scales crystal.

Keywords: Copolymer; Scale inhibitor; Calcium carbonate; Calcium sulfate

1. Introduction

Precipitation of scales is a common problem encountered in many industrial processes, such as desalination plants and cooling water systems [1–4]. The solubility of scale minerals increase or decrease with increasing temperature, and the precipitation of scales will occur on the equipment surfaces [5,6]. The depositions in cooling water systems are mainly consisted of calcium carbonate, calcium sulfate and other insoluble solids. The formation of scales is often depends on the changes of temperature, mineral concentration and pH of the water [7–9]. Precipitation of scales could cause problems of reducing the volume of equipment, shortening the life of equipment and leading to the loss of production.

There are three main routes to mitigate the problem of scaling: (1) use of water softening chemicals, (2) reverse osmosis device and (3) using chemical treatment method. Adding chemical antiscalant is the most effective and economical method to inhibit scales growth [10–12]. Numerous water-soluble polymers which contain several functional groups like phosphonate, carboxylate and sulfonate have been widely applied in controlling scales formation [13,14]. Phosphorus type scales inhibitors, such as 1-hydroxy ethylidine-1-diphosphonic acid (HEDP) and 1,2-diaminoethanetetrakis-methylene phosphonic acid have been used for the circulating cooling water systems due to their high scale inhibition efficiency and dispersing capability [15]. However, they all contain high phosphorus, resulting

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in environmental pollution and eutrophication difficulties in water [16]. Therefore, phosphorus scale inhibitors are becoming increasingly restricted.

In response to environmental guidelines, researchers have worked on preparing non-phosphate scale inhibitors [17]. Polycarboxylic acid type scales inhibitors, such as polyacrylic acid (PAA) possess relatively high inhibition efficiency toward carbonate or calcium sulfate scale as it contains carboxylic acid functional groups. Unfortunately, it will form insolubilization of polymer complexes in the existence of excessive amounts of calcium ions [18]. Therefore, the trend of inhibitor application is to develop more environmentally friendly and efficient polymers, with higher calcium tolerance.

Methallyl methoxy polyethylene glycol (HPEG) has a wider choice of comonomer, which is used to synthesize polymer than allyloxy polyethoxy ether (APEG), because it possesses the advantage of higher polymerization activity [19,20]. In recently years, lot of polycarboxylate polymers based on polyether (APEG) to prevent the deposition of calcium scales have been prepared and evaluated by our team [18,21–24]. However, there is no polymer synthesized based on HPEG used as antiscalant for cooling water systems is reported in the literatures.

The aim of this study is to prepare and evaluate a polycarboxylate antiscalant based on HPEG for cooling water systems. The new polymer was synthesized by acrylic acid (AA) and succinic anhydride–methallyl methoxy polyethylene glycol (HPEL) including functional groups of carboxyl, allyloxy and ester. The inhibition performance on calcium carbonate and calcium sulfate was evaluated. We also investigated the inhibition rate of AA–HPEL on calcium scales at wider range of pH, Ca^{2+}, HCO_3^-, SO_4^{2-} ions concentration and temperature. The influences of AA–HPEL on the crystal structure of calcium scales were also investigated by the using of scanning electron microscopy (SEM) and X-ray diffraction (XRD) methods.

2. Experimental setup

2.1. Materials

The succinic anhydride, AA, anhydrous calcium chloride, borax, sodium bicarbonate, ammonium persulfate, ethylenediaminetetraacetic acid disodium salt (EDTA·2Na) are of AR grade and were obtained from Zhongdong Chemical Reagent (Nanjing, Jiangsu, China). Methallyl methoxy polyethylene glycol (HPEG; molecular weight 300), commercial inhibitor of PAA (molecular weight 1,800), poly(epoxysuccinic acid) (PESA; molecular weight 1,500) and HEDP (molecular weight 206) were technical grade and supplied by Jianghai Reagent (Changzhou, Jiangsu, China). Distilled water was used for all the studies.

2.2. Measurements

The samples were analyzed using an Fourier transform infrared spectroscopy (FTIR) spectroscopy (VECTOR-22, Bruker Co., Germany) in the region of 4,000–500 cm^{-1}. Structures of HPEL and AA–HPEL were also explored by a Bruker NMR analyzer (AVANCE AV-500, Bruker, Switzerland) operating at 500 MHz. The XRD patterns of the $CaCO_3$ and $CaSO_4$ crystals were carried on a Rigaku D/max 2400 X-ray powder diffractometer with Cu Kα (λ = 1.5406) radiation (40 kV, 120 mA). The shape of $CaCO_3$ and $CaSO_4$ precipitation was observed by SEM method, and the images were recorded using a field emission scanning electron microscope (S-3400 N HITECH SEM).

2.3. Synthesis of HPEL and AA–HPEL

The synthesis procedure of HPEL is shown in Fig. 1. It was synthesized from methallyl methoxy polyethylene glycol (HPEG) and succinic anhydride at 70°C under nitrogen atmosphere for 4.0 h.

