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Study on the performance of $CaSO_4$ scale for phosphorus-free modified PEG scale inhibitor in cooling water system

Huchuan Wang[a,b], Jianjun Yang[a,*], Chuanrun Li[b], Mengjie Zhu[b], Qingyun Wu[a], Mingyuan Wu[a], Jianan Zhang[a]

[a]*School of Chemistry and Chemical Engineering, Anhui University, Hefei, Anhui 230601, China, emails: andayjj@163.com (J. Yang), WHC03231986@163.com (H. Wang), 1154206008@qq.com (Q. Wu), 371648331@qq.com (M. Wu), 928678731@qq.com (J. Zhang)*

[b]*School of Pharmacy, Anhui University of Chinese Medicine, Hefei, Anhui 230012, China, emails: chuanrunli@qq.com (C. Li), 3059613722@qq.com (M. Zhu)*

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ABSTRACT

The static test experiments in this study was conducted to evaluate the inhibiting the formation of calcium sulphate scale. At present commonly in the market used scale inhibitors is commonly phosphorous scale inhibitor, is not conducive to environmental protection. In this paper, synthesized a kind of no phosphorus green scale inhibitor, the scale inhibitor consists of acrylic acid (AA), polyethylene glycol ester (PEGZG maleic anhydride modified polyethylene glycol), allyl sulfonate (SAS) system for the controlled radical polymerization of aqueous phase, through Fourier transform infrared spectrometer (FT-IR) known monomer reaction completely, the best synthetic conditions for AA: PEGZG: SAS = 1:3:1 (mass ratio), 6% of the total quality of the initiator to monomer, add and reaction temperature respectively in 70° and 80°, the scale inhibitor in dosing quantity is 5 mg/L, the resistance rate of calcium sulphate scale above 95%, through the simulation of cooling water pipe figure can be concluded that adding scale inhibitors AA/PEGZG/SAS, simulating the circulating cooling water pipes become clear, generating calcium sulphate scale, the scale inhibitor can be used in high hardness water quality conditions, has a certain industrial application prospect.

Keywords: Inhibitor; Calcium sulphate scale; Cooling water systems

1. Introduction

With the shortage of freshwater resources, fresh water saving has become the subject of the chemical industry. In order to maintain the reactor at the specified temperature in the industry, if the reactor temperature needs to be reduced and the cooling water needs to be used for cooling. In the annual chemical industry, the amount of cooling water accounts for more than 70% of the total water consumption in the industry. In order to reduce the total amount of cooling water and start using the circulating cooling water system, the cooling water is generally recycled 2–4 times and then fresh cooling water is used. After the cooling water is recycled for more than two times, a large amount of inorganic salt ions (such as calcium ions, barium ions and the like) existing in the circulating water system will form inorganic salt scales with carbonate and sulfate ions such as calcium carbonate, calcium sulfate and barium sulfate [1–3]. In these fouling, calcium sulphate scale, once formed, can't be treated with dilute acid like calcium carbonate and is difficult to remove. As these inorganic scale deposits on the inner surface of the pipeline, it gradually clogs the heat exchange pipe. The heat rate dropped sharply, it is difficult to maintain the required reaction temperature, in severe cases reactor will stop

* Corresponding author.

working or even cause an explosion accident, resulting in economic losses and casualties [4–6].

In order to reduce the production of inorganic scale in the industry, water treatment chemicals, such as scale inhibitors or biocides, are generally added to the circulating water system. Most of the scale inhibitors currently used in the market was phosphorus-based scale inhibitors such as PBTC, ATMP, HEDP, etc. Although, these scale inhibitors are excellent in scale inhibitor effect, their long-term use will eutrophize the water due to their phosphorus content and will not be able to meet the environmental protection concept put forward by the state and will be gradually eliminated by the market. Environmental friendly, scale inhibitors have also gradually become the focus of research, such as PAA, PESA, PASP and other non-phosphorus scale inhibitors, these non-phosphorus scale inhibitors in the use of prone to calcium gel defects, limiting the scope of use [7–12].

