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Synthesis of glutamic-modified polyether copolymer as a novel non-phosphorous inhibitor for calcium carbonate scales in cooling water systems

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ABSTRACT

A novel non-phosphorous copolymer acrylic acid-allyloxy polyethoxy glutamate (AA-APEU) had been synthesized and developed as an efficient calcium carbonate scale inhibitor for cooling water systems. The structure of the new copolymer was characterized by Fourier transform infrared spectra and ^{1}H NMR. The inhibition property of the non-phosphorous copolymer toward $CaCO_3$ in the artificial cooling water was studied through static scale inhibition tests. It was found that AA-APEU exhibited excellent ability to control calcium carbonate scale, with approximately 71.8% calcium carbonate inhibition at a level of 8 mg/L. The micromorphology and crystal of calcium particles were investigated with a combination of scanning electronic microscopy and X-ray powder diffraction analysis, respectively.

Keywords: Calcium carbonate; Scale inhibitor; Non-phosphorous; Cooling water system; Copolymer

1. Introduction

Natural hard water, used widely in cooling water systems and heat exchangers, contains various metal ions such as Ca^{2+}, Fe^{3+}, Mg^{2+}, and Ba^{2+}, which tend to increase in concentration over time owing to evaporation and corrosion [1,2]. Consequently, the scale formation, especially the precipitation of calcium scale, occurs. This creates security issues like overheating, plugging of the equipment, unscheduled shutdown time, and ultimately pipe failure [3–7]. For these reasons, water treatment agent is added as the most common and effective control method to minimize invasive factors. In the last seven decades, there have been tremendous studies about calcium scale formation [8–10]. Organic polymer compounds, which

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contain strong functional groups and exhibit excellent affinity toward insoluble irons, have drawn much attention of researchers in recent years. These organic polymers have shown nice anti-scaling performance in current recycling water systems, such as polyacrylic acid (PAA), hydrolyzed polymaleic anhydride (HPMA), and epoxysuccinic acid (PESA) [11,12]. However, all of these antiscalants are endowed with unsatisfactory inhibition and low calcium tolerance at high temperature [13]. In addition, without effective control of hydrolysis, many phosphate-containing inhibitors, especially the polyphosphates, decompose at high temperatures and give scale-forming ions. Therefore, a new type of non-phosphorous inhibitor is required to reduce the use of substances hazardous to human health and the environment [14,15].

Our earlier works showed that non-phosphate inhibitors (AA-APEC, AA-APEL, APEG-PG-COOH, and APEM) for cooling water systems demonstrated outstanding inhibitory efficiency. However, those copolymers could not biodegrade easily [16–19]. According to all these information, the chief aim of this study was to develop a greener inhibitor (acrylic acid [AA] and allyloxy polyethoxy glutamate [APEU]), which is biodegrade to some extent because there is an amino acid component in it, more importantly, to evaluate this new inhibitor's effectiveness of scale inhibition, primarily in cooling water systems. Since the precipitation of calcium carbonate is the main problem of mineral scaling in cooling water systems, laboratory scale inhibition of this copolymer is carried out to investigate its effectiveness toward calcium carbonate [20]. The inhibitor prepared in this paper is glutamic acid-modified polyether copolymer, which is non-phosphorous and has superior calcium carbonate tolerance compared to the available commercial inhibitors.

2. Experimental

2.1. Materials

Acrylic acid (AA), glutamic acid, and ammonium persulfate (APS) were of analytically pure grade and purchased from Zhongdong Chemical Reagent (Nanjing, Jiangsu, People's Republic of China). Allyloxy polyethoxy ether (APEG, $M_W = 300$ g/mol) used in the experiment was provided by Jiangsu Jianghai Chemical (Changzhou, Jiangsu, People's Republic of China). The commercial inhibitors of PAA ($M_W = 1,800$ g/mol), HPMA ($M_W = 600$ g/mol), PESA ($M_W = 1,500$ g/mol) were of technical grade and were supplied by Jiangsu Jianghai Chemical Co., Ltd (Changzhou, Jiangsu, People's Republic of China). Acrylic acid-alkyl polyethoxy carboxylate (AA-APEL, $M_W = 18,000$ g/mol) which were synthesized by Liu in our laboratory, were supplied by Jiangsu Jianghai Chemical (Changzhou, Jiangsu, People's Republic of China) [17]. Distilled water was used throughout the investigation.

2.2. Preparation of APEU and AA-APEU

2.2.1. Synthesis of APEU

APEU was synthesized by the esterification between a terminal hydroxyl group in APEG and one of the carboxyl groups in glutamic acid with a molar ratio of 1:1. Hydrogen chloride gas was filtered into the reaction to cast away oxygen gas and water vapor to protect reactants from being oxidized, more importantly, to prevent the occurrence of acylation reaction by forming semicarbazide hydrochloride. Finally, the brown aroma product of APEU with an approximate 75.8% yield was obtained. The structure of APEU is shown in Fig. 1.

