



Copolymer of citric acid and glutamic acid as calcium scale inhibitor

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ABSTRACT

Poly(citric acid-co-glutamic acid) (PCA-GLU) was prepared successfully by using citric acid and glutamic acid as monomers. The synthesized polymers were characterized by Fourier-transform infrared spectroscopy and size exclusion chromatography. The static scale inhibition method was utilized to test the performance of PCA-GLU. The polymerization conditions, such as reaction time, reaction temperature, catalyst dosage, and monomer ratio, were optimized to gain the high-performance scale inhibitor. The scale inhibition rate exceeded 95% in simulated CaSO_4 fouling solution which initially contained $3,000 \text{ mg L}^{-1} \text{ Ca}^{2+}$ and SO_4^{2-} ions when the dosage of the optimized polymer scale inhibitor was 10 mg L^{-1} . The results of calcium ion titration experiments in static scale inhibition experiments showed that PCA-GLU can chelate with Ca^{2+} ions, increase the content of Ca^{2+} ions stayed in simulated water and reduce the amount of deposition of CaSO_4 scale. The CaSO_4 scale collected from the simulated water was observed by scanning electron microscopy and characterized by X-ray diffraction. PCA-GLU significantly inhibited the crystal growth of CaSO_4 and distorted the lattice of the crystal. Therefore, PCA-GLU is a potent inhibitor of a highly-effective green CaSO_4 scale.

Keywords: Citric acid; Glutamic acid; Scale inhibitor; Calcium sulfate

1. Introduction

Systems of the oilfield water injection and recycle cooling water have a common problem that scaling brings many adverse effects on production [1,2], which results in blockage of the good pipeline, consumption of energy, and even severely damage of equipment. The ordinary scales in oil field water include calcium carbonate scale, barium sulfate scale, calcium phosphate scale, calcium sulfate scale, iron oxide scale, ferrous carbonate scale, ferrous oxide scale, iron hydroxide scale, and iron hydroxide scale [3]. Adding scale inhibitors is a simple and effective way to reduce scale

deposition [4]. Scale inhibitor tends to prevent the deposition of scale-forming material from the water onto the metal surface of the industrial water system equipment [5,6].

In recent years, non-toxic, harmless, biodegradable, and environmental-friendly scale inhibitors have been investigated widely since the increasing shortage of water resources and the growing awareness of environmental protection. Green chemistry [7–10] has been proposed and become the basic requirement of water treatment regents synthesis [11]. Therefore, it is imperative to research and develop cheap and efficient environmental-friendly scale inhibitors.

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Citric acid is an essential organic acid and is widely used in the food industry [12]. It is a cheap and environmentally friendly substance. We have prepared poly(citric acid) used as a scale inhibitor for calcium sulfate [13], and it is a prospective green industrial water treatment agent [14]. But the synthesis method of poly(citric acid) is needed to be improved and developed. Poly(aspartic acid) is an excellent scale inhibitor for all kinds of calcium scale, but it is expensive [15]. Glutamic acid is one kind of natural amino acid and its structure is similar to aspartic acid. Glutamate can react with citric acid to form amide groups, meanwhile glutamic acid is a common cheap food additive in Japan and China.

In this paper, poly(citric acid-co-glutamic acid) (PCA-GLU) was prepared by thermal polycondensation. Glutamic acid was used to copolymerize with citric acid to improve the synthesis method and enhance the performance of the citric acid polymer. The synthesized copolymer PCA-GLU was characterized by Fourier-transform infrared spectroscopy (FTIR) spectrometer and size exclusion chromatography (SEC). The inhibition effect of PCA-GLU against CaSO_4 deposition was measured by a static scale inhibition test method. Morphology of scale was observed by scanning electron microscopy (SEM) and the crystal structure of the scale was characterized by X-ray Diffractometer (XRD).

2. Experimental

2.1. Reagents and Materials

L-glutamic acid (GLU), N,N-dimethylformamide (DMF), citric acid (CA) and other chemicals used were the analytically pure grade and used directly without further purification.