HPEL was copolymerized with AA in aqueous medium. The synthesis procedure of AA-HPEL is shown in Fig. 2. About 14.4 g AA and 15 mL distilled water were added into a 250 mL five-neck round-bottom flask, and heated to 65°C with stirring continuously under nitrogen atmosphere. Next, in fixed conditions, the initiator solution (0.3 g of ammonium persulfate in 15 mL of distilled water) was added separately at constant flow rates more than 1.5 h. At the same time, the HPEL solution (a definite proportion of HPEL in 15 mL distilled water) was also added at constant flow rates over 1.5 h. Then, the reactant was heated with stirring at 75°C for 3 h under nitrogen atmosphere, to ultimately afford an aqueous copolymer solution containing approximately 30% solid. Scale inhibitors were prepared at different mole ratio of AA:APEL (5:1, 4:1, 3:1, 2:1 and 1:1) to study the influence of mole ratio of comonomer on inhibition performance.

2.4. Static scale inhibition methods

All static scale inhibition experiments were carried out in triplicate and all inhibitor dosages given below were on a dried condition, and the ability of the AA–HPEL copolymer against $CaCO_3$ precipitation was compared with the free

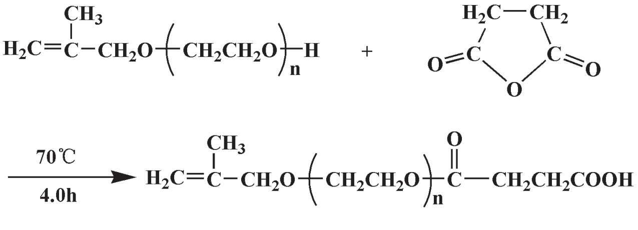

Fig. 1. Preparation of HPEL.

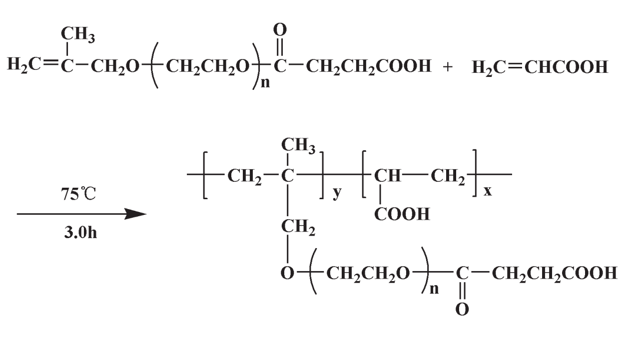

Fig. 2. Preparation of AA–HPEL.

inhibitor in flask tests according to the national standard of People's Republic of China (GB/T 16632-2008). The experiment was carried out in artificial cooling water which was prepared by dissolving the reagent grade $CaCl_2$ and $NaHCO_3$ in distilled water. The concentration of Ca^{2+} and HCO_3^- was 240 and 732 mg/L, respectively, the pH solution was kept at 9 adjusting by borate buffer solution. All tests of inhibitors were carried out in a 500 mL flask immersed at 80°C for 10 h. The concentration of Ca^{2+} ions in the solution was standardized by EDTA complexometry method as specified in code (GB/T 15452-2009). Inhibitor efficiency of AA–HPEL was calculated from the following equation:

$$\text{Inhibition efficiency (\%)} = \frac{(Ca^{2+})_1 - (Ca^{2+})_0}{(Ca^{2+})_2 - (Ca^{2+})_0} \times 100\% \qquad (1)$$

where $(Ca^{2+})_1$ was the Ca^{2+} concentration of inhibited sample, $(Ca^{2+})_0$ was the Ca^{2+} concentration of uninhibited sample and $(Ca^{2+})_2$ was the initial Ca^{2+} concentration before the test.

Calcium sulfate precipitation experiments were also carried out similar to $CaCO_3$ precipitation experiments according to the national standard of People's Republic of China concerning the code for the design of industrial oilfield-water treatment (SY/T 5673-93). Procedure of calcium sulfate inhibition precipitation test was studied in different artificial cooling water which was prepared by dissolving a certain quantity of $CaCl_2$ and Na_2SO_4 in distilled water. The concentration of Ca^{2+} and SO_4^{2-} was 6,800 and 7,100 mg/L, respectively, with solutions pH 7 were adjusted using sodium hydroxide and hydrochloric acid. After that, the different doses of AA–HPEL solutions were placed in a flask at 70°C for 6.0 h in a water bath. The determination of Ca^{2+} was done by exactly identical procedure. The inhibition efficiency of inhibitor control $CaSO_4$ scale was calculated as Eq. (1). The data used in below are the average data of the repeated tests.