2.2.2. Synthesis of AA-APEU

A typical synthetic process is as follows: 60 g of distilled water and 14 g (0.03 mol) of APEU (the mole ratio of AA and APEU was 3:1) were mixed together in a four-neck round bottom flask equipped with a thermometer, and a magnetic stirrer. The mixture was heated to 70°C with stirring under nitrogen atmosphere. After that, 7.2 g (0.1 mol) of AA in 20 mL of distilled water and the initiator solution (1.0 g of ammonium persulfate in 20 g of distilled water) were added dropwise through different necks in 1.0 h at 70°C. Then, the reaction was heated with stirring at 80°C for 3.0 h under nitrogen atmosphere. Ultimately, the yellow product of AA-APEU, containing 25% solid, was obtained. Without any isolation, these products were used for Fourier transform infrared spectra (FT-IR) and ^{1}H NMR spectra tests. The synthesis procedure of AA-APEU is given in Fig. 2.

2.2.3. Characterization

The functional groups were confirmed by a FT-IR spectroscopy (VECTOR-22, Bruker Co., Germany) in the pressed KBr pellets. Using deuterated dimethyl sulfoxide (DMSO-d_6) as the solvent, ^{1}H NMR spectra were tested on a Mercury VX-500 spectrometer (Bruker AMX500) with a tetramethylsilane internal reference. The weight distribution of the copolymer was determined by gel permeation chromatography

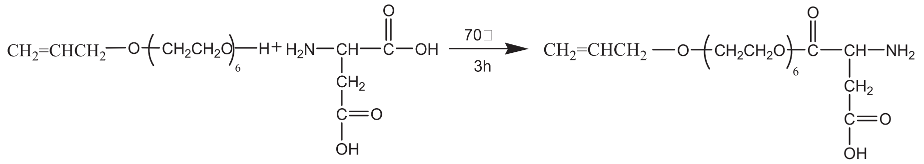

Fig. 1. Preparation of APEU.

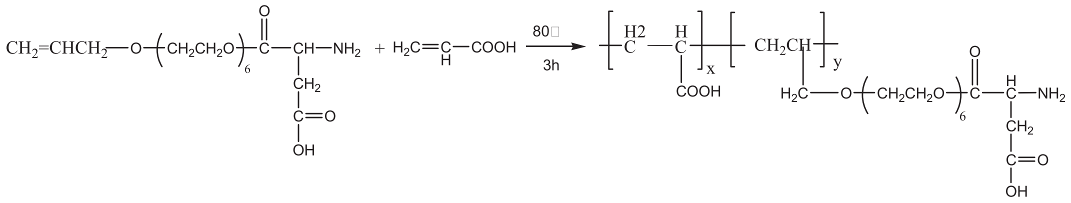

Fig. 2. Preparation of AA-APEU.

(GPC, Shodex KF-850 column, calibrated with PEG standard) with water as the mobile phase at a flow rate of 1.0 mL/min. The change in crystal morphology and size of the calcium carbonate was observed through scanning electron microscopy (S-3400N HITECH SEM). The X-ray diffraction (XRD) patterns of the calcium carbonate crystals were recorded on a Rigaku D/max 2400 X-ray powder diffractometer with Cu Kα ($k = 1.5406$) radiation (40 kV, 120 mA).

2.2.4. Inhibition test

All the inhibitor dosages given below were on a dry-inhibitor basis. In this experiment, the ability of the AA-APEU copolymer against calcium carbonate scale was compared with that of the free inhibitor in flask tests. Calcium carbonate precipitation and inhibition were studied in artificial cooling water which was prepared by dissolving a certain quantity of $CaCl_2$ and $NaHCO_3$ (Zhongdong Chemical Reagent Co.) in deionized water at equivalent concentrations of 24 milliequivalent/L (cooling water code GB/T 16632-2008). The supersaturation level of the solutions corresponded to a Langelier Index of 2.1. Each inhibition test was carried out in a 500-mL flask immersed in a temperature-controlled bath for 10.0 h. Precipitation of $CaCO_3$ was monitored by analyzing aliquots of the filtered (0.22 μm) solution for Ca^{2+} using EDTA complexometry, as specified in code GB/T 15452-2009. Inhibitor efficiency was calculated from the following equation:

$$\text{Inhibition }(\%) = \frac{[Ca^{2+}]_{\text{final}} - [Ca^{2+}]_{\text{blank}}}{[Ca^{2+}]_{\text{initial}} - [Ca^{2+}]_{\text{blank}}} \times 100\% \quad (1)$$

where $[Ca^{2+}]_{\text{final}}$ is the concentration of ions in filtrate in the presence of inhibitor after calcium carbonate supersaturated solutions heated for 10.0 h at 80℃, $[Ca^{2+}]_{\text{blank}}$ is the final calcium concentration in the absence of inhibitors after calcium carbonate supersaturated solutions heated for 10.0 h at 80℃, and $[Ca^{2+}]_{\text{initial}}$ is the concentration of calcium ions at the beginning of the experiment [21].