2.2. Synthesis of PCA-GLU

The process of typical synthesis is: citric acid and glutamic acid were placed in a round-bottom flask in a molar ratio of 1:1, and dissolved in 10 mL DMF. For the synthesis, concentrated sulphuric acid was used and the reaction solution was heated to 180°C with stirring. The mixture reacted at this temperature for 1 h until the reaction mixture became a brown viscous solution. After cooling to room temperature, the pH of the reaction solution was adjusted to neutral by dropping 1 mol L⁻¹ NaOH. Then it was transferred to a regenerated cellulose dialysis bag to retain the product with a molecular weight greater than 1,000 and dialyzed for 24 h to remove small molecules with changing bathwater per 4 h. Brown PCA-GLU was obtained after solvent (water) evaporation and dried in a vacuum for 24 h.

2.3. Characterization methods

The prepared polymer is characterized on spectrum two FTIR spectrometer (PerkinElmer Instrument Co. Ltd., Waltham, MA, USA) by the attenuated total reflection method. The samples were directly determined after being dried in a vacuum for 24 h.

The molecular weight of polymers was determined by Agilent 1260 SEC (Agilent Technologies Co. Inc., Santa Clara, CA, USA). The flowing solvent is ultra-pure water and the flowing rate is 1.0 mL min⁻¹. The standard sample is polyethylene glycol.

Thermogravimetric analysis (TGA) was carried out using a thermal gravimetric to check the products' stability. The temperature range for testing was 25°C–600°C and the whole process was carried out in a nitrogen atmosphere. The temperature rising rate was 10°C min⁻¹.

2.4. Inhibition performance of PCA-GLU against CaSO_4 scale testing

Static experiments were performed as described in Q/SY126-2014 (China) [16]. CaCl_2 solution and Na_2SO_4 solution with or without scale inhibitor PCA-GLU were put into 100 mL volumetric flasks. Briefly, an aqueous solution containing 3,000 mg L⁻¹ Ca^{2+} and SO_4^{2-} ion was prepared in a volumetric flask (capacity 100 mL). The flasks were then immersed in a water bath for 10 h at 80°C. After being cooled to room temperature, the scale solution was filtered through a 0.22 μm filter paper. Then adjust the pH of the solution by using Ammonia-ammonium chloride buffer solution, and the Ca^{2+} concentration in the filtrate was measured by ethylenediaminetetraacetic (EDTA) titration. The scale inhibition ratio can be calculated by the following formula:

$$\eta = \frac{(V_1 - V_2)}{(V_0 - V_2)} \quad (1)$$

where V_0 is the volume of EDTA standard solution used to titrate the Ca^{2+} ion in the solution without a scale inhibitor and being heated in the water bath. V_1 is the volume of EDTA solution used to titrate the Ca^{2+} ion in the solution containing a scale inhibitor and heated in the water bath, and V_2 is the volume of EDTA standard solution used to titrate the Ca^{2+} ion in the solution without a scale inhibitor and being heated in the water bath.

2.5. Characterization by SEM

SEM images were recorded using a field emission scanning electron microscope SU 150 (SITP) Hitachi Co. Ltd., Tokyo, Japan. Imaged by SEM before, the samples were sputtered with a thin layer of gold.

2.6. Characterization by XRD

The crystallographic measurement was studied through Bruker Co. Ltd., (Karlsruhe, Germany) D8 Advance powder X-ray diffractometer (made in Germany), using graphite monochromatized Cu Kα radiation XRD ($\lambda = 0.1546$ nm), and the data was collected from 5 to 90 with a scanning rate of 1 per min and analyzed with jade6.5 standard card.

3. Results and discussion

3.1. Synthesis of PCA-GLU

There are three carboxylic groups and one hydroxyl group on each citric acid molecule. The glutamic acid molecule has a similar chemical structure. That is, there are two carboxylic groups and one amino group. The condensation reaction occurred between the carboxylic group and the hydroxyl group or between the carboxylic group and

amino-group on the different citric acid molecules or glutamic acid molecules. So the polymer PCA-GLU prepared by citric acid and glutamic acid could be obtained. Fig. 1 shows the possible polymerization principle and PCA-GLU structure fragments. The polymer is not only line-typed as shown in Fig. 1 but also is possibly branched since there are multiple carboxylic groups suspended on the polymer which could continue to esterify and amidated with other citric acid or glutamic acid molecule. Anyhow, there are many carboxylic, ester and amide groups in PCA-GLU polymer molecules.