3. Results and discussion

3.1. FTIR analysis of inhibitor

The FTIR spectra of HPEG, HPEL and AA–HPEL are exhibited in Figs. 3(a)–(c), respectively. The 1,730 cm^{-1} strong intensity absorption peak (–C=O) in curve (b) clearly reveals that HPEL has been synthesized successfully. The fact that the (–C=C–) stretching vibration at 1,650 cm^{-1} appears in curve (b) but disappears completely in curve (c) reveals that radical polymerization between AA and HPEL has happened [18].

3.2. ^{1}H NMR studies

The ^{1}H NMR spectra of HPEG, HPEL and AA–HPEL are presented in Fig. 4. HPEG ($(CD_3)_2SO$, δ ppm): 2.50 (solvent residual peak of $(CD_3)_2SO$), 3.30–3.57 ($–OCH_2CH_2–$, ether groups), 1.66 and 3.80–4.94 ($CH_2=C(CH_3)–CH_2–$, propenyl protons) and 4.53–4.59 (–OH, active hydrogen in HPEG) (Fig. 4(a)).

HPEL ($(CD_3)_2SO$, δ ppm): 2.35–2.55 ($–CH_2CH_2–$, protons in $–COCH_2CH_2COOH$), 2.50 (solvent residual peak of $(CD_3)_2SO$), 3.43–4.15 ($–OCH_2CH_2–$, ether groups), 1.66 and 4.80–4.94 ($CH_2=C(CH_3)–CH_2–$, methylallyl protons) (Fig. 4(b)).

AA–HPEL ($(CD_3)_2SO$, δ ppm): 2.10–2.55 ($–CH_2CH_2–$, protons in $–COCH_2CH_2COOH$), 2.50 (solvent residual peak of $(CD_3)_2SO$), 1.60–1.73 ($–CH_3$, methyl proton) and 3.30–3.90 ($–OCH_2CH_2–$, ether groups) (Fig. 4(c)).

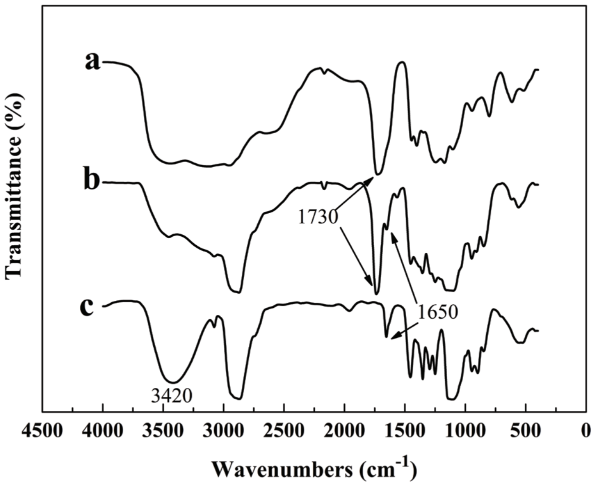

Fig. 3. FTIR spectra of HPEG (a), HPEL (b) and AA–HPEL (c).

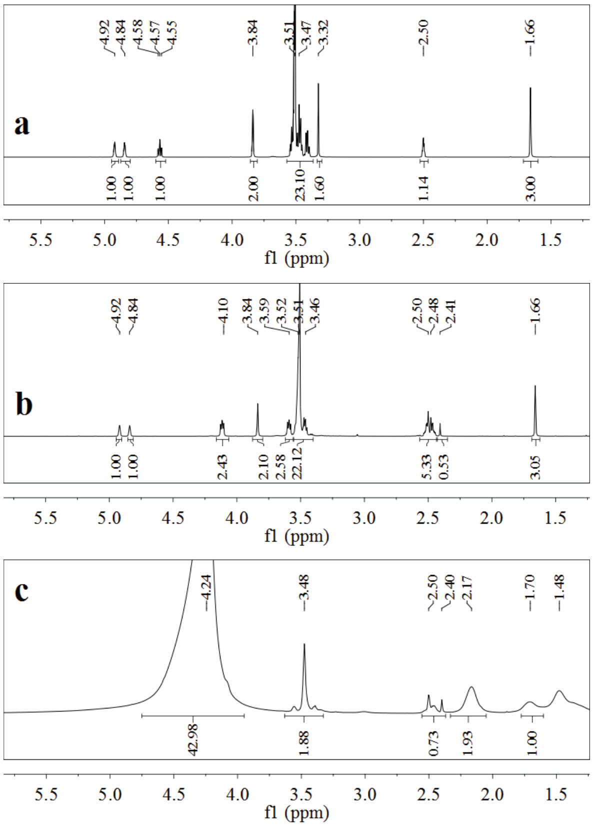

Fig. 4. ^{1}H NMR spectra of HPEG (a), HPEL (b) and AA–HPEL (c).

The complete disappearance of 4.53–4.59 ppm active hydrogen (–OH) in (a) and the appearance of 2.35–2.55 ppm methylene proton ($–CH_2CH_2–$) in (b) proves that HPEG has reacted with succinic anhydride. 4.80–4.94 ppm in (b) double bond absorption peaks completely disappeared in (c) [25]. These results reveal that free radical polymerization among

AA and HPEL has happened. From FTIR and ^{1}H NMR analysis, it certifies that synthesized AA–HPEL has expected structure.

