

Synthesis and characterization of an ionic liquid–carboxylic acid copolymer scale inhibitor and its scale inhibition performance

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ABSTRACT

A phosphorus-free scale inhibitor (ionic liquid–carboxylic acid copolymer) was successfully synthesized by the reaction of 1-sulfobutyl-3-vinylimidazolium hydrogen sulfate (SVIS) and acrylic acid (AA). The structure of the product was characterized by Fourier transform infrared spectroscopy (FTIR), hydrogen nuclear magnetic resonance (^1H NMR) and carbon-13 nuclear magnetic resonance (^{13}C NMR). Then the scale inhibition efficiency of 1-sulfobutyl-3-vinylimidazolium hydrogen sulfate–acrylic acid (SVIS-AA) copolymer against CaCO_3 and CaSO_4 was determined. The results indicated that SVIS-AA copolymer showed better scale inhibition efficiency than poly (acrylic acid) (PAA). After that, the effects of temperature and Ca^{2+} concentration on the scale inhibition efficiency against CaCO_3 were studied. Results showed that when the temperature reached 90°C , the scale inhibition efficiency could still remain 91% at a concentration of 18 mg L^{-1} . When the concentration of Ca^{2+} reached $1,200\text{ mg L}^{-1}$, the scale inhibition efficiency could remain 70% at a concentration of 20 mg L^{-1} . At last, the effect of SVIS-AA copolymer on the morphologies of CaCO_3 and CaSO_4 scale was studied by scanning electron microscopy (SEM) and X-ray diffraction (XRD).

Key words | circulating cooling water system, copolymer, ionic liquids, scale inhibitors

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INTRODUCTION

Because of pollution, global warming and other reasons, the shortage of water resources is becoming more and more serious (Ren *et al.* 2018). In order to save water, circulating cooling water systems have been widely used in industry (Zhang *et al.* 2016).

However, a common problem we are facing in circulating cooling water systems is scale deposition. Scale deposition can bring many problems, for example, it can reduce the efficiency of heat transfer (Amjad & Koutsoukos 2014). The most effective method to inhibit the formation of scale is to use scale inhibitors, so scale inhibitors are widely used in circulating cooling water systems (Popov *et al.* 2017).

Currently, there are many types of scale inhibitors that are used to inhibit the formation of scale. Among them,

phosphorus scale inhibitors, such as amino trimethylene phosphonic acid, are one of the most widely used scale inhibitors due to their good scale inhibition performance. Unfortunately, phosphorus scale inhibitors may cause eutrophication of water because they contain phosphorus (Zhao *et al.* 2016). Because of the major concern over global ecological and environmental problems, phosphorus scale inhibitors are gradually restricted in use (Wang *et al.* 2014). Therefore, it is necessary to prepare novel phosphorus-free scale inhibitors.

In recent years, phosphorus-free copolymer scale inhibitors have attracted great interest (Guo *et al.* 2014). Because they do not contain phosphorus, this can avoid eutrophication of water, so they are beneficial to protect the water

environment and maintain the balance of the ecological environment. Besides, they usually show excellent scale inhibition performance because they contain double or multiple types of functional groups (Guo *et al.* 2012). Recently, a copolymer scale inhibitor was reported (Guo *et al.* 2014). It does not contain phosphorus and it shows excellent scale inhibition efficiency against CaCO₃. An novel environmental friendly and hydrophilic terpolymer inhibitor has been reported (Yang *et al.* 2017). It does not contain phosphorus, and it also shows excellent scale inhibition efficiency against CaCO₃. Therefore, we can draw the conclusion that phosphorus-free copolymer scale inhibitors show many advantages and are promising in the future.

Ionic liquids are low-temperature liquid salts with the advantages of both liquids and salts (Wang *et al.* 2018). As anions and cations of ionic liquids can be replaced flexibly, it is believed that scale inhibitors containing various functional groups can be prepared (Berthod *et al.* 2008). Therefore, it is necessary to study the application of ionic liquids in scale inhibitors.