3. Results and discussion

3.1. FT-IR analysis of the copolymer

The FT-IR spectra of glutamic acid (a), APEG (b), APEU (c), and AA-APEU (d) are shown in Fig. 3. The 1,720 cm^{-1} strong intensity absorption peak (–C=O) which belongs to glutamic acid and the peak at

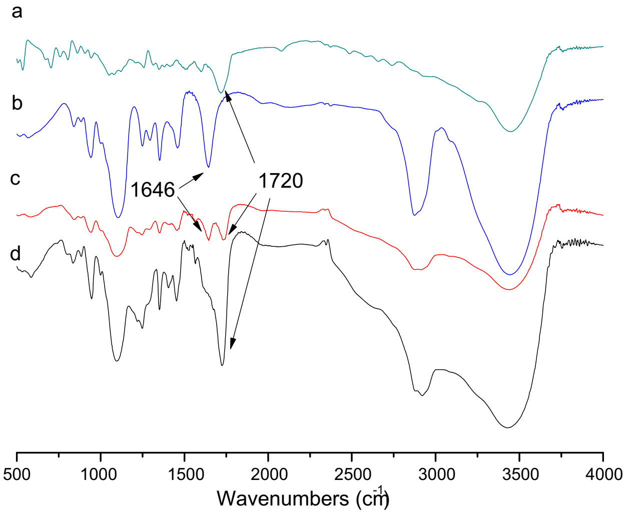

Fig. 3. The FT-IR spectrums of (a) glutamic acid, (b) APEG, (c) APEU, and (d) AA-APEU (AA:APEU = 3:1, 1 h initiator dropping time, 5 wt% initiator, and 3 h reaction time; 25% solid content).

1,646 cm^{-1} from the stretching vibration of –C=C– groups originated from APEG both appear in curve c. This result reveals clearly that APEU has been synthesized successfully. The fact that the band at 1,646 cm^{-1} of –C=C– groups appears in curve *b* and *c* but disappears completely in curve *d* indicates that free radical polymerization between AA and APEU has happened.

3.2. ^{1}H NMR analysis of the copolymer

The structures of the synthesized copolymers were further characterized by the ^{1}H NMR spectra of APEG (a), APEU (b), and AA-APEU (c) were showed in Fig. 4.

APEG (a) [$(CD_3)_2SO$, δ ppm]: 2.50 (solvent residual peak of $(CD_3)_2SO$), 3.19–3.61 ($–OCH_2CH_2–$, ether groups), 3.88–4.01 ($CH_2=CH–CH_2–$, propenyl protons), 4.51–4.60 (–OH, active hydrogen in APEG), 5.09–5.95 ($CH_2=CH–CH_2–$, propenyl protons) (Fig. 4(a)).

APEU (b) [$(CD_3)_2SO$, δ ppm]: 1.90–2.10 ($–CH_2–CH–$, alkane protons), 2.50 (solvent residual peak of $(CD_3)_2SO$), 3.19–3.61 ($–OCH_2CH_2–$, ether groups), 3.88–4.01 ($CH_2=CH–CH_2–$, propenyl protons), 5.09–5.95 ($CH_2=CH–CH_2–$, propenyl protons), 6.90–8.70 ($NH_2–$, amino protons) (Fig. 4(b)).

AA-APEU (c) [$(CD_3)_2SO$, δ ppm]: 1.90–2.10 ($–CH_2–CH–$, alkane protons), 2.50 (solvent residual peak of $(CD_3)_2SO$), 3.18–3.51 ($–OCH_2CH_2–$, ether groups), 3.88–4.01 ($CH_2=CH–CH_2–$, propenyl protons), 6.90–8.70 ($NH_2–$, amino protons) (Fig. 4(c)).

The disappeared peak at 4.51–4.60 ppm (–OH) in Fig. 4(b) reveals that active hydroxyl group of APEG has reacted with glutamic acid, which confirms the FT-IR analysis of emerging 1,720 cm^{-1} strong intensity absorption peak (–C=O) in Fig. 3(c). The fact that the double bond absorption peak at 5.09–5.95 ppm (–CH=CH–) completely disappeared in Fig. 4(c) confirms the vanishing (–C=C–) stretching vibration at 1,642 cm^{-1} in Fig. 3(d). Besides, the active hydrogen peak at 6.90–8.70 ($–NH_2$) in Fig. 4(b) can further confirm the occurrence of esterification and also proves the successful synthesis of AA-APEU copolymer in Fig. 4(c). All of these data suggest that AA-APEU was synthesized successfully.

After the analysis from both FT-IR and ^{1}H NMR, the new copolymer AA-APEU has been synthesized as expected.

3.3. GPC analysis of AA-APEU

The AA-APEU copolymer shown in Table 1 was prepared through free radical solution copolymerization at different AA/APEU mole ratios under the condition of 1 h initiator dropping time, 5 wt% initiator, and 3 h reaction time. These crude products obtained from free radical solution copolymerizaiton were purified by acetone. After that, the molecular mass distribution of the polymer were tested by GPC and the results are show in Table 1.