3.3. Calcium scales inhibition at different dosage and mole ratio of AA:HPEL

The properties of AA–HPEL against $CaCO_3$ and $CaSO_4$ scales were prepared at different AA:HPEL mole ratio was shown in Figs. 5 and 6, respectively. The results reveal that mole ratio of comonomer have large impact on the inhibition properties. As can be seen from Fig. 5, compared with the others mole ratio (1:1, 2:1, 4:1 and 5:1), the inhibition efficiency of the polymer (AA:HPEL = 3:1) for $CaCO_3$ scale can get highest value about 93.6% at the concentration of 8 mg/L. The inhibition efficiency for $CaSO_4$ is 100.0% at a level of 5 mg/L (AA:HPEZ = 3:1), while it is 90.8%, 85.4%, 94.5% and 80.5% at the same concentration with different mole ratio of AA:HPEL (1:1, 2:1, 4:1 and 5:1), respectively. Copolymers can have the same composition but with different sequence structure which displays different properties and the ratio of functional groups in the long-chain polymer is also different. Therefore, there is a best mole ratio for calcium scales inhibition. The results of calcium scales inhibition tests demonstrate that AA–HPEL (AA:HPEL = 3:1) shows superior inhibition efficiency on both $CaCO_3$ and $CaSO_4$ precipitation than other mole ratio.

3.4. Comparisons of inhibition efficiency

During the last decade, investigations on polymer inhibitors to control calcium scales have caught much attention of water treatment researchers [26]. Common inhibitors used in industry such as PAA, PESA and HEDP often synthesized by diverse monomers with different functional groups. Figs. 7 and 8 present calcium carbonate and calcium sulfate inhibition of AA–HPEL (AA:HPEL = 3:1) and commercial scale inhibitors. The inhibition efficiency of AA–HPEL to

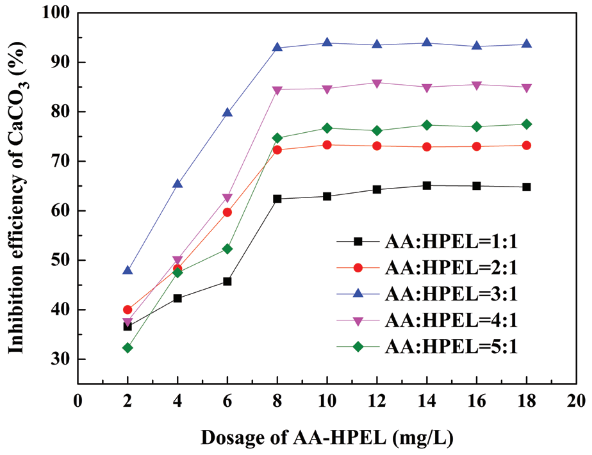

Fig. 5. Influence of the dosage and mole ratio on the inhibition tests of $CaCO_3$.

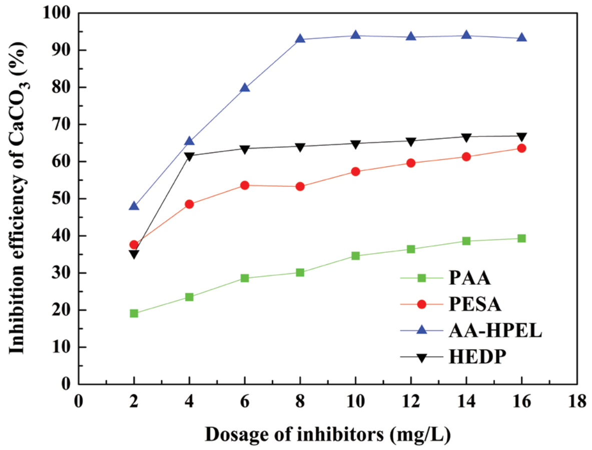

Fig. 7. Comparison of scale inhibition efficiency on $CaCO_3$ of AA–HPEL and different commercial inhibitors.

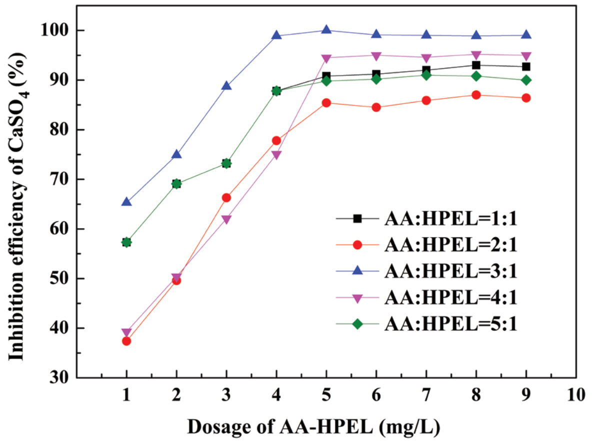

Fig. 6. Influence of the dosage and mole ratio on the inhibition tests of $CaSO_4$.