In this paper, a new non-phosphorus scale inhibitor AA/PEGZG/SAS was synthesized. The scale inhibitor is free of phosphorus and has a large number of carboxyl functional groups. It can chelate the inorganic salt in recycled water system, chelated scale inhibitor contains a large number of water-soluble polyethylene glycol, sulfonic acid groups, the chelating calcium ion scale inhibitors can be dissolved in water to avoid the generation of calcium gel, the scale inhibitor is phosphorus-free environment protection so it is a new industrial scale inhibitor.

2. Experimental

2.1. Materials

PEGZG synthesis of reference 13, terminal two hydroxyl groups in PEG subjected to Maleic Anhydride (MA) by the esterification with a molar ratio of 1:2 in great yields exceeding 98%. AA, SAS Nanjing ZhongDong Company, 1-hydroxyethylidine-1, 1-diphosphonic acid (HEDP) and 2-phosphonobutane-1, 2, 4-tricarboxylic acid (PBTC) were acquired from Jiangsu Jianghai Chemical Co., Ltd, the entire experiment using deionized water. Fourier transform infrared spectrometer Vertex 80 (Germany BRUKER company).

2.2. Precipitation of $CaSO_4$ experiments

Resistance to calcium sulfate scale performance was tested according to the literature 14.

2.3. Preparation of AA/PEGZG/SAS

In a nitrogen atmosphere, according to the certain ratio weighed AA, PEGZG, SAS, PEGZG and appropriate amount of deionized water was added to a three-necked flask and then SAS dissolved in AA, placed in a constant pressure burette. Ammonium persulfate was dissolved in deionized water and placed in a constant pressure buret. The water bath was heated to 70°C. The reagents in the constant pressure burette were dropped within 60 min. After the addition, the temperature was raised to 80°C and incubated for 1.5 h. The reaction was completed to give a light yellow liquid AA/PEGZG/SAS with a solids content of 26.6%. AA:PEGZG:SAS = 1:3:1, 3:3:1, 5:3:1, 7:3:1 were prepared according to the experimental procedures above. The mass ratio of AA:PEGZG:SAS = 1:3:1, molecular weight (g/mol) of the polymer was investigated through gel permeation chromatography (GPC-Waters-2410) and the result was 13,702 (see Fig. 1).

3. Results and discussion

3.1. Fourier transform infrared spectrometer measurements

As can be seen from the infrared spectra of PEGZG and AA/PEGZG/SAS in Fig. 2, PEGZG has a significant unsaturated double bond vibration stretching absorption peak (-C=C-) at 1,648 cm^{-1} in the infrared spectrum, and AA/PEGZG/SAS in Fig. 2 at 1,648 cm^{-1} at double bond absorption peak disappears, indicating AA and PEGZG, SAS reaction was completed.

3.2. Influence of different ratio of monomer on $CaSO_4$ inhibition

Different ratio of monomer, scale inhibitor scale synthesis effect is also different, through the past experience of synthetic scale inhibitor, we choose a fixed titration time 1 h, holding time 1.5 h, titration temperature 70°C and reaction temperature 80°C, and static scale inhibition time 6 h, static scale inhibition temperature 70°C, initiator dosage 6% of the total mass, Ca^{2+} concentration 2,000 mg/L, SO_4^{2-} concentration 5,000 mg/L. Test AA, PEGZG, SAS of different mass ratio of synthetic scale inhibitor resistance $CaSO_4$ performance, the results shown in Fig. 3.