As can be seen from Table 1, the mass average molecular weight (M_W) ranges from 1.77×10^4 to 1.95×10^4, while the number average molecular weight (M_n) spreads between 1.68×10^4 and 1.80×10^4. The total mass average molecular weight trend increased with the increase in the acrylic acid because the acrylic acid monomer was more active. However, the difference was not huge. This might be due to the fact that the molecular weight of APEU ($M_W = 429$ g/mol) was higher than that of AA ($M_W = 72$ g/mol) and PEG ($–(OCH_2CH_2)_6–$, $M_W = 264$ g/mol) chain played a dominant role. One of the GPC response curves of AA-APEU (the mole ratio of AA and APEU was 1:3) is shown in Fig. 5. Molar mass at the maximun peak (M_P), viscosity average molecular weight (M_v), the z average molecular weight (M_z), and polydispersity index ($PD = M_W/M_n$) are also presented in the curve profiles.

3.4. Inhibition performance of the copolymer against calcium carbonate scales

Fig. 6a–6d shows that calcium carbonate inhibition efficiency varies under polymerization conditions. Variable-controlling method was used under the conditions of 1 h initiator dropping time, 5 wt% initiator, and 3 h reaction time at the feed AA:APEU mole ratio of 3:1. The details of the preparation and solid content of these polymer samples are exhibited in Table 2.

As shown in Fig. 6a, the inhibition of calcium carbonate increases with the mole ratio of AA and APEU and the inhibition efficiency of AA-APEU (3:1) is the best among other mole ratios. This may owe to the fact that the molecular weight of AA-APEU is more suitable to capture Ca^{2+} when the mole ratio is 3:1. Therefore, there is a best molecular weight of the copolymer to obtain the maximum effect for $CaCO_3$, that is 1.86×10^4 according to Table 1 [22]. Fig. 6b illustrates that there is no obvious difference in scale inhibition by extending initiator dropping time. Considering the stability of experiment, the initiator is added in 1 h. Fig. 6c shows the variation of inhibition efficiency against $CaCO_3$ scale with different amount of initiators. It is found that, the most appropriate dosage of initiator is 5 wt% and the inhibition value reaches approximately 70.1% at a level of 8 mg/L. This may owe to the fact that lack of sufficient