In this study, we prepared a phosphorus-free copolymer scale inhibitor. It was synthesized from 1-sulfobutyl-3-vinylimidazolium hydrogen sulfate (SVIS) and acrylic acid. SVIS is an ionic liquid, and its molecule contains a sulfonic group. Then the scale inhibition efficiency against CaCO₃ and CaSO₄ of SVIS-AA copolymer and PAA were compared. The effects of temperature and Ca²⁺ concentration were also studied. At last, the effect of SVIS-AA copolymer on the structure of CaCO₃ and CaSO₄ scale was studied by scanning electron microscopy (SEM) and X-ray diffraction (XRD).

METHODS

Measurements

The structure of the product, SVIS, and AA were characterized by Fourier transform infrared spectroscopy (FTIR) (TENSOR 27, Bruker Co., Germany), ¹H NMR (AVANCE400, Bruker Biospin AG Co., Switzerland) and ¹³C NMR (AVANCE400, Bruker Biospin AG Co., Switzerland). The morphologies of CaCO₃ and CaSO₄ were characterized by SEM (Quanta 450 FEG, FEI Co., Hong Kong) and XRD (Da Vinci, Bruker AXS Co., Germany).

Static scale inhibition method

The common methods to evaluate the scale inhibition efficiency of scale inhibitors include the static scale inhibition method and the bubbling method (Tang *et al.* 2008; Zhao *et al.* 2016). The static scale inhibition method presents the advantage of simple operation, so the static scale inhibition method was selected to evaluate the scale inhibition efficiency. The static scale inhibition method was performed to estimate the scale inhibition efficiency of SVIS-AA copolymer against CaCO₃ and CaSO₄ according to GB/T 16632-2008 (China) and SY/T 5673-93 (China), respectively. The static scale inhibition method for CaCO₃: the test solution was formulated with NaHCO₃, CaCl₂ and deionized water, and the concentrations of Ca²⁺ and HCO₃⁻ were 240 mg L⁻¹ and 732 mg L⁻¹, respectively. A certain amount of SVIS-AA copolymer was added into the test solution. The pH of the solution was adjusted to 9 with borax buffer solution. The test solution was heated in a water bath at 80 °C for 10 h. The concentration of Ca²⁺ was titrated with ethylene diamine tetraacetic acid (EDTA) standard solution. When the color of the solution changed from purple to blue, the titration was finished. The static scale inhibition method for CaSO₄: the test solution was formulated with CaCl₂, Na₂SO₄ and deionized water, and the concentrations of Ca²⁺ and SO₄²⁻ were 6,800 mg L⁻¹ and 7,100 mg L⁻¹, respectively. A certain amount of SVIS-AA copolymer was added into the test solution. The pH of the solution was adjusted to 7 with NaOH or HCl. The solution was heated in a water bath at 70 °C for 6 h. The concentration of Ca²⁺ was titrated with EDTA standard solution. The scale inhibition efficiencies against CaCO₃ and CaSO₄ were calculated by the following equations:

$$\eta = \frac{A_4 - A_3}{A_0 - A_3} \times 100\% \quad (1)$$

where A_4 and A_3 are Ca²⁺ concentration in the presence and absence of SVIS-AA copolymer after heating, respectively. A_0 is the initial Ca²⁺ concentration before heating; η is the scale inhibition efficiency against CaCO₃.

$$\eta = \frac{B_4 - B_3}{B_0 - B_3} \times 100\% \quad (2)$$

where B_4 and B_3 are Ca^{2+} concentration in the presence and absence of SVIS-AA copolymer after heating, respectively. B_0 is the initial Ca^{2+} concentration before heating; η is the scale inhibition efficiency against CaSO_4 .