As can be seen from Fig. 3, the main functional group of the chelating calcium ion in the scale inhibitor is a carboxyl group and the carboxyl group in AA/PEGZG/SAS is derived from AA. However, in the synthesis, the more AA content is not the more excellent the scale inhibiting effect is. A certain range, it is possible that the increase of AA content leads to

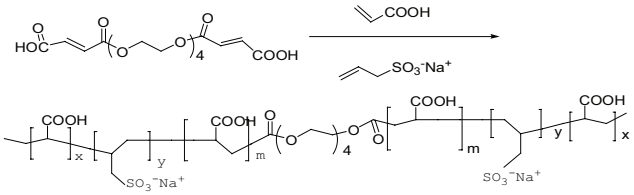

Fig. 1. Preparation of AA/PEGZG/SAS.

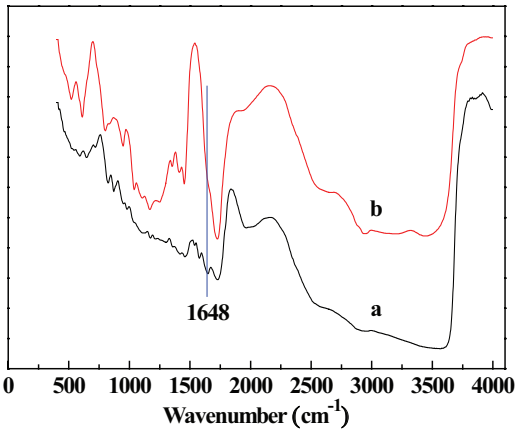

Fig. 2. FT-IR spectrums of (a) PEGZG and (b) AA/PEGZG/SAS.

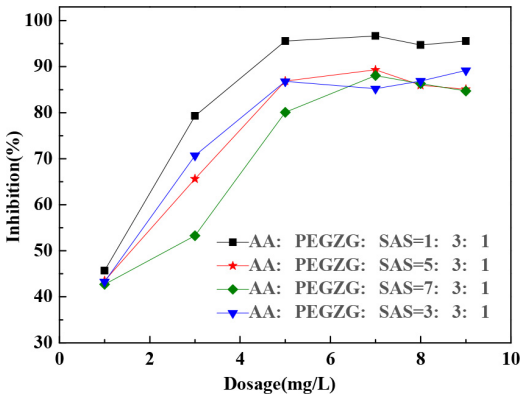

Fig. 3. Comparison of $CaSO_4$ inhibition between different molar ratio inhibitors.

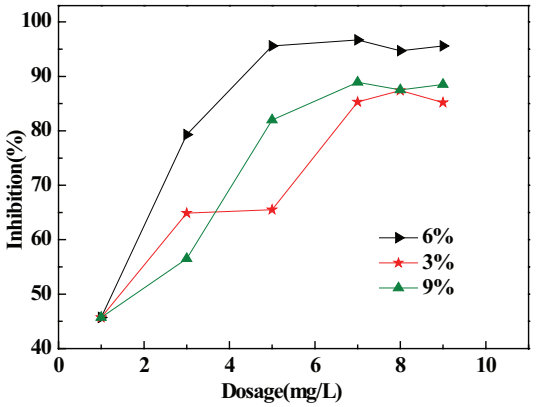

Fig. 4. Comparison of $CaSO_4$ inhibition between different initiator inhibitors.

the excessive molecular weight of the scale inhibitor. When carboxyl groups chelate a large amount of calcium ions, the soluble PEG and sulfonic acid groups contained in the AA/PEGZG/SAS hardly make the whole chelating calcium ion. As shown in Fig. 3, AA/PEGZG/SAS had the most excellent calcium sulfate scale inhibition effect when AA:PEGZG:SAS = 1:3:1. When the scale inhibitor was dissolved in circulating water, AA/PEGZG/SAS dosage of 5mg/L, the calcium sulfate resistance scale reached more than 95%, then with the dosage increases, the scale effect basically unchanged, in line with the previously reported scale inhibitor "threshold effect" [14], so we use the actual circulating water treatment agent, the general choice of dosage is about 5 mg/L.

3.3. Influence of different initiator on $CaSO_4$ inhibition

The addition amount of initiator had a great influence on the scale inhibitor. According to the synthetic procedure of 3.2, AA/PEGZG/SAS was selected as AA:PEGZG:SAS = 1:3:1, the amount of agent added, the study of its impact on the performance of the scale inhibitor. The results are shown in Fig. 4.