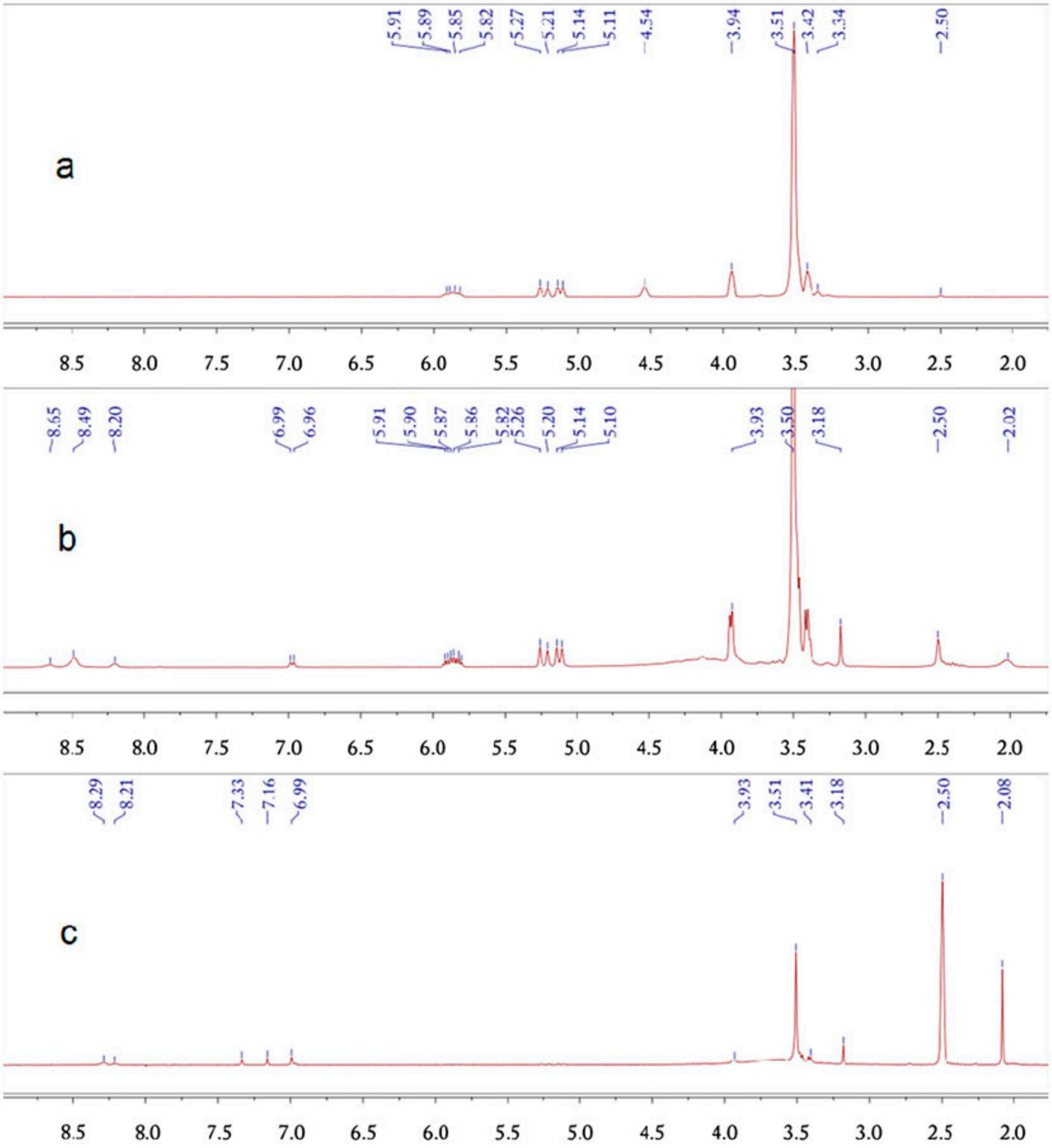

Fig. 4. ^{1}H NMR spectra of (a) APEG, (b) APEU, and (c) AA-APEU (AA:APEU = 3:1, 1 h initiator dropping time, 5 wt% initiator, and 3 h reaction time; 25% solid content).

Table 1
Average molecular weight and solid content of AA-APEU

AA/APEU molar ratio momm	5:1	3:1	1:1	1:3	1:5
$M_W \times 10^{4a}$	1.95	1.86	1.82	1.77	1.79
$M_n \times 10^{4a}$	1.80	1.74	1.69	1.71	1.68
Solid content (%)	26.7	25.1	27.3	28.9	31.8

Note: [a]Determined by GPC eluted with water based on PEG standards.

initiators would decelerate the aggregation process, while excessive initiators would result in too broad molecular weight distribution. Fig. 6d presents the variation trend of the inhibition efficiency with the polymerization time of copolymer. The result indicates that 3 h is the perfect polymerization reaction time. This may be due to the degree of polymerization which is relatively high at 3 h.

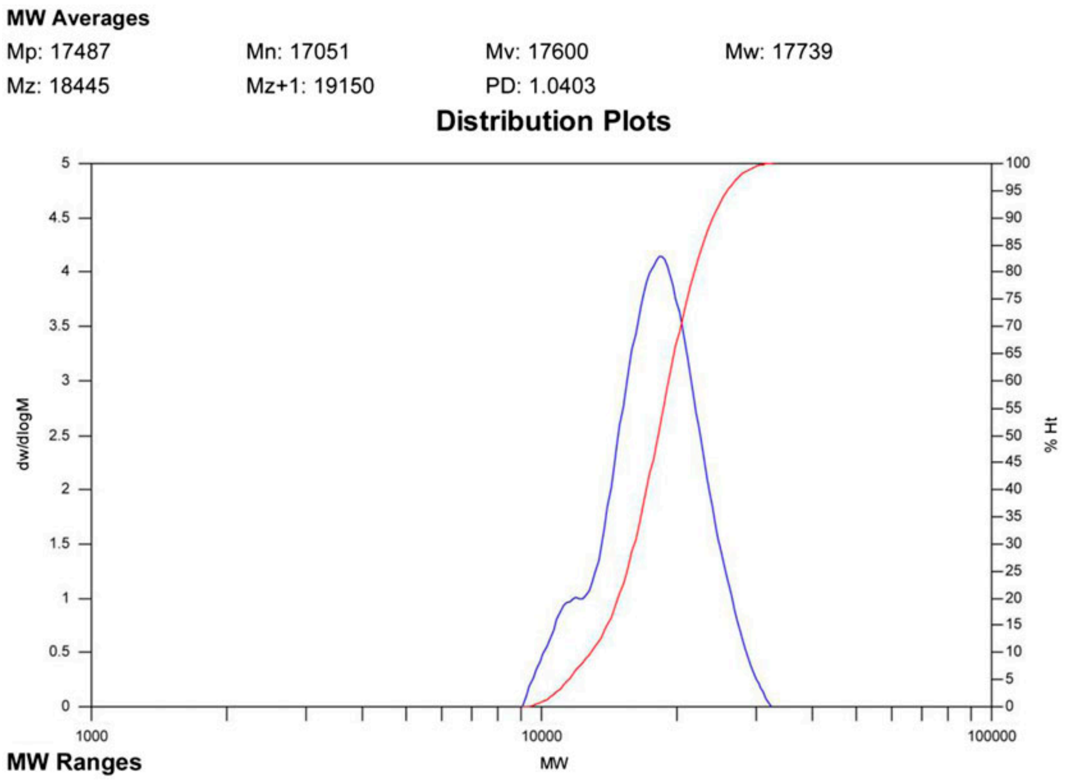

Fig. 5. Retention curve profiles of AA-APEU (AA:APEU = 3:1, 1 h initiator dropping time, 5 wt% initiator, and 3 h reaction time; 25% solid content).