The FTIR spectrum of the citric acid, glutamic acid, and PCA-GLU copolymer could illustrate that the polymerization was carried on successfully (Fig. 2). Depending on the curve of the GLU infrared (IR) spectrum, the absorption peak appearing at $3,027\text{ cm}^{-1}$ is the frequently doubled and combined vibration peak of NH_2 . The IR absorption peak of $-\text{COOH}$ is at $1,798$ and $1,640\text{ cm}^{-1}$ (Fig. 2a). The three carboxyl groups on the citric acid monomer molecule are not similar. They are at $1,755$, $1,730$, and $1,681\text{ cm}^{-1}$ respectively (Fig. 2b). For polymer PCA-GLU, $3,364\text{ cm}^{-1}$ (Fig. 2c) is the N-H stretching vibration absorption peak of the secondary amide. $1,697\text{ cm}^{-1}$ (Fig. 2c) is the stretching vibrational absorption peak of C=O of amide and C=O in the carboxylic group. The broad resonance peak of $1,377\text{ cm}^{-1}$ C-O-C group illustrates an ester carbonyl group by condensation. It is a polymerization between a carboxylic group and a hydroxyl group.

The product of polymerization was measured by SEC. The weight-average molecular weight (M_w) of PCA-GLU was $4.675 \times 10^3\text{ g mol}^{-1}$, and the number-average molecular weight (M_n) was $3.746 \times 10^3\text{ g mol}^{-1}$. The polydispersity coefficient of the polymer was 1.25. So the efflux curve was narrow.

The products' stability was checked by TGA. As shown in Fig. 3, when the temperature was lower than 200°C , the polymer and GLU were much stabler than CA. Meanwhile, the temperature we used in this work was 80°C . Therefore, the stability of PCA-GLU was good enough.

3.2. Effect of preparation conditions on scale inhibition performance

The test result of the static scale inhibition method indicates that the product of polymerization PCA-GLU is a scale

inhibitor. The polycondensation condition was optimized to gain the polymer with highly-effective scale inhibition performance.

3.2.1. Polymerization time

The reaction time was set at 30 min to 5 h (30 min, 1, 2, 3, 4, and 5 h). In this work, 30 min was first chosen as the reaction time. But the polymer product was too little to be separated. So 1 h was chosen as the minimum reaction time. Polymer product PCA-GLU had the best CaSO_4 scale inhibition performance when the reaction time was 1 h (Fig. 4), which exceeded 95%. The main polycondensation reaction was reversible. Water was continuously generated during the reaction, and the reactants were all hydrophilic substances. Therefore, it is difficult to remove the water, which will prevent the reaction from progressing. At the same time, if the

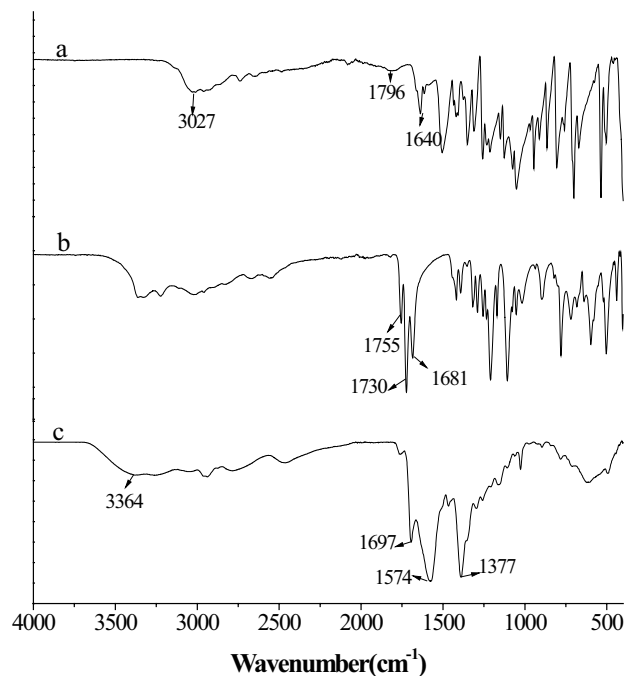


Fig. 2. FTIR spectra of (a) GLU, (b) CA, and (c) PCA-GLU.