It can be seen from Fig. 4 that the amount of the initiator added has a great influence on the scale inhibition effect of the synthetic scale inhibitor, and the amount of the initiator directly affects the molecular weight of the synthesized scale inhibitor. The molecular weight is too large or too small, which is unfavorable to the scale inhibitor of the calcium sulfate scale inhibition, when the initiator is added in an amount of 6%, AA/PEGZG/SAS calcium sulfate scale the best effect, 3% initiator, calcium sulfate scale inhibition effect is the lowest, probably because the initiator addition is too small, resulting in inadequate polymerization of monomers, which scale inhibition effect is lower.

3.4. Influence of different titration and reaction temperature on $CaSO_4$ inhibition

Different titration and reaction temperature have some influence on the scale inhibitor. According to the synthetic procedure of 3.2, AA/PEGZG/SAS was selected as AA:PEGZG:SAS = 1:3:1. Different titration and reaction temperature, the study of its impact on the performance of the scale inhibitor is shown in Fig. 5.

It can be seen from Fig. 5 that the titration and the reaction temperature have a great influence on the scale inhibitor synthesized. The temperature is too low or too high, which is not conducive to scale inhibitor scale inhibition. The temperature may affect the polymerization of the initiator or the monomer too large, resulting in the synthesis of the scale inhibitor performance of large differences in the actual synthesis and we choose to drop 70°, the reaction of 80° more appropriate.

3.5. Influence of different Ca^{2+} and SO_4^{2-} concentration on $CaSO_4$ inhibition

China's water quality and environment vary greatly. In order to save water cost, factories generally use groundwater and tap water to mix cooling water. In the north, for example, due to the hardness of groundwater and the high content of inorganic salt ions, synthetic scale inhibitors can be used in circulating water system under high hardness environment. We investigated the effect of scale inhibitors under different calcium ions and sulfate ion water quality, and choose AA:PEGZG:SAS = 1:3:1 set of effectiveness tests. The results are shown in Figs. 6 and 7.

As can be seen from Figs. 6 and 7, the scale inhibitor AA/PEGZG/SAS still has a good calcium sulfate scale inhibition effect in the water with high hardness. When the calcium ion concentration is 8,000 mg/L, the calcium sulfate scale inhibition effect is still close 80% scale inhibition rate, in the sulfate ion 12,000 mg/L inhibition efficiency also nearly 80%, the scale inhibitor for the North and other relatively large hardness of the water environment, expanding its scope of application.

3.6. Influence of different inhibitor on $CaSO_4$ inhibition

Fig. 8 shows that the influence of different inhibitor on the scale inhibition efficiency. Scale inhibition changes when the copolymer concentration changes. AA/PEGZG/SAS shows superior ability to influence $CaSO_4$ deposition with 95% inhibition at threshold dosage of 5 mg/L, whereas it is 80% and 68% for HEDP and PBTC at the same dosage. Also, nowadays HEDP and PBTC is not suitable for scale inhibition because it contains phosphorus in these structures.

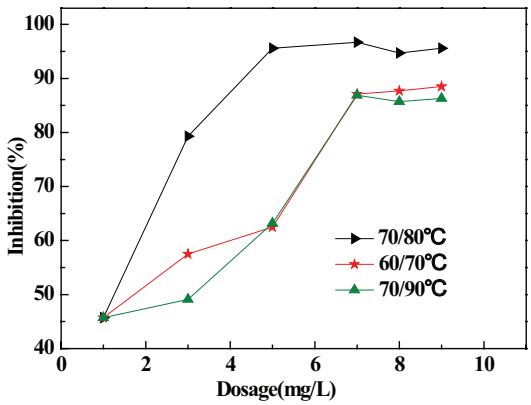

Fig. 5. Comparison of $CaSO_4$ inhibition between different titration and reaction temperature.