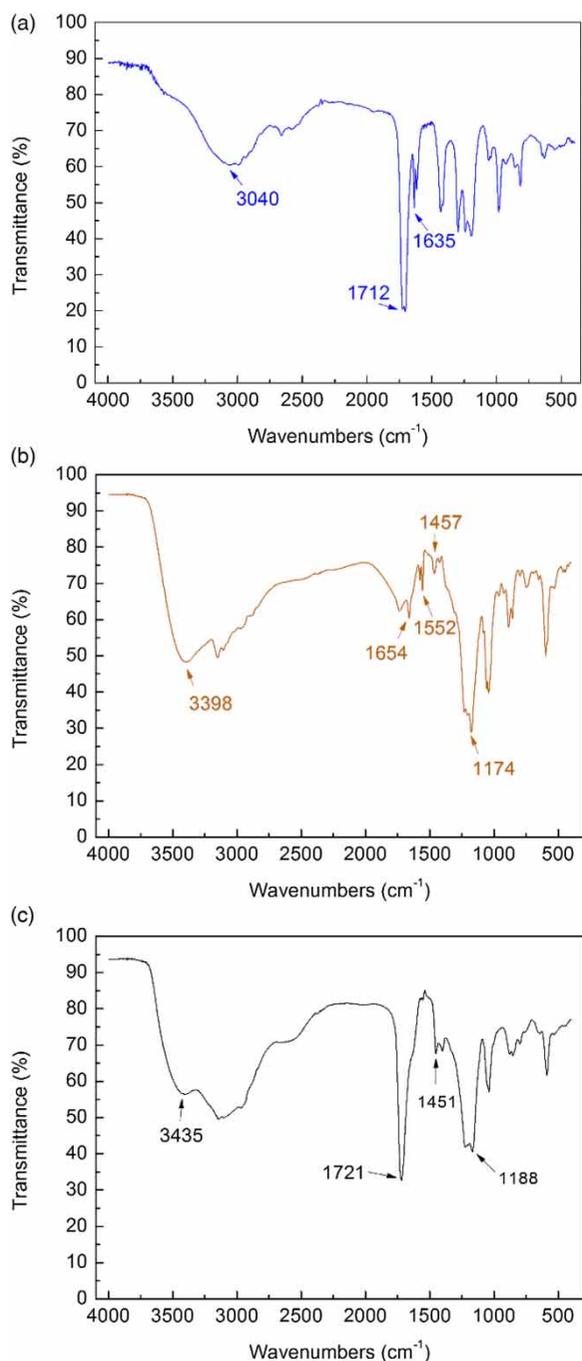


Figure 1 | FTIR spectra of (a) AA, (b) SVIS and (c) the product.

Synthesis of SVIS-AA copolymer

About 6.56 g (0.02 mol) SVIS and 1.38 g sodium hypophosphite (SHP) were initially dissolved in 50 ml deionized water in a four-necked flask, which was then heated to 60 °C under a nitrogen atmosphere. After that, the aqueous solution with about 7.2 g (0.1 mol) AA and 1.38 g ammonium persulfate (APS) was slowly added to the flask through a dropping funnel for 40 minutes. Then the reactant was heated to 85 °C and maintained for four hours before it was cooled down to room temperature. Afterwards, the pH of the system was adjusted to 7 with NaOH or HCl, followed by rotary evaporation in order to remove the solvent. Finally, the product could be obtained after the product was dried by a vacuum drying oven.

RESULTS AND DISCUSSION

FTIR analysis

The FTIR spectra of (a) AA, (b) SVIS and (c) the product are shown in Figure 1. The peaks of functional groups are listed in Table 1. It is obvious that the stretching vibration peaks of $-\text{C}=\text{C}-$ in AA and $-\text{C}=\text{C}-$ in vinyl have disappeared.