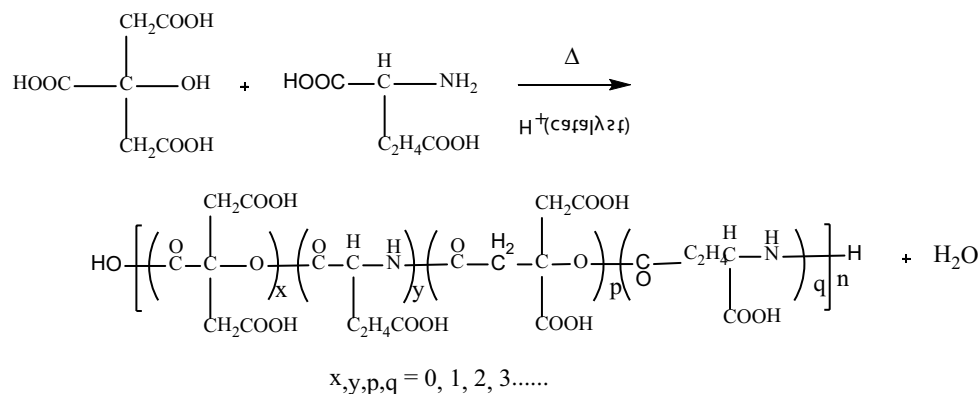


Fig. 1. Possible synthesis of PCA-GLU.

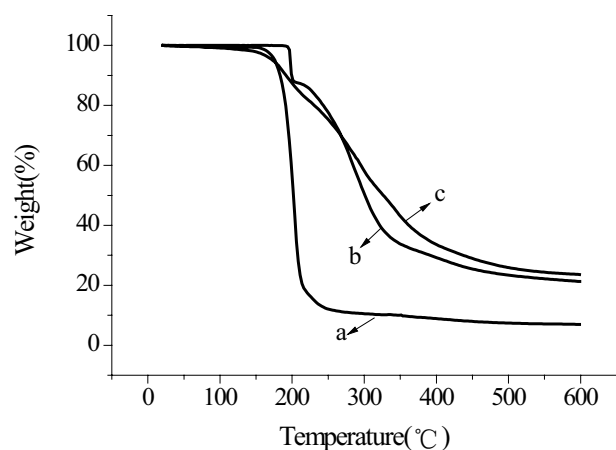


Fig. 3. Stability analysis of (a) CA, (b) GLU, and (c) PCA-GLU.

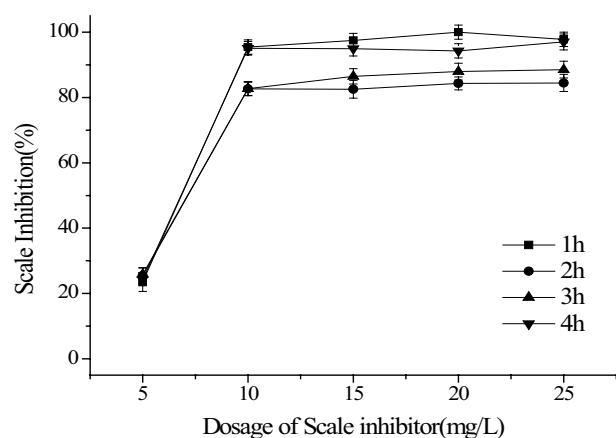


Fig. 4. Performance of PCA-GLU on calcium sulfate scale affected by different polymerization times.

reaction time is already too long, and the degree of polymerization of PCA-GLU is too deep, the water-solubility of the scale inhibitor is deteriorated and functional groups are encapsulated. Besides, if the reaction time is too long, the probability of side reactions (such as carbonization reaction [17,18]) occurrence will increase. So the optimized synthesis time is 1 h.

3.2.2. Reaction temperatures

The reaction temperature ranged from 110°C to 190°C (110°C, 120°C, 140°C, 160°C, 180°C, and 190°C). According to the static scale inhibition test results (shown in Fig. 5), when the reaction temperature is 180°C, PCA-GLU has the best inhibitory effect on calcium sulfate scale. As the temperature increases, the monomer conversion also increases. According to the thermodynamic point of view, when the reaction temperature is higher than 100°C, the reaction enthalpy of the esterification reaction is greater than 0 kJ mol⁻¹, indicating that the reaction is endothermic, the elevated temperature will facilitate the progress of the reaction. In this case, the elevated temperature will facilitate the progress of the reaction [19]. When the reaction temperature is higher than 180°C,