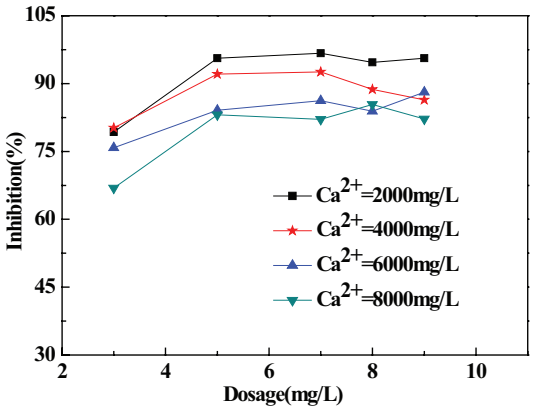

Fig. 6. AA/PEGZG/SAS inhibition at different dosage as a function of solution Ca^{2+} concentration.

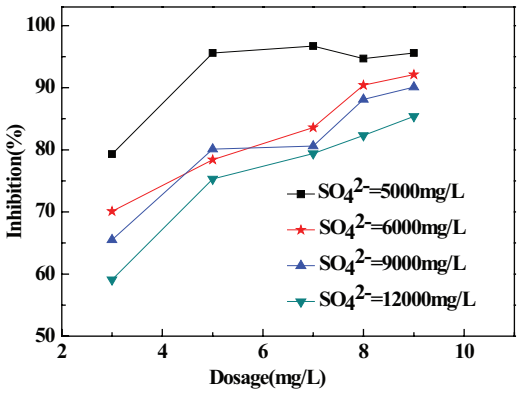

Fig. 7. AA/PEGZG/SAS inhibition at different dosage as a function of solution SO_4^{2-} concentration.

3.7. Simulate the pipeline of the circulating water system scale inhibitor process

In order to make the scale effect more intuitive, we use a colorimetric tube to simulate the pipeline of the circulating water system. The scale digital image is shown in Fig. 9.

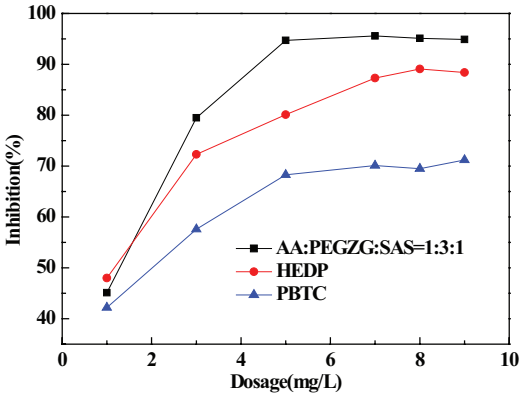

Fig. 8. Relationship between $CaSO_4$ scale inhibition efficiency in the presence of different inhibitor.

