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Performance of an environmentally friendly anti-scalant in $CaSO_4$ scale inhibition

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ABSTRACT

The precipitation of calcium sulfate ($CaSO_4$) scale on heat transfer surfaces widely occurs in numerous industrial processes. For the control of calcium sulfate scale, a novel environmentally friendly type of scale inhibitor Acrylic acid–oxalic acid–allypolyethoxy carboxylate (AA-APEM9) was synthesized and characterized, and the anti-scale property of the AA-APEM9 copolymer towards calcium sulfate in the artificial cooling water was studied through static scale inhibition tests. It was shown that AA-APEM9 exhibited excellent ability to control calcium sulfate scale, with approximately 97.1% calcium sulfate inhibition at a level of 4 mg/L AA-APEM9. Scanning electron microscopy and X-ray powder diffraction studies have been performed to identify the change in crystal surfaces by the addition of the copolymer. Inhibition mechanism is proposed that PAA can recognize and react with positively charged calcium ions on the surface of inorganic minerals and water-compatible PEG segments increase its solubility in water.

Keywords: Copolymer; Water soluble; Scale inhibitor; Calcium sulfate; Cooling water systems

1. Introduction

Increasing scarcity of freshwater supply for use in cooling water systems has led to the search for reuse of cooling water many times (typically 4–8 times). Because of the evaporative loss of water, the elevated concentration and high water temperature could cause severe mineral deposition (scaling) problems. When these scales appear on a pipe surface, scale can lead to loss of system efficiency, unscheduled shutdown, localized corrosion attack, and obstruction of fluid flow and, in some cases, can even cause disastrous operational failures in cooling water systems [1–4]. The commonly occurring scales are calcium carbonate, calcium sulfate, barium sulfate, calcium phosphate, calcium oxalate, etc. and among them, calcium sulfate is considered the most prominent [5–8]. To eliminate or to reduce these problems, waters used in cooling systems are treated with inhibitive formulations. Therefore, the consumption of inhibitors to reduce scaling has increased in recent years. Several studies about

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calcium sulfate scales formation in the absence and presence of inhibitors have been carried out [4,9–14].

Investigations of more environmentally acceptable scale inhibitors are of great practical interest. One of the effective methods to prevent precipitation is the use of carboxylic polymers such as poly acrylic acid (PAA) [7,15]. The exact mechanism by which these polymers function is still incompletely understood, but several mechanisms may plausibly play a role: chelation of calcium ions by PAA, specific adsorption of PAA to active sites on the surface of crystallites to retard growth or alter crystal habit, and nucleation of calcium oxalate crystallites by Ca^{2+}:PAA complexes [7,16]. Current environmentally friendly carboxylic polymers inhibitor such as PESA or PAA, which has a low calcium tolerance, will react with calcium ions to form insoluble calcium-polymer salts [17].

Our earlier studies showed that no phosphate- and nitrogen-free scale inhibitor (APECn, APELn, and APEG-PG-COOH) for cooling water systems were prepared from allyloxy polyethoxy ether, NaOH, and chloroacetic acid, glycidol or succinic anhydride (SA) and allylpolyethoxy carboxylate, a double-hydrophilic block copolymer, has high molecular weight and the (–COOH) anionic active groups are at lateral and exposed [4,18–20]. However, the preparation process still has two defects. (a) chloroacetic acid is toxic and harmful to human body and environment. (b) Glycidol and SA are very expensive and difficult to turn into a large-scale business. Thus, new types of double-hydrophilic block copolymer need to be developed.

In response to environmental guidelines, the purpose of the present study presents the results of "green" chemicals study that was undertaken to investigate the ability of new inhibitors (acrylic acid [AA], oxalic acid, and allypolyethoxy carboxylate [APEM9]) to inhibit the scale problems found in cooling water systems. As calcium sulfate is the major scale in cooling water system, thrust is to be given towards the performance of the scale inhibitor with respect to this scale. The principal aim in the present work is to investigate the effectiveness of a structurally well-defined calcium sulfate which is phosphorus-free and has a superior calcium tolerance. Inhibitor employed in this paper is double-hydrophilic block copolymer of acrylic acid, oxalic acid, and allylpolyethoxy carboxylate.

