Synthesis and properties of the IA/AMPS copolymer

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Abstract: Based on itaconic acid (IA) and 2-acrylamido-2-methyl propane sulfonic acid (AMPS) as raw material, the IA/AMPS copolymer was prepared. The scale inhibition of copolymer was studied under different experimental conditions. The optimum conditions of synthesis of IA/AMPS were obtained: the raw material quality ratio was IA:AMPS = 5:1; the addition amount of ammonium persulfate as the initiator was 5% of the total mass of the monomer; the polymerization temperature was 95°C; the time of epoxidation was 4 h. Under this condition, the scale inhibition rate on CaCO₃ was 100% when the IA/AMPS copolymer was 10 mg·L⁻¹. The scale inhibition rate on Ca₃(PO₄)₂ was 100% when the IA/AMPS copolymer was 30 mg·L⁻¹. The light transmittance of the supernatant after the dispersion of Fe₂O₃ was 25%, indicating that the copolymer obtained under this experimental condition has good scale inhibition and dispersion performance.

1. Introduction

At present, in the field of water treatment, the scaling phenomenon of water system is usually alleviated by adding scale inhibitor. The scale inhibitor is mainly divided into inorganic salt, organic compound, natural polymer and synthetic polymer. Inorganic salts and organic phosphine compounds have been rarely used because they can easily promote the reproduction of algae and eutrophication in the system[1]. Although the natural polymer is cheap and easy to obtain, but its scale inhibition effect is poor, and its impurity content is high. Therefore, synthetic macromolecule scale inhibitors with low phosphorus and environmental protection have been paid more and more attention. For example, synthetic organic polymers such as poly (acrylic acid), poly (methacrylic acid) and other non-phosphorus scale inhibitors, single functional group leads to limited processing ability, so binary terpolymer scale inhibitor is produced[2]. This kind of copolymer contains many kinds of scale inhibition functional groups, such as carboxyl group, hydroxyl group, sulfonic acid group, amino group and so on. The combination of different groups can not only prevent the weak hydrophilic groups from forming insoluble calcium gel, but also help to dissolve and prevent scale effectively[3-5].

Itaconic acid is an unsaturated dicarboxylic acid[6]. At present, starch fermentation is widely used at home and abroad. With the maturity of fermentation technology, the production cost of itaconic acid becomes lower and lower, which makes the use of itaconic acid more common. In the molecule of itaconic acid, not only the functional group of carbon double bond required by free radical
polymerization is contained, but also a carboxylic acid group is attached on both sides of the double bond, which endow the copolymer with excellent negative dispersion performance and the ability of complexation with other ions. In order to achieve efficient scale inhibition effect, it is not enough to only contain carboxylic groups, so carboxylic acid type polymer scale inhibitor is modified with sulfonic acid groups, and the combination of different acidic groups can effectively prevent the formation of calcium gel[7-9].

In this paper, under the premise of not affecting the biodegradability of itaconic acid, it is proposed to introduce 2-acrylamido-2-methylpropane sulfonic acid (AMPS) containing sulfonic acid groups with itaconic acid (IA) as the main raw material. The IA/AMPS copolymer was prepared and the properties of the copolymer were investigated.

2. Material and Methods

2.1. Main reagents and instruments
Itaconic acid (IA), 2-acrylamido-2-methylpropane sulfonic acid (AMPS), hydrogen peroxide (mass fraction of 30%), ammonium persulfate, sodium hydrogen sulfite, calcium chloride hexahydrate, etc., all of which are of analytical grade.

HH-S8 electric heating constant temperature water bath, Beijing Kewei Yongxing Instrument Co., Ltd.; TU-1900 double beam UV-visible spectrophotometer, Beijing Pu Analysis General Instrument Co., Ltd.; 724 visible spectrophotometer, Shanghai Optical Instrument Factory; BSA423S-CW type electronic balance, Sartorius Scientific Instruments (Beijing) Co., Ltd.; JB-3A type timing constant temperature magnetic stirrer, Shanghai Lei Magnetic Xinyi Instrument Co., Ltd., etc.

2.2. Synthesis of IA/AMPS copolymer
A certain amount of itaconic acid (IA) and 2-acrylamido-2-methylpropanesulfonic acid (AMPS) were added into a four-necked flask equipped with a condenser and a thermometer, and then deionized water, ammonium persulfate and isopropanol were added. Then put the flask into the magnetic stirrer with water bath to heat the flask at a constant temperature. After the liquid temperature reached the set value in four bottles, two injection pumps were used to drop sodium bisulfite solution and hydrogen peroxide. Make sure that both of them were added at the same time within a certain period of time. Then the polymerization continued at constant temperature for some time. When the solution dropped to room temperature, the liquid was discharged and the light yellow transparent liquid was the water solution of the polymer.