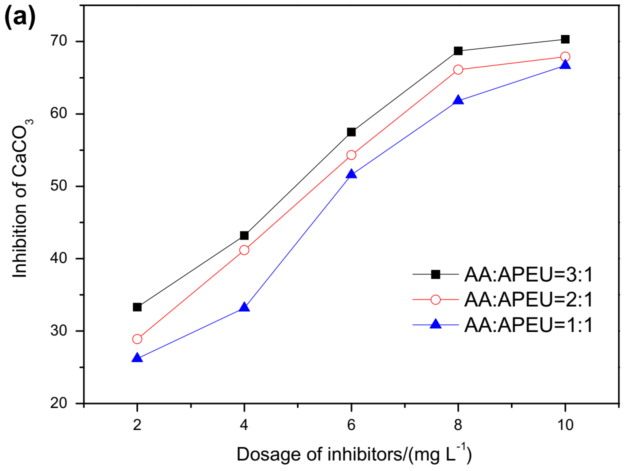

Fig. 6a. Influence of mole ratio of AA-APEU (samples 1, 2, and 3 in Table 2) on calcium carbonate inhibition.

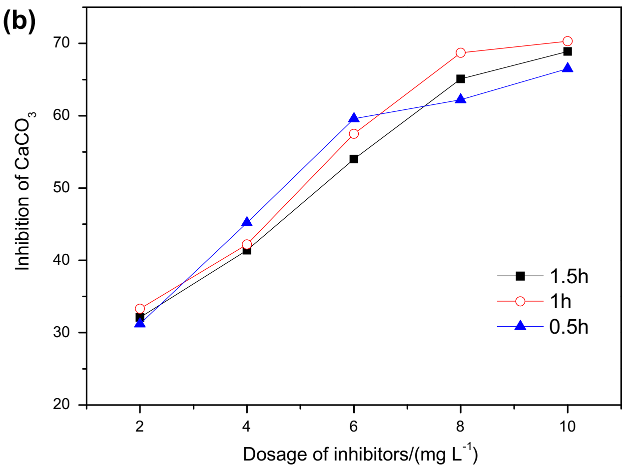

Fig. 6b. Influence of initiator dropping time of polymerization (samples 1, 4, and 5 in Table 2) on calcium carbonate inhibition.

Therefore, the AA-AEPU used in Figs. 7, 8, and Fig. 9 was radical polymerized at the feed AA:APEU with the mole ratio of 3:1 under the conditions of 1 h initiator dropping time, 5 wt% initiator, and 3 h reaction time.

Fig. 7 illustrates the precipitation condition of calcium carbonate in the presence of different inhibitors.

As can be seen from Fig. 6a–6d, the ability to control calcium carbonate precipitation followed the order AA-APEU > AA-APEL > PESA > HPMA > PAA.

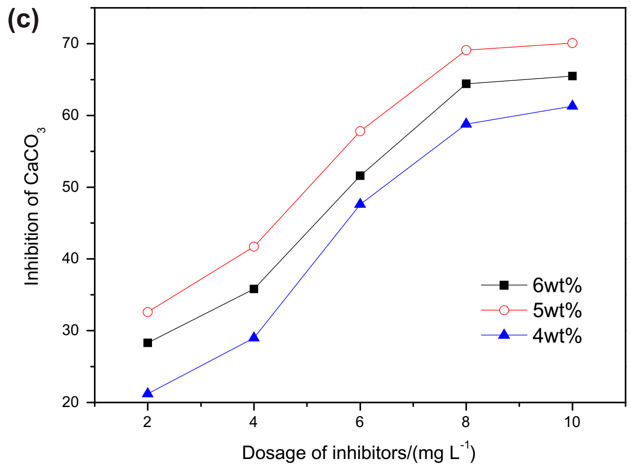

Fig. 6c. Influence of initiator dropping dosage of polymerization (samples 1, 6, and 7 in Table 2) on calcium carbonate inhibition.

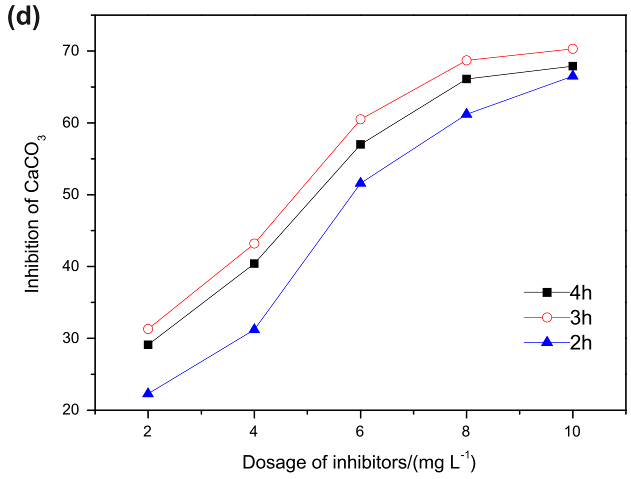

Fig. 6d. Influence of reaction time of polymerization (samples 1, 8, and 9 in Table 2) on calcium carbonate inhibition.