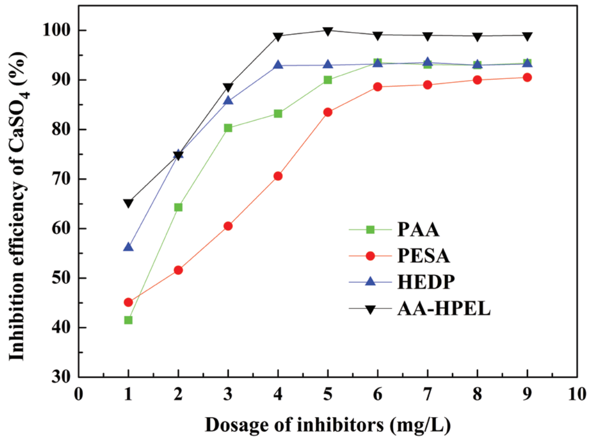

Fig. 8. Comparison of scale inhibition efficiency on $CaSO_4$ of AA–HPEL and different commercial inhibitors.

calcium carbonate and calcium sulfate is better than that of PAA, PESA and HEDP beyond the threshold dosage. It is worth mentioning that the molecular structures of PAA, PESA and AA–HPEL all contain carboxyl groups, but the efficiency of PAA and PESA to control calcium carbonate scale is poor even at a high dosage. It may be that the side-chain polyethylene (PEG) segments and carboxyl groups of AA–HPEL play an important role during the control of calcium carbonate scales [27]. The functional groups of polymeric inhibitors have a significant influence on reducing calcium scales precipitation. Taking Figs. 7 and 8 into account, it can be concluded that the AA–HPEL can be utilized as an efficient scale inhibitor for both calcium carbonate and calcium sulfate in cooling water systems.

3.5. Influence of solution property on calcium carbonate inhibition

Solution properties have a significant impact on the precipitation of calcium carbonate. We investigated the influence of the solution parameters on the calcium carbonate inhibition of AA–HPEL. The results are shown in Fig. 9.

Figs. 9(a) and (b) indicate that AA–HPEL provides superior calcium carbonate inhibition under conditions of water with a much higher Ca^{2+} or HCO_3^-. Fig. 9(c) clearly demonstrates that the AA–HPEL shows great inhibition performance even for the solution with higher temperature. When increasing the temperature of solution from 50°C to 90°C, there is only 15% loss in calcium carbonate inhibition. As shown in Fig. 9(d), the inhibition efficiency of calcium carbonate reduces by 19% when the pH of solution elevated from 4 to 11. The reason is probably that the solubility of calcium carbonate decreases with the increasing of the pH value. In the range of 8–9, the usual pH values of the cooling water, AA–HPEL still shows excellent calcium carbonate inhibition. Thus, the incorporation of the high performance antiscalant AA–HPEL into recycling water ensures a better overall system performance. Thus, AA–HPEL can be used as a high efficiency antiscalant under complex water conditions.

3.6. Influence of solution property on calcium sulfate inhibition

The data in Fig. 10 show that the scale inhibition efficiency of calcium sulfate is affected by the temperature, pH and ions concentration of water. From Figs. 10(a) and (b), it can be found that Ca^{2+} and SO_4^{2-} ions concentration have a great effect on calcium sulfate inhibition. Figs. 10(a) and (b) indicate that AA–HPEL provides calcium sulfate inhibition under conditions of water with a much higher Ca^{2+} and SO_4^{2-} concentration. Fig. 10(c) clearly demonstrates the superior thermal stability of the AA–HPEL copolymers. When the solution temperature increased from 70°C to 90°C, there is only 19.5% loss in calcium sulfate inhibition. However, when the temperature in the range of 50°C–70°C, which is a usual temperature range of cooling water systems, copolymer shows superior calcium sulfate inhibition efficiency about 100%. In the usual pH values range (7–9) of the cooling water, AA–HPEL still shows excellent calcium sulfate inhibition. From the above results, we can conclude that AA–HPEL can be used as an efficient inhibitor against calcium sulfate scale under complex water conditions.