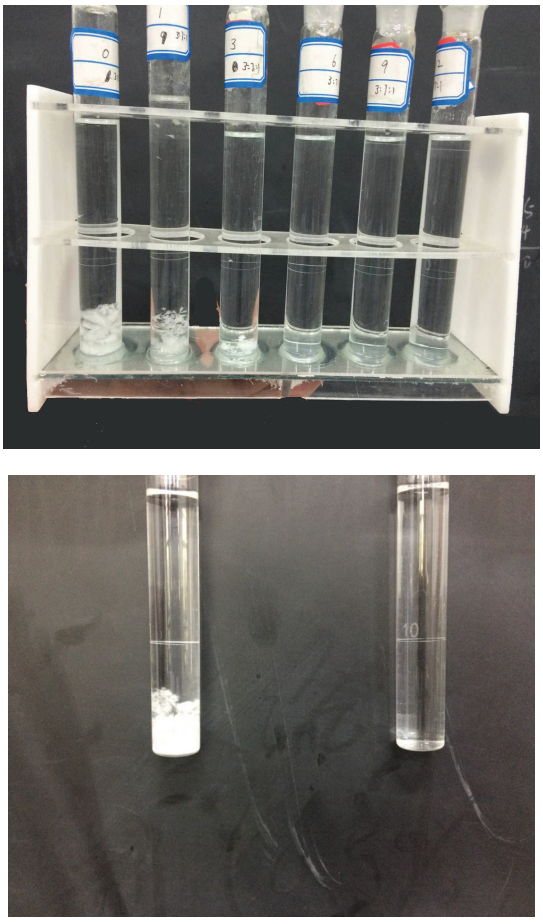

Fig. 9. Photographs for the $CaSO_4$ scale inhibition.

We can clearly see from Fig. 9 left with the dosage of scale inhibitor gradually increased that the colorimetric calcium sulfate disappeared, right and left in Fig. 9 is not added scale inhibitor. With the gradual production of calcium sulfate, these calcium sulfate scales will be deposited on the pipe surface, blocking the pipeline, and right in Fig. 9 added 4 mg/L scale inhibitor AA/PEGZG/SAS, you can find no calcium sulfate pipe scale production. Fig. 10 shows the SEM

images of the $CaSO_4$ crystals in the presence and absence of AA/PEGZG/SAS. Fig. 10 illustrates that in the absence of copolymer a regular with smooth surface shape is recognized (Fig. 10(a)), while that in the presence of different copolymer the $CaSO_4$ crystal appears large numbers of small defects and the size is reduced (Fig. 10(d)). These results indicate that the crystals of $CaSO_4$, with the increase of copolymer concentration, presents a messy state, formed are large and unstable crystal and therefore are more easy to be washed away by the running water.

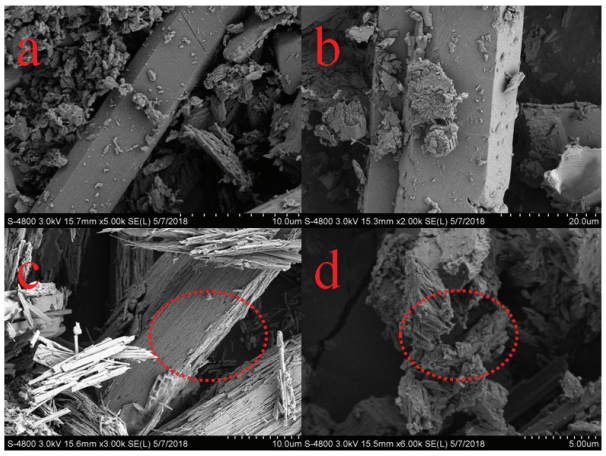

Fig. 10. SEM image of $CaSO_4$ with different concentration AA/PEGZG/SAS: (a) 0 mg/L; (b) 1 mg/L; (c) 3 mg/L; and (d) 5 mg/L.

3.8. Inhibition mechanism toward $CaSO_4$ scale

In order to explain that scale inhibitor AA/PEGZG/SAS has excellent scale inhibition. Fig. 11 simulates the mechanism explanation for scale inhibition.

Scale inhibitor AA/PEGZG/SAS contains a large number of hydrophilic groups PEG- and sulfonic acid group, which scale inhibitor AA/PEGZG/SAS has a large number of chelating calcium ion carboxyl, as shown in Fig. 11(a), when scale inhibitor AA/PEGZG/SAS added to the circulating cooling water, the circulating cooling water has a lot of free calcium ions, scale inhibitor AA/PEGZG/SAS contains a large number of carboxyl groups will chelate calcium ions in the cooling water, as shown in Fig. 11(b). As scale inhibitor AA/PEGZG/SAS is a linear polymer, when scale inhibitor AA/PEGZG/SAS is dissolved in circulating water, there is a large amount of random linear shape. When AA/PEGZG/SAS chelated to calcium ion becomes Ca^{2+}-AA/PEGZG/SAS macrocycle insoluble in circulating water, whereas a large number of water soluble sulfonic acid groups present in scale inhibitor AA/PEGZG/SAS may pack living water insoluble Ca^{2+}-AA/PEGZG/SAS large groups, the formation of a stable putamen structure (similar to the polymer self-assembly phenomenon), as shown in Fig. 11(c), a large number of soluble sulfonic acid groups and PEG groups can make the entire chelated large group dissolved in circulating water, through the chelating solubilization, reducing the presence of free calcium ions, circulating water sulfate ions difficult to combine with free calcium ions, thus avoiding the generation of inorganic salt calcium scale.