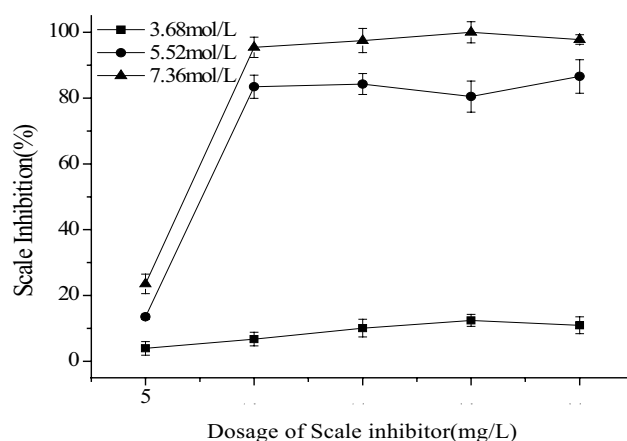


Fig. 5. Performance of PCA-GLU on calcium sulfate scale affected by polymerization temperatures.

the carbonization reaction is observed, and the phenomenon is more and more serious with the rise of temperature. Therefore, the reaction at 180°C for 1 h is most beneficial to the synthesis of the polymer.

3.2.3. Dosage of catalyst

The concentration of catalyst used ranged from 1.84 to 9.20 mol L⁻¹ (1.84, 3.68, 5.52, 7.36, and 9.20 mol L⁻¹). The dosage of catalyst affected the polymer PCA-GLU scale inhibition performance (Fig. 6). When the amount of catalyst was 7.36 mol L⁻¹, the effect of PCA-GLU on calcium sulfate was the best, reaching 95.45% (the usage of scale inhibitor is 10 mg L⁻¹). Depending on the theory of polymerization [20], when the amount of catalyst used is too low (1.84 mol L⁻¹), the esterification and amidation reactions are not sufficiently promoted, and the yield of the reaction is lowered. With the increase of the amount of catalyst, the copolymerization reaction between CA and GLU will be accelerated. However, when the dosage of the catalyst increases to 9.2 mol L⁻¹, side reactions, such as dehydration and carbonization, will increase. Therefore, the usage of a catalyst is optimized to be 7.36 mol L⁻¹.

3.2.4. Monomer molar ratios and different dosage

The different original monomer molar ratio (CA to GLU are 1:0, 2:1, 1:1, 1:2, and 0:1, respectively) of the scale inhibitors greatly influenced the performance of PCA-GLU. It can be seen from Fig. 7. When the molar ratio is 1:1, the scale inhibition performance is the best among the five polymer products. Also, scale inhibition efficiency of calcium sulfate can reach 95% when the polymer inhibitor dosage is more than 10 mg L⁻¹. According to the polycondensation mechanism mentioned above, the reaction is mainly carried out by -NH₂ and -OH with -COOH groups. Poly(citric acid) and poly (glutamic acid) were obtained by citric acid and glutamic acid homo polymerization condensation respectively. Except containing carboxyl groups, poly(citric acid) or poly(glutamic acid) with the individual ester groups or amide groups possess less scale inhibition performance. The scale inhibition efficiency is all less than 20% (monomer

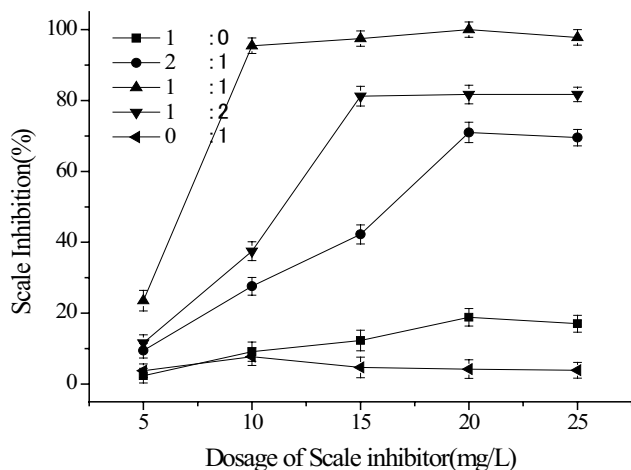


Fig. 6. Performance of PCA-GLU on calcium sulfate scale affected by different catalyst amounts.