^1H NMR analysis

The structure of (a) AA, (b) SVIS and (c) the product were characterized by ^1H NMR with D_2O as the solvent. The

Table 1 | The peaks of the functional groups

The types of functional groups	The peaks of functional groups (cm^{-1})		
	AA	SVIS	SVIS-AA
$-\text{OH}$	3,040	3,398	3,435
$-\text{C}=\text{O}$	1,712		1,721
$-\text{C}=\text{C}-$	1,635		
$-\text{C}=\text{C}-$ in vinyl		1,654	
$-\text{C}=\text{C}-$ in the imidazole ring		1,457	1,451
$-\text{C}=\text{N}-$		1,552	
$-\text{S}=\text{O}$		1,174	1,188

results are shown in Figure 2. The chemical shifts of the hydrogen atoms are listed in Table 2. As can be seen from Figure 2 and Table 2, the peaks of $\text{CH}_2 = \text{CH}-$ have basically disappeared in the product.

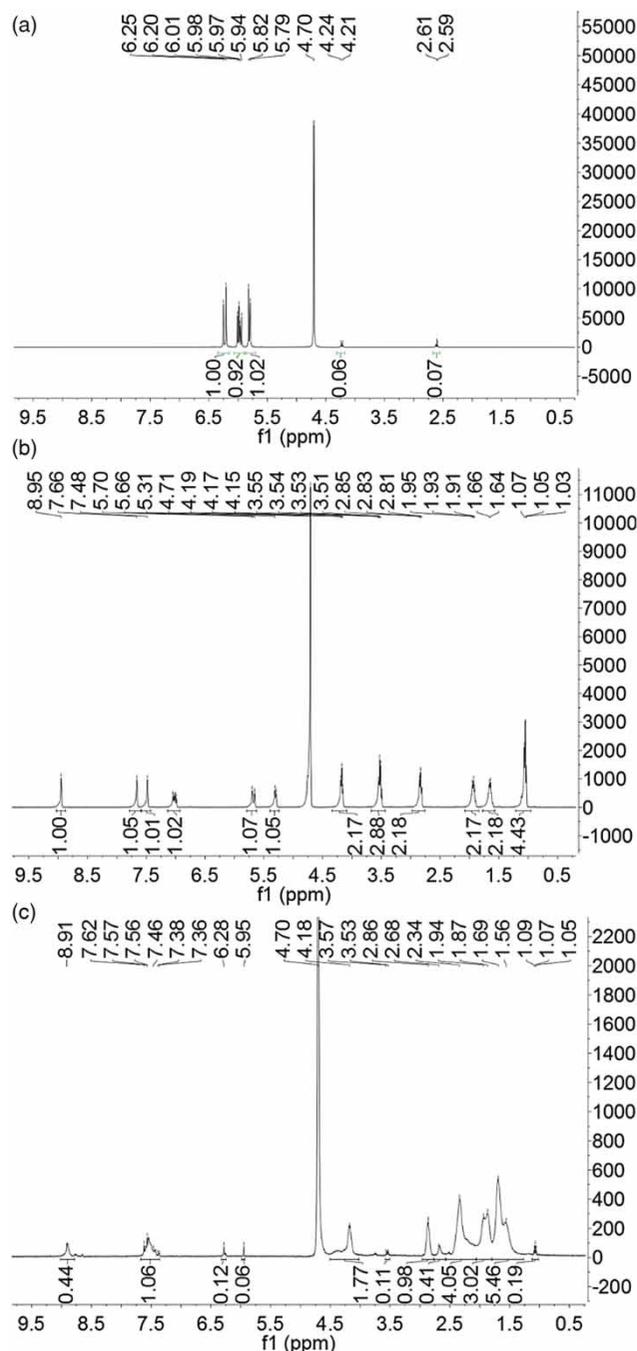


Figure 2 | ^1H NMR of (a) AA, (b) SVIS and (c) the product.