3.7. Characterization of scales

3.7.1. SEM studies

The addition of antiscalant influences the growth and morphology of $CaCO_3$ crystals. Fig. 11 shows the SEM

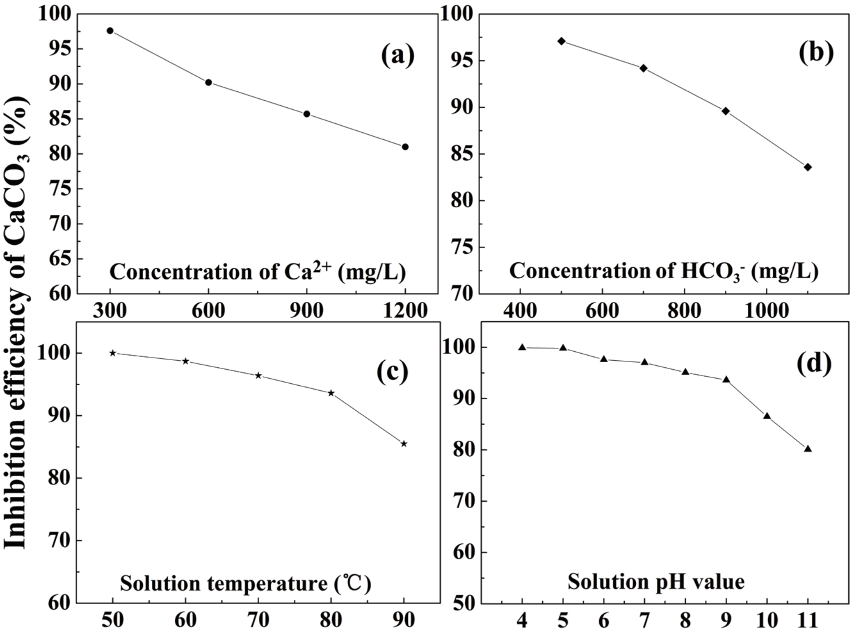

Fig. 9. Inhibition of calcium carbonate at a level of 8 mg/L AA–HPEL as a function of Ca^{2+} (a), HCO_3^- concentration (b), temperature (c) and pH (d).

micrographs of $CaCO_3$ precipitate formed in artificial cooling water. It can be observed from Fig. 11(a) that the precipitates collected from the experiments without AA–HPEL copolymer added shows the characteristic of well-regulated orthorhombic calcite crystal [28]. In contrast, in the presence of the AA–APEL copolymer (Figs. 11(b)–(d)), obvious changes can be seen in size and morphology of the $CaCO_3$ precipitate comparing with Fig. 11(a). The $CaCO_3$ precipitate

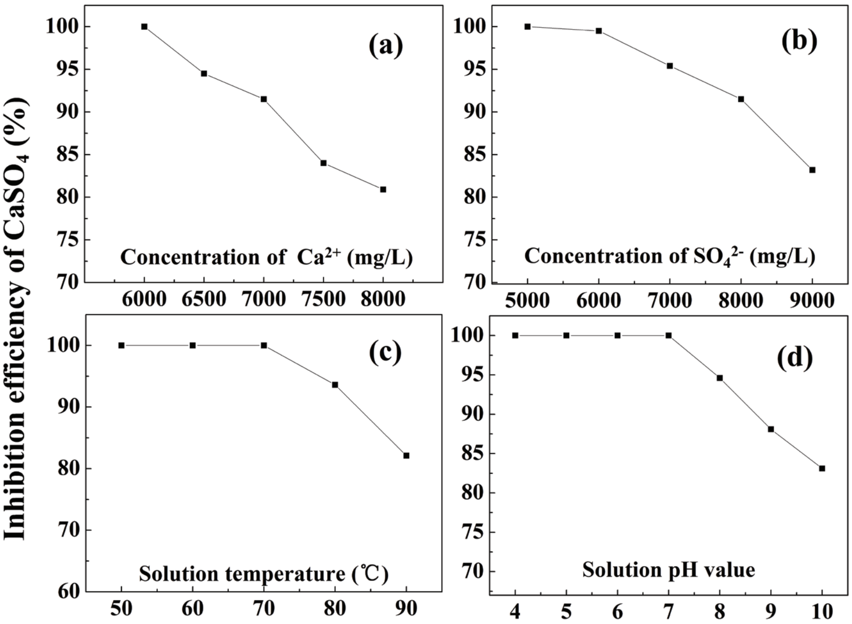

Fig. 10. Inhibition of calcium sulfate at a level of 5 mg/L AA–HPEL as a function of Ca^{2+} (a), SO_4^{2-} concentration (b), temperature (c) and pH (d).