2. Materials and methods

2.1. Materials

APEM9 and AA-APEC9 were synthesized from allyloxy polyethoxy ether (APEG9) in our laboratory according to K. Du's procedure [21]. AA was in analytically pure grade and was supplied by Zhongdong Chemical Reagent Co., Ltd (Nanjing, Jiangsu, China). Commercial inhibitors of T-225, poly (acrylic acid) (PAA, 1800 MW), hydrolyzed polymaleic acid (HPMA, 600 MW), and polyepoxysuccinic acid (PESA, 1500 MW) were in technical grade and supplied by Jiangsu Jianghai Chemical Co., Ltd. Distilled water was used for all the studies.

2.2. Preparation of APEM9 and AA-APEM9

The carboxylic acid functionalization of the surface hydroxyl groups was realized with oxalic acid. The preparation procedure of APEM9 is shown in Fig. 1.

A five-neck round-bottom flask, equipped with a thermometer and a magnetic stirrer, was charged with 90 mL distilled water and 0.1 mol APEM9 and heated to 60˚C with stirring under nitrogen atmosphere. After that, 1.5 mol AA was added in 20 mL distilled water (the mole ratio of APEM9 and AA was 1:15) and the initiator solution (3.5 g ammonium persulfate in 20 mL distilled water) was added separately at constant flow rates over a period of 1.0 h. The reaction was then heated to 80˚C and maintained at this temperature for an additional 2 h, ultimately affording an aqueous polymer solution containing approximately 28.6% solid. At last, the product of AA-APEM9 was obtained. The preparation procedure of AA-APEM9 is shown in Fig. 2.

2.3. Fourier transform infrared (FT-IR) and ^1H NMR characterization

The samples were analyzed using a FT-IR spectroscopy (VECTOR-22, Bruker Co., Germany) in the region of 4,000–500 cm^{-1}. Prior to the measurement, the samples were dried under vacuum until reaching to a constant weight. The dried samples were pressed into the powder, mixed with KBr powder, and then compressed to make a pellet for FT-IR characterization. Structures of APEG, APEM9, and AA-APEM9 were also explored by a Bruker NMR analyzer (AVANCE AV-500, Bruker, Switzerland) operating at 500 MHz.

2.4. Morphology observation and other characterization

The morphologies of the calcium sulfate crystals were analyzed by scanning electron microscopy (SEM). The samples were coated with a layer of gold and observed in a S-3400 N HITECH SEM. The X-ray diffraction (XRD) patterns of the calcium sulfate crystals were recorded on a Rigaku D/max 2,400 X-ray

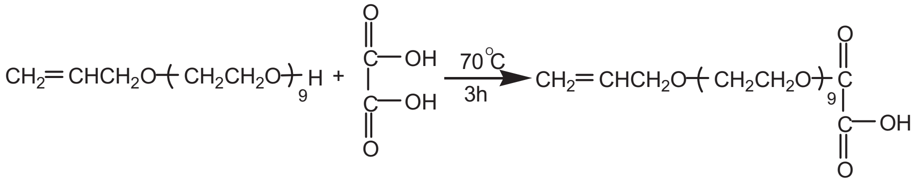

Fig. 1. Preparation of APEM9.

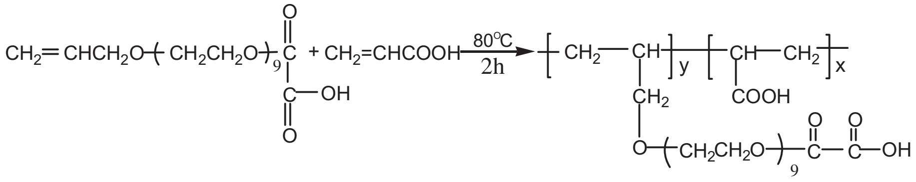

Fig. 2. Preparation of AA-APEM9.

powder diffractometer with Cu Kα ($\lambda = 1.5406$) radiation (40 kV, 120 mA).