2.3. Measurement of performance of the IA/AMPS copolymer

2.3.1. Measurement of the rate of static scale inhibition on CaCO₃
Water sample used in the experiment was confecting water (C(Ca²⁺)=600mg·L⁻¹, C(HCO₃⁻)=1200mg·L⁻¹). 500mL confecting water with an amount of pharmacy was heated to 80°C and then kept 80°C for 10 hours. Using EDTA titration to detect the content of calcium ion in the cooling and filtrating water.

2.3.2. Measurement of the rate of static scale inhibition on Ca₃(PO₄)₂
Water sample used in the experiment was confecting water (C(Ca²⁺)=250mg·L⁻¹, C(PO₄³⁻)=150mg·L⁻¹, pH=9.0(regulated by 25g·L⁻¹ sodium borate solution)). 500mL confecting water with an amount of pharmacy was heated to 80°C and then kept 80°C for 10 hours. The content of PO₄³⁻ in the cooling and filtrating water was determined by 721 spectrophotometer.

2.3.3. Calculation of scale inhibition
The rate of scale inhibition is calculated by equation 1.
Rate of scale inhibition = \( \frac{C_1 - C_0}{C_2 - C_0} \times 100\% \)  \( (1) \)

Equation 1. Calculation of the scale inhibition rate

Where \( C_0, C_1 \) and \( C_2 \) represent the mass concentrations of \( \text{Ca}^{2+} \) or \( \text{PO}_4^{3-} \) in the blank water sample after heated, the water sample with the inhibitor after heated and the blank water sample before heated, respectively.

2.3.4. Determination of dispersibility on \( \text{Fe}_2\text{O}_3 \)

Water sample was confecting water (\( C(\text{Ca}^{2+})=150\text{mg} \cdot \text{L}^{-1}, C(\text{Fe}^{2+})=10\text{mg} \cdot \text{L}^{-1}, \text{pH}=9.0 \) (regulated by sodium borate solution)). 500mL confecting water with an amount of pharmacy was heated to 50\(^\circ\)C and then kept 50\(^\circ\)C for 5 hours. After cooling to room temperature, the upper layer solution was taken and the transmittance was measured by 724 type visible spectrophotometer under 450nm. The smaller the transmittance is, the better the dispersion effect is (100\% light transmittance is 100\% with distilled water as reference).

3. Results and discussions

The properties of IA/AMPS copolymer against calcium carbonate were tested under different conditions, and the optimum synthesis conditions of the copolymer were obtained.

3.1. The effect of mass ratio of IA and AMPS on the properties of IA/AMPS copolymer

Fixed the initiator of ammonium persulfate as monomer for the amount of 5\% of the total quality, then the polymerization temperature was 95\(^\circ\)C and the copolymerization time was 4 h. The resistance on \( \text{CaCO}_3 \) of copolymer was tested by changing the mass ratio of raw materials. The results are shown in figure 1.

![Figure 1. The relationship between the mass ratio and the scale inhibition performance on \( \text{CaCO}_3 \) when the dosage was 10mg/L](image)

From figure 1 above, it can be seen that with the increase of the ratio of amps, the scale inhibition performance on \( \text{CaCO}_3 \) of the copolymers decreases, while that of \( \text{Ca}_3(\text{PO}_4)_2 \) and dispersed \( \text{Fe}_2\text{O}_3 \) increases, and when the mass ratio of the IA to AMPS is 5, the scale inhibition and dispersion property can reach the best. It is shown that the addition of sulfonic acid group can improve the performance of inhibiting \( \text{Ca}_3(\text{PO}_4)_2 \) and dispersing \( \text{Fe}_2\text{O}_3 \), but reduce the ability of inhibiting \( \text{CaCO}_3 \) to some extent. Therefore, the proportion of AMPS should not be too large. When the mass ratio IA:AMPS is 5, the comprehensive performance of the copolymer can reach the best.
3.2. The effect of the addition quality of the initiator ammonium persulfate on the properties of IA/AMPS copolymer

Fixed material quality IA: AMPS=5:1, then the polymerization temperature was 95 ℃ and the copolymerization time was 4 h. When the scale inhibitor was added at 10 mg/L, the resistance on CaCO₃ of copolymer was tested by changing the amount of ammonium persulfate as the initiator. The results are shown in figure 2.

![Figure 2](image)

As can be seen from figure 2, when the amount of initiator is 1% to 5% of the total mass of monomer, with the increase of the amount of initiator, the scale inhibition performance of copolymer shows an obvious upward trend. When the amount of initiator is more than 5%, the amount of initiator has no effect on the properties of copolymer. Therefore, the amount of initiator is selected as 5% of the total mass of raw materials.