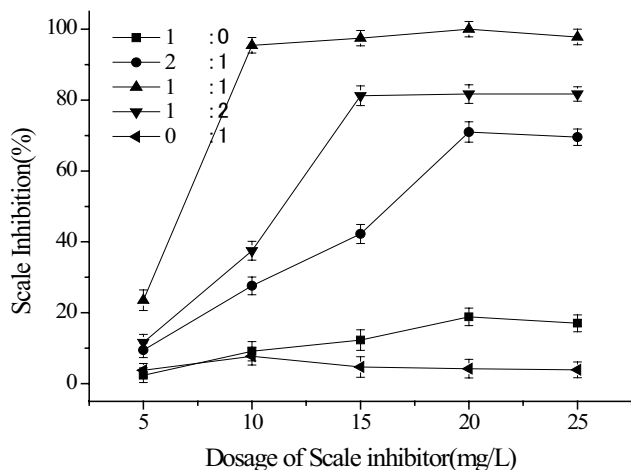


Fig. 7. Effect of PCA-GLU molar ratio on calcium sulfate scale inhibition.

molar ratio of 1:0 and 0:1 in Fig. 6, respectively). But the synergistic effect of ester groups and amide groups on a polymer molecule is beneficial to improve scale inhibition (monomer molar ratio of 1:2, 1:1 and 2:1 in Fig. 6, respectively).

3.3. Scale inhibition performance of optimized PCA-GLU and commercial-scale inhibitors

The effect of the most relevant variables of the process, such as reaction time, reaction temperature, amount of catalyst and the molar ratio between CA and GLU, has been analyzed at 3.2. For changes in reaction time, even though this is an effect we have studied in this article, the final scale inhibition efficiency does not follow an endothermic behavior as expected. Changes in the reaction temperature showed a stronger influence than on reaction time. The results showed that the final efficiency grew as the temperature increased. A variation on the amount catalyst showed a great effect on the reaction when more catalyst was added to the reaction, the higher efficiency was

obtained. Last, variations on the molar ratio showed that when the monomer molar ratio was 1:1, synthesized polymer had the best performance of scale inhibition. So the optimal synthesis reaction conditions are that the monomer molar ratio is 1:1, the catalyst dosage is 7.36 mol L^{-1} , the reaction temperature is 180°C and the reaction time is 1 h. The scale inhibition effect of synthetic PCA-GLU on calcium sulfate is significantly better than that of commercial-scale inhibitors, such as Poly(aspartic acid) (PASP) and Polyepoxysuccinic acid (PESA) (Fig. 8). Additionally, the citric acid monomer has a poor scale inhibition effect on calcium sulfate, which confirms that the polymerization is meaningful for improving the performance of scale inhibition.

3.4. Analysis of calcium sulfate scale

3.4.1. Morphology of calcium sulfate scale

Calcium sulfate dehydrate $\text{CaSO}_4(\text{H}_2\text{O})_2$ scales were obtained in the static scale inhibition tests that were all performed at 80°C since the crystal form of the calcium sulfate scale precipitated from the solution is greatly affected by fouling temperature [21], and calcium sulfate dihydrate $\text{CaSO}_4(\text{H}_2\text{O})_2$ is mainly precipitated when the temperature of the solution is between 25°C to 100°C [22].

The surface morphology of calcium sulfate scales collected from the static test solution was observed by an SEM. The morphology of the calcium sulfate scale obtained from the blank test solution is a slim prism shape with a smooth surface shown in Fig. 9a. However, the calcium sulfate scales imaged in Figs. 9b and c are short-thick prism shape with obvious defects (b) or irregular fragments (c), which were obtained from the test solution with different scale inhibitor dosages, 2 mg L^{-1} (b) and 10 mg L^{-1} (c), respectively. When the scale inhibitor PCA-GLU exists in the system, calcium sulfate crystals will have an uneven surface and become loose. Although there is still a prism shape, the surface has been destroyed, with holes appearing (Fig. 9b). When the scale inhibitor dosage reached 10 mg L^{-1} (Fig. 9c), the scale morphology was already flower-like. This phenomenon is because the active groups of the scale inhibitor

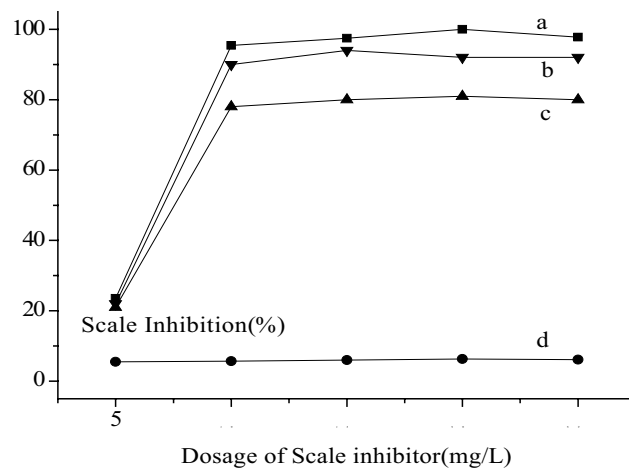


Fig. 8. CaSO_4 scale inhibition performance of (a) PCA-GLU, (b) PASP, (c) PESA, and (d) CA.