2.5. Inhibition test

The ability of the AA-APEM9 copolymer to inhibit calcium sulfate scale was compare with that of the free-inhibitor in flask tests [18]. The inhibitor dosages given were on dry-inhibitor basis. Calcium sulfate precipitation and inhibition were studied in artificial cooling water which was prepared by dissolving a certain quantity of $CaCl_2$ and Na_2SO_4 in deionized water. Two concentrations of $CaC1_2$ (6,800 mg/L Ca^{2+}) and Na_2SO_4 (7,100 mg/L SO_4^{2-}) were used according to the national standard of P.R. China concerning the code for the design of industrial recirculating cooling-water treatment (GB/T 16632-2008).

The artificial cooling water containing different quantities of the AA-APEM9 copolymer was thermostated at 60℃ for 10 h. $CaCl_2$ and Na_2SO_4 used to prepare the scaling test solution were of analytical reagent grade. The phosphorous-free and nonnitrogen copolymer had been synthesized in the laboratory.

Solution was analyzed after every set of experiments with respect to soluble calcium ions using a standard solution of EDTA according to standard methods (Water Treatment Reagent Unit of Standardization Research Institute of Chemical Industry of China Chemical Industry Press, 2003). The inhibition efficiency μ was defined as:

$$\mu = \frac{\rho 1(\mathrm{Ca}^{2+}) - \rho 2(\mathrm{Ca}^{2+})}{\rho 0(\mathrm{Ca}^{2+}) - \rho 2(\mathrm{Ca}^{2+})} \tag{1}$$

$\rho 0(\mathrm{Ca}^{2+})$ was the total concentrations of $\mathrm{Ca}^{2+}(\mathrm{mg\,L}^{-1})$, $\rho 1(\mathrm{Ca}^{2+})$ was the concentrations of $\mathrm{Ca}^{2+}(\mathrm{mg\,L}^{-1})$ in the presence of the AA-APEM9 copolymer, and $\rho 2(\mathrm{Ca}^{2+})$ was the concentrations of $\mathrm{Ca}^{2+}(\mathrm{mg\,L}^{-1})$ in the absence of the AA-APEM9 copolymer.

3. Results and discussion

3.1. Structure analysis of the copolymer

The FT-IR spectra of APEG9 (a), APEM9 (b), and AA-APEM9 (c) were shown in Fig. 3. The bands at 1,648 cm^{-1} are from the stretching of –C = C– groups. The 1,731 cm^{-1} strong intensity absorption peak (–C = O) in curve b reveals clearly that APEM9 has been synthesized successfully. On the basis of FT-IR studies, the (–C = C–) stretching vibration at 1,647 cm^{-1} appears in curve b but disappears completely in curve c, which reveals that free radical polymerization between APEM9 and AA has happened.

H^1 NMR spectra for (a) APEG9, (b) APEM9, and (c) AA-APEM9 are shown in Fig. 4. APEG9 (Fig. 4(a)) ($(CD_3)_2SO$, δ ppm): 2.50 (solvent residual peak of

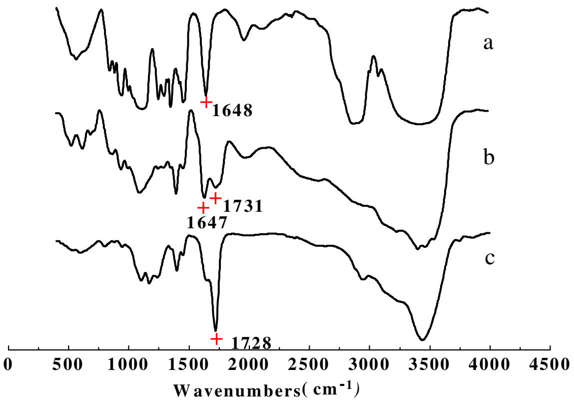

Fig. 3. The FT-IR spectrums of (a) APEG9 (b) APEM9, and (c) AA-APEM9.