3.3. The effect of polymerization temperature on the properties of IA/AMPS copolymer

When the mass ratio of the fixed raw materials was IA:AMPS= 5:1, and the addition amount of initiator was 5% of the total mass of monomer, the influence of polymerization temperature on the resistance of the copolymer to calcium carbonate is shown in figure 3. At this time, the copolymerization time is 4h and the addition amount of scale inhibitor is 10mg/L.

![Figure 3](image)

As can be seen from figure 3, when the polymerization temperature is between 60℃ and 100℃, the scale inhibition performance of copolymer shows an obvious upward trend. Therefore, the polymerization temperature is selected as 90℃.
From figure 3, when the temperature is less than 95℃, the scale inhibition rate of the copolymer on CaCO₃ increases gradually with the increase of reaction temperature, and the scale inhibition rate of the product reaches 100% at 95℃. Therefore, the selected polymerization temperature is 95℃.

3.4. The effect of polymerization temperature on the properties of IA/AMPS copolymer
When the mass ratio of the fixed raw materials was IA:AMPS=5:1, and the addition amount of initiator was 5% of the total mass of monomer. The influence of polymerization time on the resistance of the copolymer to calcium carbonate is shown in figure 4. At this time, the copolymerization temperature was 95℃ and the addition amount of scale inhibitor was 10mg/L.

![Graph showing the relationship between polymerization time and scale inhibition rate](image)

Figure 4. The relationship between polymerization temperature on the scale inhibition performance on CaCO₃ when the dosage was 10mg/L

As shown in figure 4, with the prolongation of polymerization time, the scale inhibition performance of copolymer on CaCO₃ first becomes better and then worse, and the scale inhibition performance is the best at reaction time of 4 hours. This is because with the increase of polymerization time, the higher the monomer conversion rate is, and the higher the degree of polymerization is. At this time, the number of functional groups such as carboxyl, amide group and sulfonic acid group in the synthesized copolymer is more, and the effect of inhibiting calcium carbonate scale is better. However, if the reaction time is too long, the polymer molecular chain will be larger, which will affect its complexation with metal ions. Thus, the ability of the copolymer to complex calcium ions is reduced, and the scale inhibition rate is reduced. Therefore, the polymerization reaction time was determined to be 4h, and the scale inhibition rate of the polymer could reach 100%.

4. Conclusion
According to the experimental results, the optimum synthesis conditions of the polymer can be obtained: the raw material mass ratio is IA:AMPS=5:1; the addition amount of ammonium persulfate as the initiator is 5% of the total mass of the monomer; polymerization temperature is 95℃; the copolymerization time is 4h. Under this condition, the scale inhibition rate on CaCO₃ of the polymer could reach 100% when the dosage was 10mg/L; when the dosage was 30mg/L, the scale inhibition on Ca₃(PO₄)₂ was 100%, and the light transmittance of the supernatant after the dispersion of iron oxide was 25%. It is shown that the copolymer has good scale inhibition performance for CaCO₃ and Ca₃(PO₄)₂ under the condition of the experiment, and has good dispersion property to the iron oxide.

References
[1] H. Shao, Y. Wang, Y. Zhou, YX. Leng, J. Zhong, Preparation and inhibition performance of IA-HEPC copolymer scale inhibition, Acta Petrolei Sinica(Petroleum Processing
[2] N. N. Lin, Z. L. Nie, Y. M. Wu, Study on scale inhibition of IA-SSS-MA terpolymer, Science Technology and Engineering, 9(11):3134-3137, 2009

[3] W. X. Zhang, J. T. Chen, H. Li, Study on Synthesis of Sulphonate-containing Copolymer and Its Scale Inhibition Performance, Corrosion Research, 25(3): 36-39, 2011

[4] A. Q. Zhang, G. H. Zhang, H. Wei, L. J. Liu, Preparation and performance of a new sulfonate copolymer scale inhibitor, Chemical Industry and Engineering Progress, 30(8): 1858-1861, 2011

[5] Z. C. Han, P. Li, S. L. Li, F. Li, Research on the synthesis of IA/MA/AMPS terpolymer scale inhibitor, Applied Chemical Industry, 44(2): 268-270+272, 2015

[6] W. Wu, H. Sun, A. S. Li, P. P. Liu, X. Y. Zhang, Synthesis of AA-SAS-IA terpolymer and evaluation of its scale inhibitive property, Applied Chemical Industry, 45(9): 1611-1618, 2016

[7] Y. M. Song, Progress on the development and application of green scale inhibitor, Industrial Water Treatment, 25(9): 9-12, 2005

[8] P. Li, Z. C. Han, S. L. Li, F. Li. Research on the synthesis of scale inhibitor copolymer IA/MA/MAA/AMPS and its scale inhibition capacity, Industrial Water Treatment, 35(7): 47-50, 2015

[9] L. Meng, Synthesis and scale inhibition performance of IA/ASP/AMPS terpolymer, Chemical Research and Application, 30(9): 1487-1492, 2018