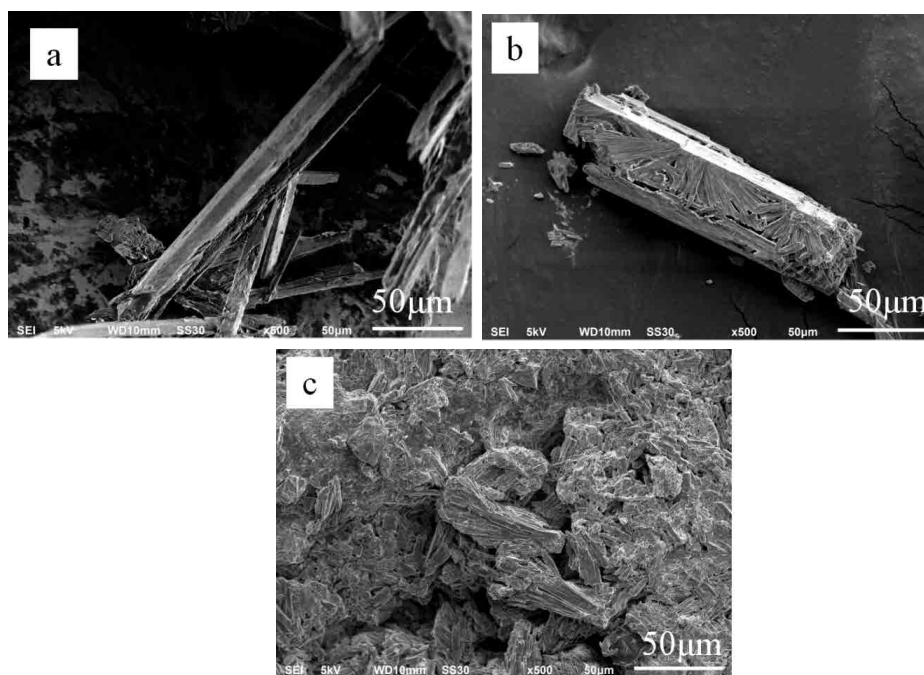


Fig. 9. Morphography of calcium sulfate scale obtained from blank solution (a), 2 mg L⁻¹ (b) and 10 mg L⁻¹ (c) PCA-GLU polymer inhibitions.

are mainly carboxyl groups and amide groups, which can chelate with calcium ions in water and adsorb to the scale crystal surface during scale formation [23]. On the one hand, the crystallites carry the same kind of charge under the action of scale inhibitor, which repels each other to prevent the formation of crystal nuclei and reduce the growth rate of crystals. On the other hand, the inhibitor can cause the scale to be distorted and make it unable to form normally. The scale inhibitor PCA-GLU has a significant influence on the growth process of the calcium sulfate crystals and leads to morphological distortion [24].

3.4.2. XRD of calcium sulfate scale

To further illustrate the form distortion of the calcium sulfate scale crystal under the effect of PCA-GLU, the calcium sulfate scale was characterized by XRD (Fig. 10). Figs. 10a–c shows the diffraction pattern of calcium sulfate scale obtained from static test solutions with 0, 2, and 10 mg L⁻¹ scale inhibitor PCA-GLU respectively. According to a standard card, the XRD pattern shows that calcium sulfate scale without scale inhibitor is calcium sulfate hydrate, with the significant lattice plane, (100), (301), (400) and (–141). The scale with a 2 mg L⁻¹ scale inhibitor is composed of gypsum, syn. The primary lattice planes are (020), (–121), (040), (–141) and (002). After the addition of 10 mg L⁻¹ scale inhibitor, the crystal form is anhydrite, syn. The major lattice planes are (100), (110), (200), (102), (300) and (212). The scale crystal lattice varies with the concentration of the anti-scaling agent. The intensity of the diffraction peak weakened, which indicates that the scale crystal regularity is deteriorated. In summary, the addition of PCA-GLU is not only the external appearance of calcium sulfate scale but also changes the crystal form.