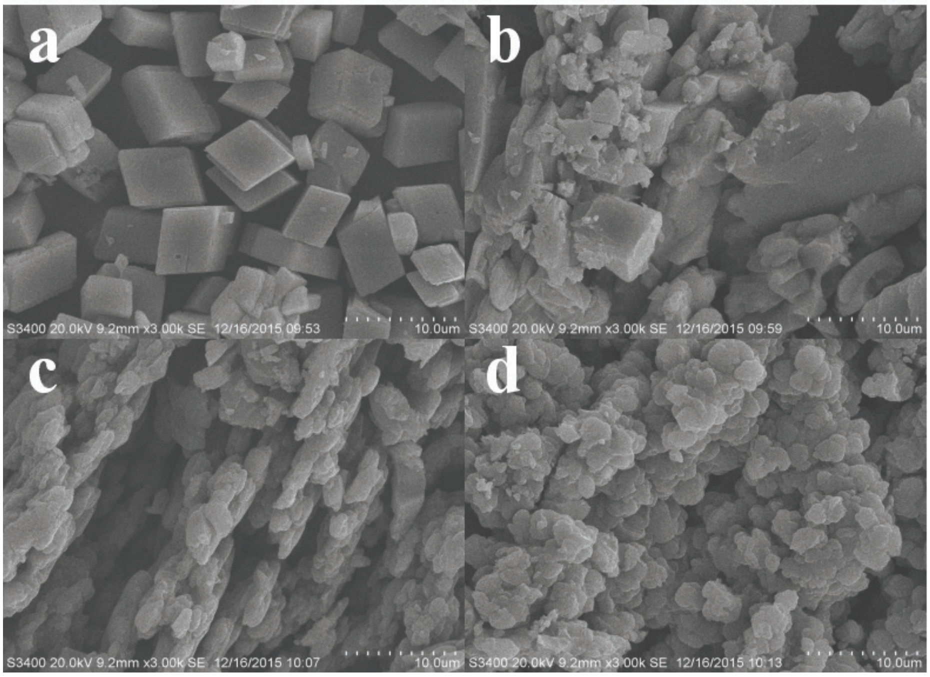

Fig. 11. SEM photographs for the $CaCO_3$ precipitates: in the absence of AA–HPEL (a), in the presence of 2 mg/L (b), 4 mg/L (c) and 6 mg/L (d).

lost its sharp edges, and the form is distorted. When the AA–HPEL dosage increased to 6 mg/L, sharp edges and acute corners of the crystals disappeared completely (Fig. 11(d)).

Calcium sulfate deposits were analyzed by SEM to characterize morphological changes that taken place during growth without and with the addition of AA–HPEL (Fig. 12). It is found that the $CaSO_4$ deposits without inhibitor addition are thin needle-shaped crystals with an elongated monoclinic structure (Fig. 12(a)) [29]. In the presence of 1 mg/L AA–HPEL, small cracks occur in the surface of crystals. With the concentration of AA–HPEL increased to 2 mg/L AA–HPEL, massive cracks and fractured layer structure are observed, while the dosage of AA–HPEL increased to 3 mg/L, the crystals are completely changed to irregular particles (Fig. 12(d)).

SEM images indicate that the use of AA–HPEL has a significant impact on the $CaSO_4$ crystal morphology and size. These facts indicate that the side-chain PEG segments of HPEL and carboxyl groups of AA might play an important role in the inhibition process of $CaSO_4$ deposits. The structure of $CaSO_4$ scales changes from thin needle-shaped crystals into irregular particles in the presence of AA–HPEL demonstrates that the precipitation of $CaSO_4$ can easily be washed away by water.

3.7.2. XRD studies

In order to further research $CaCO_3$ crystals, the collected $CaCO_3$ scale was characterized by XRD analyses. The XRD results for the $CaCO_3$ crystals in the absence and presence of AA–HPEL are given in Fig. 13. It is generally known that $CaCO_3$ exists in three types of crystal forms: calcite, aragonite and vaterite [30]. Calcite is the most thermodynamically stable, and vaterite is the least stable form. As can be seen from Fig. 13 curve (a), in the absence of AA–HPEL copolymer, calcite is the main crystal form, which is the most thermodynamically stable crystal. However, with the addition of inhibitors, a series of diffraction peaks appear at 24.9° (110), 27.2° (112), 32.8° (114) and 43.9° (300) corresponding to vaterite (curve (b)). These results show that, some calcite crystals are changed into vaterite crystals in the presence of AA–HPEL polymer. Thus, the impact of $CaCO_3$ precipitates on equipment surfaces can be controlled.

The effect of the AA–HPEL polymers on the morphology of the $CaSO_4$ scale was also investigated by XRD. The structure of calcium sulfate scales formed in the absence and presence of inhibitors are presented in Fig. 14. Compared with the curves (a) and (b), there is no modification in the crystal structure and morphology with the addition of inhibitor, but modification of the crystal habit or morphology can be observed from the SEM photographs (Fig. 12).

4. Conclusion

The study presents the high inhibition of calcium carbonate and calcium sulfate scales by AA–HPEL. The results demonstrate the following:

- AA–HPEL provides the best calcium carbonate and calcium sulfate inhibition when the mole ratio of AA:HPEL is 3:1, approximately 93.6% calcium carbonate inhibition and 100% calcium sulfate inhibition at the dosage of 8 and 5 mg/L, respectively.
- AA–HPEL possesses both excellent calcium carbonate and calcium sulfate inhibition compared with the commercial products (PAA, PEAS and HEDP).