$(CD_3)_2SO$), 3.00–3.80 (–OCH_2CH_2–, ether groups), 3.80–6.00 (CH_2=CH–CH_2–, propenyl protons), and 4.40–4.60 (–OH, active hydrogen in APEG).

APEM9 (Fig. 4(b)) (($(CD_3)_2SO$, δ ppm): 2.50 (solvent residual peak of $(CD_3)_2SO$), 3.50–3.90 (–OCH_2CH_2–, ether groups), because of oxalic acid reaction with APEG9 was successful, –COCOOH affects the four hydrogen in –OCH_2CH_2– group which is near –COCOOH group; and 4.10–6.00 (CH_2=CH–CH_2–, propenyl protons). The fact that the δ 4.40–4.60 ppm (–OH) active hydrogen in (a) disappeared completely proves that –OH in APEG has been entirely replaced by –COCOOH.

AA-APEM9 (Fig. 4(c)) (($(CD_3)_2SO$, δppm): 2.50 (solvent residual peak of $(CD_3)_2SO$), δ 4.10–6.00 ppm in (b) double bond absorption peaks completely disappeared in (c). This reveals that free radical polymerization among APEM9 and AA has happened. From FT-IR and ^{1}H NMR analysis, it can conclude that synthesized AA-APEM9 has anticipated structure.