Furthermore, both AA-APEU and AA-APEL display excellent control power in retarding the growth of calcium carbonate, almost 20% more than other inhibitors. This result reveals that the polyethylene glycol (PEG) on AA-APEU and AA-APEL plays an important role on inhibition of calcium carbonate scale despite the fact that AA-APEU, AA-APEL, PESA, HPMA, and PAA all contain carboxyl groups [17]. However, AA-APEU (71.8%) seems more effective than AA-APEL (69.7%) for calcium carbonate inhibition. We assume that this may be due to the unique stereo structure of AA-APEU which can chelate Ca^{2+} more selectively and effectively. Besides, AA-APEU is biodegraded more easily than AA-APEL because of amino groups. From the above statement, inhibitor AA-APEU exhibits the best ability to control calcium carbonate scale among other non-phosphorus inhibitors investigated, namely AA-APEL, PESA, HPMA, and PAA.

3.5. Scale surface morphology characterization

The SEM photographs for calcium carbonate with and without the presence of the inhibitor are presented in Fig. 7. As can be noted, in the absence of inhibitor, a regular calcite-like particle of cubic shape is observed. However, in the presence of 4 mg/L AA-APEU (Fig. 8(b)), the regular appearance transforms into ellipsoidal shape which corresponds to vaterite [23]. The presence of inhibitor apparently affects the morphology and the size of calcium crystals significantly. It also makes the precipitates have a higher disperse property in water solution. As a consequence, the precipitates can be easily disturbed by water turbulence. Further details are expounded below.

Fig. 9 is the XRD spectra of calcium carbonate crystals without and with the AA-APEU copolymer. There are three types of calcium carbonate crystal formed: calcite, aragonite, and vaterite, of which calcite is the most thermodynamically stable, while vaterite is the least one. It is traditionally recognized that vaterite crystals are the initial phase form in $CaCO_3$ saturation solutions, and they can spontaneously transform into calcite if there is no interference [24]. From Fig. 8, the threshold scale of inhibition of the copolymer can be observed, which is due to the adsorption of the polymer on the growing crystal phases. This adsorption results in the retardation and distortion of the crystal growth. XRD pattern further affirms the change of crystal morphology, which is in accordance with the result of SEM photographs. In the absence of inhibitors (Fig. 9(a)), calcite is the only crystal formed, and the reflection peaks appeared at 23 (0 1 2), 29 (1 0 4), 36 (1 1 0), 39 (1 1 3), 43 (2 0 2), 47.5 (0 1 8), and 48.5 (1 1 8). With the use of AA-APEU, vaterite crystal appears with the peaks at 25 (1 1 0), 27 (1 1 2), 33 (1 1 4), 44 (3 0 0), and 50 (1 1 8) (Fig. 9(b)). Compared with previous spectra, it's clear that the calcium carbonate scales are a mixture of calcite and vaterite crystals with inhibitors.

All these results suggest that the addition of AA-APEU alters calcium carbonate forms to some extent.

3.6. The mechanism of calcium carbonate inhibition

There are two main anti-scaling mechanisms in the process of controlling mineral scale: one is that inhibi-

Table 2
Solid contents of AA-APEU under different reaction conditions

Sample number	Mole ratio of AA:APEU	Initiator dropping time (h)	Initiator dosage (wt%)	Reaction time (h)	Solid content (%)
1	3:1	1	5	3	25.1
2	2:1	1	5	3	26.8
3	1:1	1	5	3	27.3
4	3:1	0.5	5	3	24.4
5	3:1	1.5	5	3	25.9
6	3:1	1	4	3	22.5
7	3:1	1	6	3	29.6
8	3:1	1	5	2	21.4
9	3:1	1	5	4	27.3

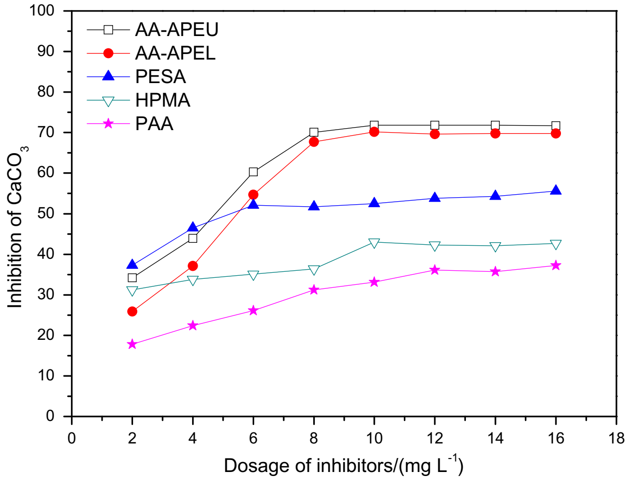

Fig. 7. Comparison of calcium carbonate inhibition of AA-APEU (AA:APEU = 3:1, 1 h initiator dropping time, 5 wt% initiator, and 3 h reaction time; 25% solid content), AA-APEL and different inhibitors at different concentrations.

tors can keep more scale-forming positive ions (e.g. Ca^{2+} and Mg^{2+}) in the solution from being precipitated through complexation action; the other one is that the anti-scaling chemicals can interact with mineral nuclei to disrupt the crystallization process and then make the crystal particles disperse in the aqueous suspension, rendering them less prone to sedimentation onto the equipment surfaces [25–27]. The latter is more widely accepted.