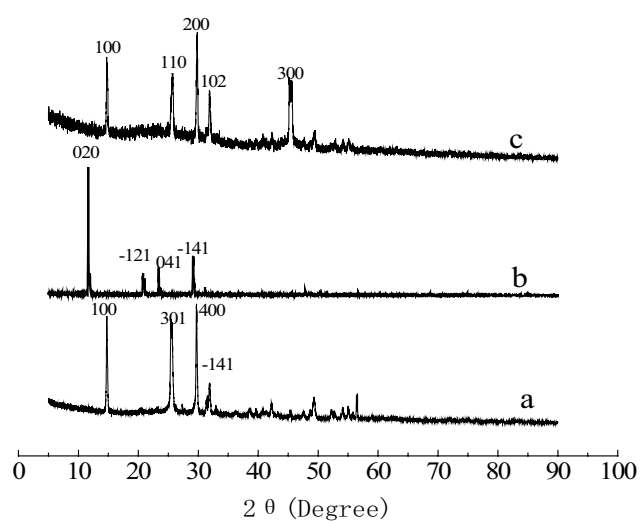


Fig. 10. XRD of calcium sulfate scale crystals obtained from blank solution (a), solutions with 2 mg L⁻¹ (b) and 10 mg L⁻¹ (c) PCA-GLU polymer inhibitors.

3.4.3. FTIR of calcium sulfate scale

Fig. 11 shows the FTIR spectra of CaSO₄ scale obtained with and without scale inhibitor. There are significant differences in vibration absorption peaks at 3,428; 3,236; 1,639; 1,614; 670; and 586 cm⁻¹. The intensity of those IR absorption peaks altered by using the intensity of peaks at 1,154 and 1,088 cm⁻¹ as standards when a scale inhibitor added. In other words, the crystal structure of the CaSO₄ scale changes significantly under the influence of PCA-GLU

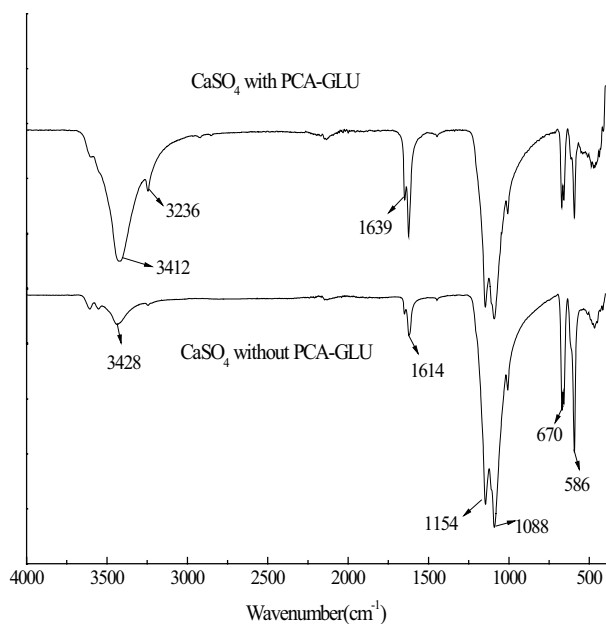


Fig. 11. FTIR spectra of CaSO_4 scale.

adsorption, which also draws the same conclusion by the study on SEM images and XRD patterns.

4. Conclusions

A new polymer scale inhibitor, PCA-GLU, was successfully prepared by using citric acid and glutamic acid as monomers. Several influential factors on CaSO_4 scale inhibition performance of PCA-GLU were investigated, such as polymerization reaction time, reaction temperature, and the amount of catalyst and original monomer molar ratio. Scale inhibition efficiency achieves over 95% when the dosage of PCA-GLU is up to 10 mg L^{-1} . It is superior to commercial calcium sulfate scale inhibitors. In the same test condition and operation, the scale inhibition efficiency of the commercial scale inhibitor PASP is 90%, and PESA is only 80%. The scale inhibition mechanism was studied using SEM, XRD, and FTIR. The crystal morphology and form of calcium sulfate changed with the addition of PCA-GLU, to achieve the purpose of scale inhibition. All of the aforesaid indicate that PCA-GLU could be used as an efficient polymer scale inhibitor and it is promising. But the yield of the polymer product is not high enough, so relevant researches will be still needed for practical application.

Acknowledgments

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