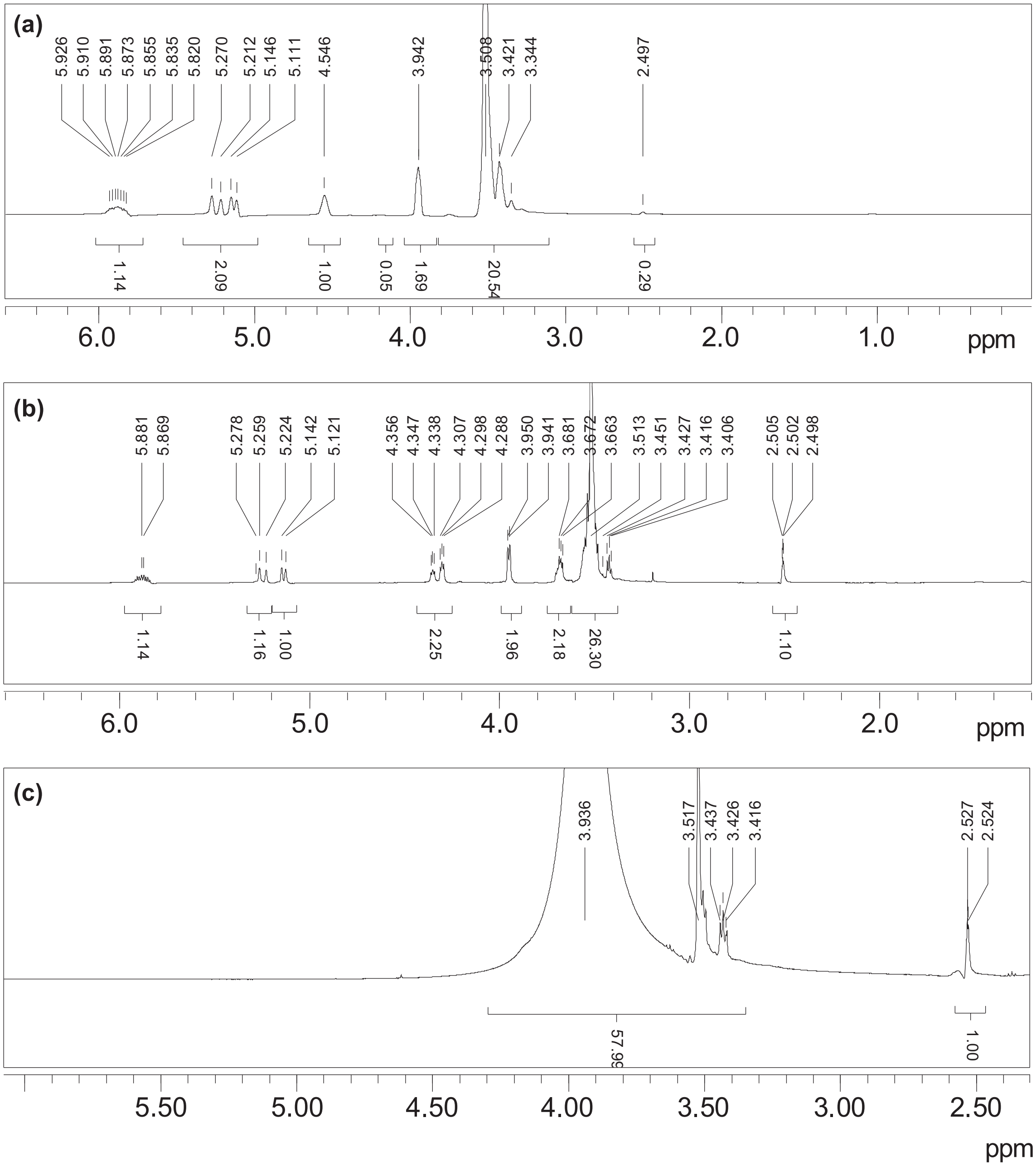

Fig. 4. The H^1 NMR spectra of (a) APEG9, (b) APEM9, and (c) AA-APEM9.

3.2. Effect of inhibitor on calcium sulfate scales

Fig. 5 illustrates the effect of calcium sulfate precipitation on the performance between different inhibitors. All the data in Fig. 5 show that the ability to control calcium sulfate precipitation followed the order AA-APEM9 > AA-APEC9 > T-225 > HPMA ≈ PAA > PESA (at low dosage). As can be seen from Fig. 5, little inhibition on calcium sulfate precipitation by the presence of PESA is observed (6 mg/L only 80% calcium sulfate inhibition). However, both AA-APEM9 and T-225 showed strong inhibition. Especially at a level of 2 mg/L, T-225(76.5%) seemed more effective than AA-APEM9 (49.1%) for the calcium sulfate inhibition. But, when overcoming 4 mg/L, AA-APEM9 (97.1%) showed great inhibition ability than T-225(82.3%). Also, we found that AA-APEM9 was more potent than both HPMA (80.1%) and PAA (87.9%) at the same dosage (4 mg/L). Therefore, inhibitor AA-APEM9 displayed the best ability to control calcium sulfate scale among nonphosphorus inhibitors investigated, namely, T-225, HPMA, PAA, and PESA.

3.3. Scale surface morphology characterization

SEM is one of the widely used nondestructive surface examination techniques. The change of crystal size and modifications, brought about by the AA-APEM9 copolymer addition, was examined through SEM. Fig. 6 showed the SEM images of calcium sulfate after 10 h crystallization and precipitation without (Fig. 6(a)) or with (Fig. 6(b)–(d)) AA-APEM9 added.

The SEM photographs for calcium sulfate scale with and without the presence of the inhibitor are presented in Fig. 6. The crystal types of calcium sulfate depend on the evaporation rate of water and forms, dehydrate, hemihydrates, and anhydrate. In the absence of inhibitor, regular rod-shaped calcium sulfate was obtained (Fig. 6(a)), and in the presence of 2 mg/L AA-APEM9, the loose calcium sulfate particles was produced (Fig. 6(b)). When the AA-APEM9 concentration increased to 4 mg/L, sharp edges and acute corners of the crystals disappeared almost completely. The loose particles became the main part of the calcium sulfate when the concentration of AA-APEM9 was 12 mg/L. It also indicated that the use of only 2 mg/L AA-APEM9 had a great effect on the calcium sulfate morphology.