Table 2 | The chemical shifts of different types of hydrogen atoms

The types of hydrogen atoms	The chemical shifts (ppm)		
	AA	SVIS	SVIS-AA
D_2O	4.70	4.71	4.70
$\text{CH}_2 = \text{CH}-$	5.77–5.82, 5.94–6.01, 6.20–6.25	5.29–5.31, 5.66– 5.70, 6.99–7.05	
$-\text{CH} = \text{N}-$		8.95	8.91
$-\text{CH} = \text{CH}-$		7.48, 7.66	7.36–7.62
$-\text{CH}_2-$		1.64–1.66, 1.91– 1.95, 2.81–2.85, 4.15–4.19	1.56–1.94, 2.86, 4.18

^{13}C NMR analysis

The structure of (a) AA, (b) SVIS and (c) the product were characterized by ^{13}C NMR with D_2O as the solvent. The results are shown in Figure 3. The chemical shifts of the carbon atoms are listed in Table 3. The peaks of $\text{CH}_2 = \text{CH}-$ have basically disappeared according to Figure 3 and Table 3. By reading the results of FTIR, ^1H NMR and ^{13}C NMR, we mainly found that $\text{CH}_2 = \text{CH}-$ in SVIS and $\text{CH}_2 = \text{CH}-$ in AA have all disappeared. This proved that the free radical polymerization between SVIS and AA had occurred, so SVIS-AA copolymer had been successfully synthesized. The reaction equation is shown in Figure 4.

Scale inhibition efficiency against CaCO_3

The scale inhibition efficiency of SVIS-AA copolymer and PAA (molecular weight = 1,800) were tested according to GB/T 16632-2008 (China). The results are shown in Table 4. As the concentration of SVIS-AA copolymer and PAA increased, the scale inhibition efficiency increased at first. Then with the increase of the concentration of SVIS-AA copolymer and PAA, the scale inhibition efficiency gradually became unchanged, and this is due to the threshold effect. Compared with PAA, SVIS-AA copolymer showed the higher scale inhibition efficiency at the same concentration. The scale inhibition efficiency of SVIS-AA could reach 96% at the threshold concentration of 18 mg L^{-1} , but the value was only 46% for PAA in the same conditions. The excellent scale inhibition performance of SVIS-AA