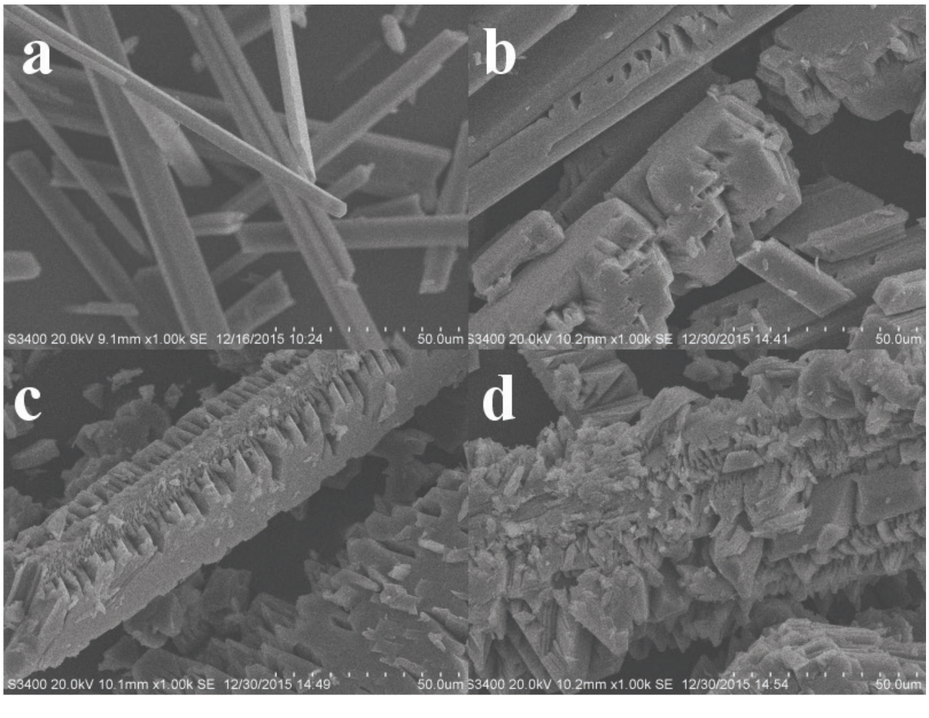

Fig. 12. SEM photographs for the $CaSO_4$ precipitates: in the absence of AA–HPEL (a), in the presence of 1 mg/L (b), 2 mg/L (c) and 3 mg/L (d).

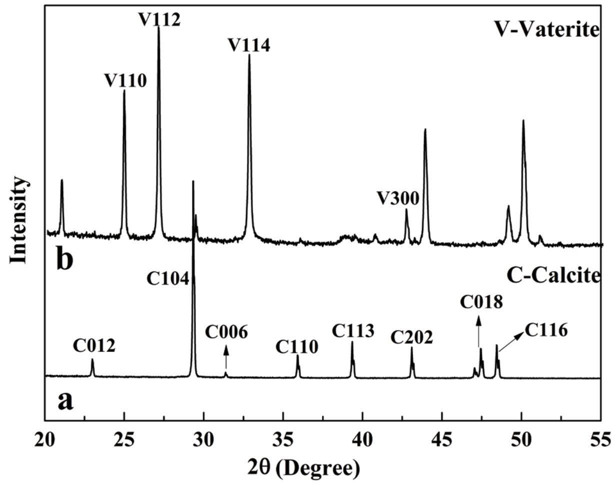

Fig. 13. XRD spectrum of $CaCO_3$ precipitates: in the absence of inhibitor (a) and in the presence of 4 mg/L (b) AA–HPEL.

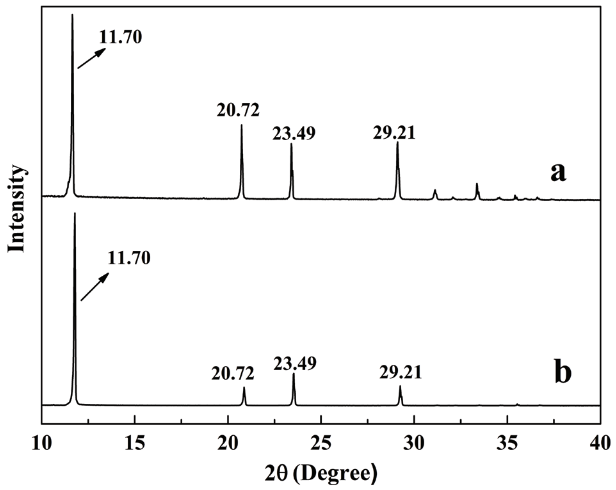

Fig. 14. XRD spectrum of $CaSO_4$ precipitates: in the absence of inhibitor (a) and in the presence of 3 mg/L (b) AA–HPEL.

- AA–HPEL is a new efficient antiscalant for calcium carbonate and calcium sulfate inhibition under the conditions of wider range of pH, higher temperature and suitable Ca^{2+}, HCO_3^-, SO_4^{2-} ions concentration in the industry cooling water systems.
- XRD and SEM analyses indicate that the presence of AA–HPEL has a great impact on the morphology of calcium crystals. It is clear that AA–HPEL can be used as a scale inhibitor for cooling water systems.

Acknowledgments

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