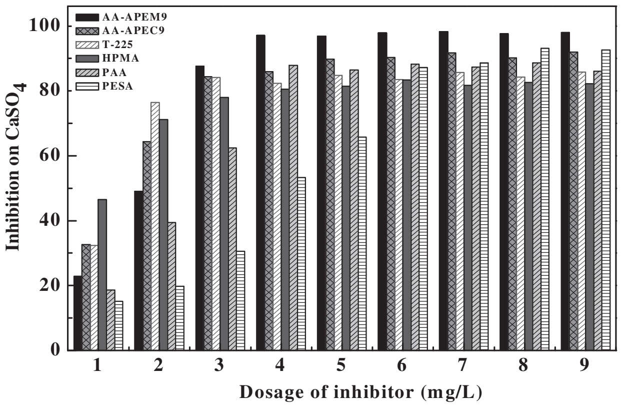

Fig. 5. Comparison of calcium sulfate inhibition between different inhibitors.

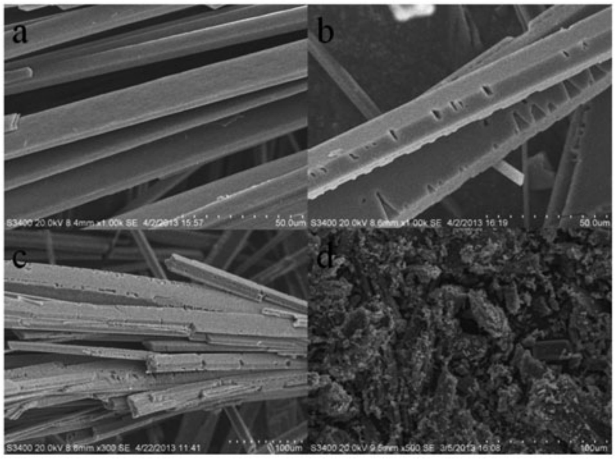

Fig. 6. SEM photographs for the calcium sulfate (a) and with the presence of AA-APEM9 (b) 2 mg/L, (c) 4 mg/L, and (d) 6 mg/L.

Fig. 7 is the XRD spectra for calcium sulfate crystals without and with the presence of the AA-APEM9 copolymer. For calcium sulfate scale, the d and θ values conform to the structure of $CaSO_4 \cdot 2H_2O$ (calcium sulfate dihydrate) [22,23]. In the case, the addition of copolymer did not alter the crystal structure, as

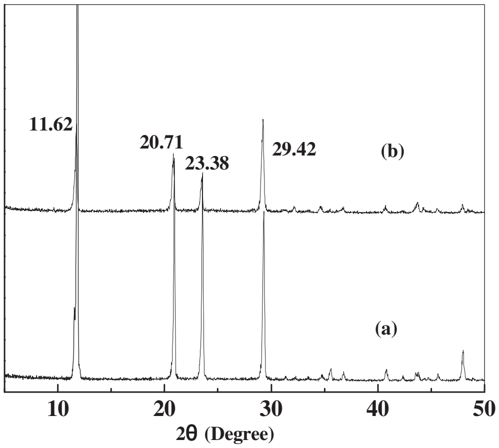

Fig. 7. XRD spectrum: (a) for calcium sulfate and (b) in presence of AA-APEM9.