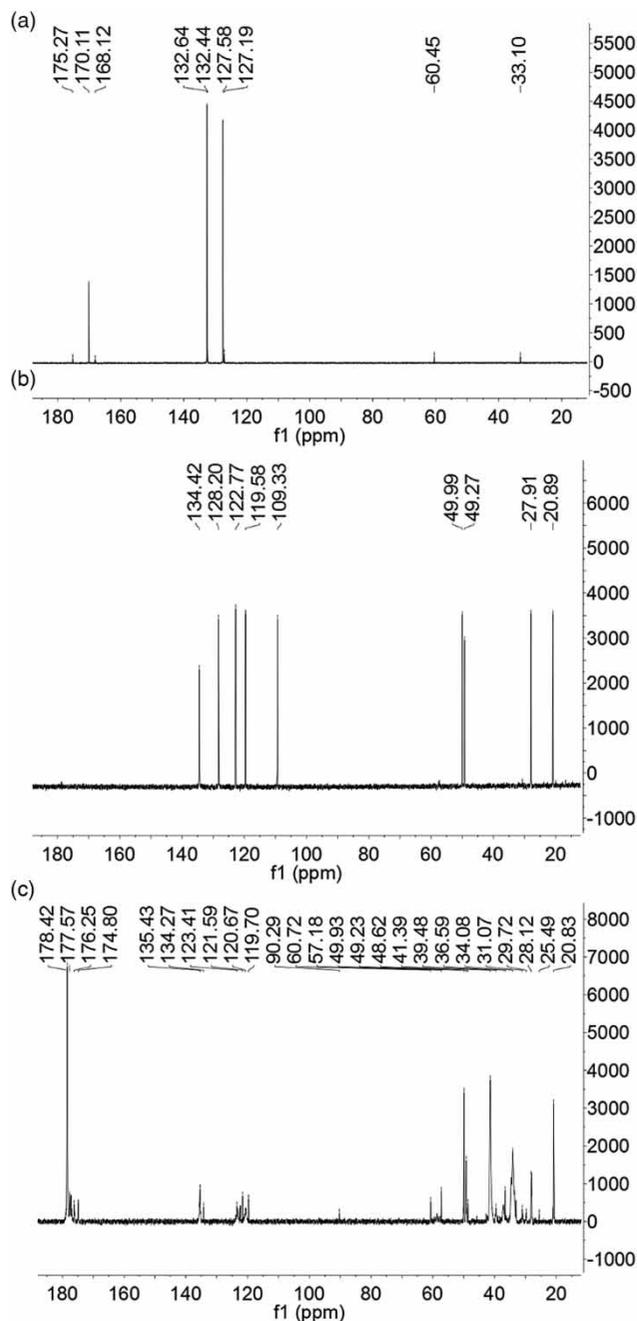


Figure 3 | ^{13}C NMR of (a) AA, (b) SVIS and (c) the product.

copolymer may be assigned to the reason that carboxyl and sulfonic groups can both chelate Ca^{2+} to inhibit the formation of CaCO_3 . In addition to the excellent scale inhibition efficiency, it does not contain phosphorus, which could avoid eutrophication of water to a certain extent, so it is beneficial for protecting the water environment. Based

Table 3 | The chemical shifts of different types of carbon atoms

The types of carbon atoms	The chemical shifts (ppm)		
	AA	SVIS	SVIS-AA
-COOH	170.11		174.80–178.42
$\text{CH}_2=\text{CH}-$	132.64, 127.58	128.20, 109.33	
-CH=N-		134.42	135.43, 134.27
-CH=CH-		122.77, 119.58	119.70–123.41
-CH ₂ -		20.89, 27.91, 49.27, 49.99	20.83, 28.12, 41.39, 48.62–49.93

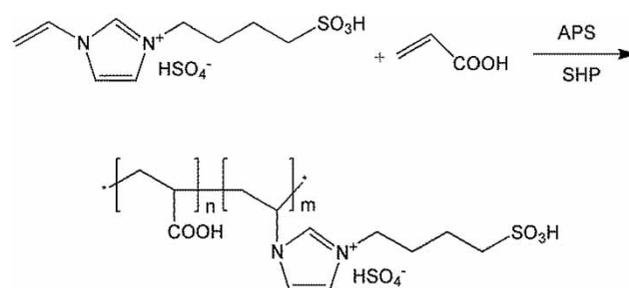


Figure 4 | The reaction equation of SVIS and AA.

on the above reasons, it can be used to inhibit the formation of CaCO_3 scale in circulating cooling water systems.

Scale inhibition efficiency against CaSO_4

The scale inhibition efficiency against CaSO_4 of SVIS-AA copolymer and PAA were tested according to SY/T 5673-93 (China). The results are exhibited in Table 5. As the concentration of SVIS-AA copolymer and PAA increased, the scale inhibition efficiency increased at first. Then with the increase of the concentration of SVIS-AA copolymer and PAA, scale inhibition efficiency gradually became unchanged. Similarly as above, SVIS-AA copolymer showed better scale inhibition efficiency than PAA. For example, the scale inhibition efficiency was 98% for SVIS-AA but 85% for PAA at the threshold concentration of 5 mg L^{-1} . Aside from the excellent scale inhibition efficiency, it does not contain phosphorus, which could avoid eutrophication of water to a certain extent, so it is beneficial for protecting the water environment. Based on the above reasons, it can