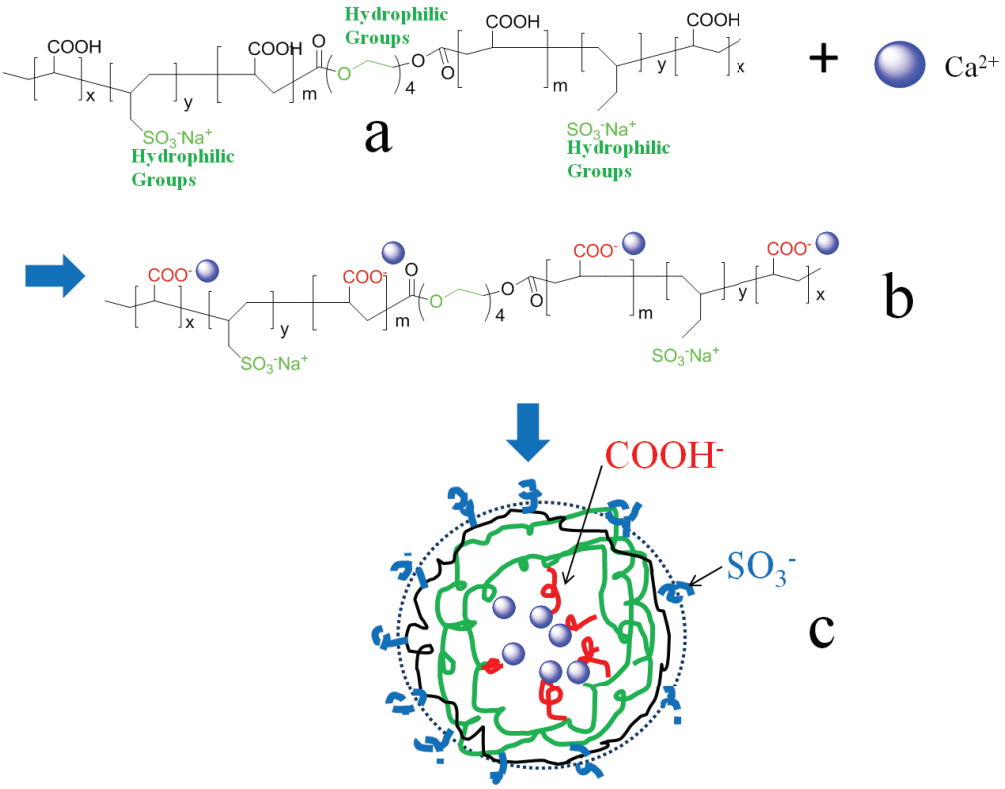

Fig. 11. Encapsulation calcium irons route via carboxyl groups.

4. Conclusion

In this paper, scale inhibitor AA/PEGZG/SAS was synthesized. The scale inhibitor does not contain phosphorus and nitrogen, and the optimum synthesis conditions for the scale inhibitor were AA:PEGZG:SAS = 1:3:1, the initiator is 6% of the total mass of the monomer, the dropping temperature and the reaction temperature are 70° and 80°, respectively. The infrared reaction shows that the monomer reaction is complete. When the dosage of the scale inhibitor is 5 mg/L, Calcium scaling rate of 95% or more, can be used in high hardness water environment, the scale inhibitor synthesis process is simple, non-phosphorus, is a kind of environmentally friendly industrial scale inhibitor.

Acknowledgments

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