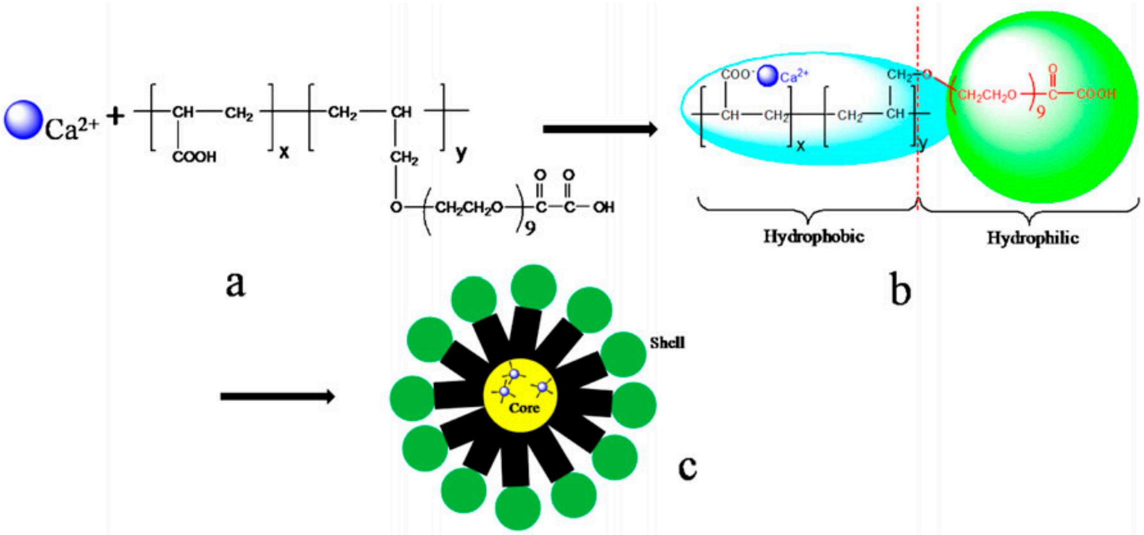

Fig. 8. Inhibition mechanism towards calcium sulfate scale.

confirmed by no alteration in its *d* and *θ* values. Only the crystal habit or morphology is changed, as is evident from the SEM photographs.

3.4. The mechanism of calcium sulfate inhibition

It is generally accepted that the inhibition of scale formation is influenced by both the location of the adsorbed inhibitor at the crystal surface and the extent of chemical bonding with the surface. The more effective the inhibitor is, the higher the surface-binding capability is [24,25]. The AA-APEM9 copolymer contains a large number of carboxyl groups and its surface-binding capability is stronger and possesses higher inhibition effect under identical conditions. Carboxyl segments and PEG are important parts on matrices of AA-APEM9. The functional groups of anti-scalant exhibit a significant impact on their inhibitory power in terms of controlling the scale precipitation. AA-APEM9 is a structurally well-defined biblock copolymer, depicted in Fig. 8(a); the main chains are composed of allyl-terminated AA, denoted as PAA, and the side chains are made of PEG segments. Both PAA and PEG segments are hydrophilic blocks and exist randomly in cooling water. PAA can recognize and react with positively charged calcium ions on the surface of inorganic minerals, such as calcium sulfate and the like (Fig. 8(b)). After encapsulation or interaction between calcium ions and carboxyl groups can lead to the spontaneous formation of AA-APEM9-COOCa complexes. At the same time, water-compatible PEG segments have the very strong hydrophilicity and thus increase its solubility in water (Fig. 8(c)). As result, the existing minerals do not precipitate with AA-APEM9 through its excellent ability to disperse solid particles such as calcium sulfate scales. Thus, AA-APEM9 possesses excellent ability to control calcium sulfate scale.

4. Conclusions

The copolymer AA-APEM9 has been synthesized and characterized through FT-IR and ^{1}H NMR studies. It is believed to represent a potentially new environmentally safe water treatment agent suitable for cooling water systems. The copolymer AA-APEM9 exhibited 97.1% calcium sulfate inhibition at a threshold dosage of 4 mg/L. Compared to the recent nonphosphorus inhibitor of AA-APEC9, PAA, HPMA, PESA, and T-225, AA-APEM9-possessing PEG shows a superior inhibitory efficiency; the inhibition mechanism is proposed that encapsulation or interaction happened between PAA and Ca^{2+} and the core–shell structure is formed. SEM and XRD studies show the crystal structures are not much altered but the copolymer bring about changes in crystal habits or crystal morphology.

Acknowledgments

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