The AA and APEU blocks, which are hydrophilic chain segments, disperse in cooling water solution at first. Due to the high-alkaline industry cooling water, the carboxkyl groups are dissociated into negatively charged carboxylate ions. Once confronting with calcium ions, these negatively charged carboxylate ions of AA-APEU can recognize and capture calcium ions. Meanwhile, the long polyethylene glycol (PEG) chain reacts and encapsulates the positive calcium to form stable AA-APEU-Ca^{2+} complexes. Both carboxyl segments and PEG are important parts on forming coordination compounds. Surrounded by several AA-APEU molecules, the complexes do not precipitate because, the long PEG chains and a large number of amino groups combine with water to form hydrogen bonds. Although both the long PEG chains and amino groups can be monohydrated in aqueous solution and show high hydrophilic properties, it should be noted that amino hydrogens are preferred to adapt to energy minimization and side chain mismatching [28–31]. The

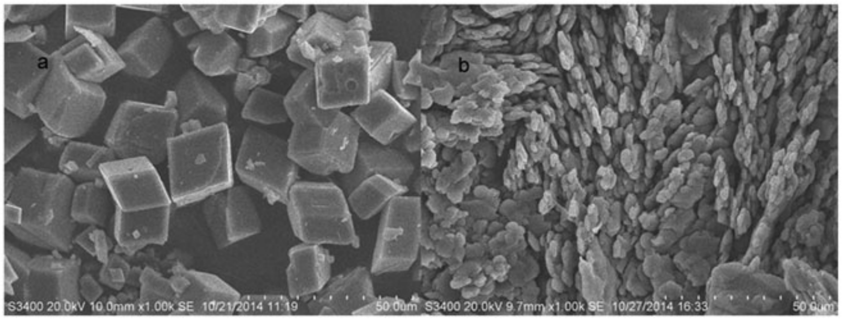

Fig. 8. SEM photographs for calcium carbonate (a) and in the presence of AA-APEU (b) 4 mg/L.

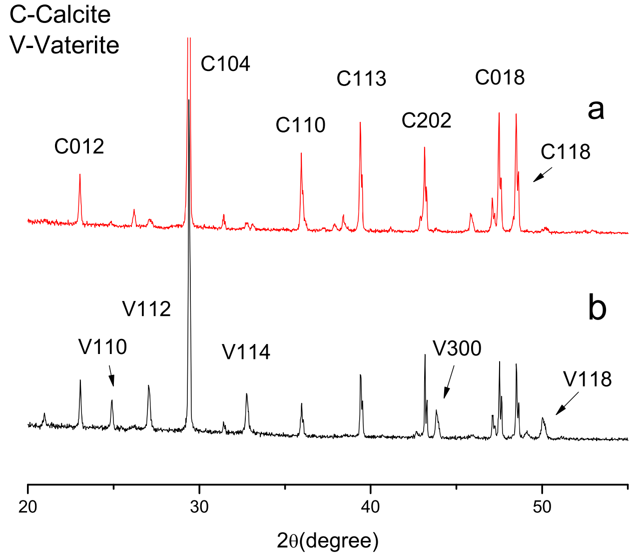

Fig. 9. XRD spectrum: (a) for calcium carbonate and (b) in presence of AA-APEU 4 mg/L.

complexes and amino groups take calcium ions away as the water is running.

4. Conclusions

In this paper, the AA-APEU copolymer is synthesized and characterized through FT-IR spectroscopy and ^{1}H NMR. AA-APEU shows the best calcium carbonate inhibition when the mole ratio of AA:APEU is 3:1, the amount of initiator is 5 wt%, the initiator dropping time is 1 h, and the time of polymerization is 3 h. The results of static scale inhibition tests reveal that the copolymer is effective in the calcium scales inhibition compared with other commercial inhibitors. The calcium carbonate inhibition of AA-APEU reaches approximately 72% at a level of 8 mg/L since the popular non-phosphorus inhibitors of PAA, HPMA, and PESA reach only 20–60%. SEM and XRD studies indicate that the metastable crystal forms of vaterite appear in the presence of inhibitors.

Until now, a similar glutamic-modified polymer AA-APEU used as a scale inhibitor in cooling water has not been reported in literature before, it is believed to be a new effective environmental water treatment agent. Also, limitations in estimating the microstructure of this new polymer accurately remains a challenge and requires further work.

Acknowledgments

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