Table 4 | Scale inhibition efficiency against CaCO₃ of SVIS-AA and PAA

Scale inhibitors	Scale inhibition efficiency against CaCO ₃ (%)											
	2 (dosage of scale inhibitors, mg L ⁻¹)	4	6	8	10	12	14	16	18	20	22	24
PAA	12.1	19.5	25.3	31.7	40.3	46.5	46.4	47.5	46.6	47.4	47.1	46.5
SVIS-AA	13.2	18.1	29.4	42.4	68.5	80.6	91.2	94.3	96.5	96.8	96.3	97.1

Table 5 | Scale inhibition efficiency against CaSO₄ of SVIS-AA copolymer and PAA

Scale inhibitors	Scale inhibition efficiency against CaSO ₄ (%)						
	1 (dosage of scale inhibitors, mg L ⁻¹)	2	3	4	5	6	7
PAA	25.4	46.4	75.3	84.7	85.9	86.2	85.5
SVIS-AA	43.2	73.6	88.3	94.2	98.6	98.3	97.8

be used to inhibit the formation of CaSO₄ scale in circulating cooling water systems.

Effect of temperature on scale inhibition efficiency against CaCO₃

The effect of temperature on scale inhibition efficiency of SVIS-AA copolymer against CaCO₃ was investigated, and the results are presented in Table 6. It was found that the scale inhibition efficiency decreased with the increase of temperature. It could be attributed that with the increase of temperature, the growth rate of CaCO₃ was enhanced as the solubility of calcium carbonate reduced (Zhang *et al.* 2016), even though the scale inhibition efficiency could remain 91% at the threshold concentration of 18 mg L⁻¹, which indicated the good resistance of SVIS-AA copolymer to high

temperature. Therefore, it can be used in high-temperature water environments to inhibit the formation of CaCO₃ scale.

Effect of Ca²⁺ concentration on scale inhibition efficiency against CaCO₃

The effect of concentration of Ca²⁺ on scale inhibition efficiency of SVIS-AA against CaCO₃ was studied, and the results are shown in Table 7. With the increase of Ca²⁺ concentration, the scale inhibition efficiency of SVIS-AA copolymer decreased. The reason should be that with the increase of Ca²⁺ concentration, the reaction probability among ions increased, so the growth of CaCO₃ would accelerate (Zhang *et al.* 2016). Moreover, carboxyl groups were likely to react with Ca²⁺ and the formed polymer salt was insoluble in water, which could also cause the decrease of scale inhibition efficiency. At different Ca²⁺ concentrations, the threshold concentration of SVIS-AA copolymer is 18 mg L⁻¹. Under the conditions of the threshold concentration of SVIS-AA copolymer, the scale inhibition efficiency decreased with the increase of Ca²⁺ concentration, but the scale inhibition efficiency could be 70% even when Ca²⁺ concentration was 1,200 mg L⁻¹. This demonstrated that SVIS-AA copolymer has good resistance to high hardness. Therefore, it can be used in high hardness water environments to inhibit the formation of CaCO₃ scale.

Table 6 | Effect of temperature on scale inhibition efficiency of SVIS-AA copolymer against CaCO₃

Temperature (°C)	Scale inhibition efficiency (%)											
	2 (dosage of scale inhibitors, mg L ⁻¹)	4	6	8	10	12	14	16	18	20	22	24
60	37.1	50.6	71.9	87.6	95.4	100	100	100	100	100	100	100
70	26.4	30.5	53.2	71.6	83.5	89.9	93.6	100	100	100	99.9	100
80	13.2	18.1	29.4	42.4	68.5	80.6	91.2	94.3	96.5	96.8	96.3	97.1
90	6.5	10.2	20.4	35.8	52.5	75.5	83.2	86.8	91.7	91.4	90.8	91.9

Table 7 | Effect of Ca^{2+} concentration on scale inhibition efficiency of SVIS-AA against CaCO_3

Ca^{2+} (mg L^{-1})	Scale inhibition efficiency (%)												
	2 (dosage of scale inhibitors, mg L^{-1})	4	6	8	10	12	14	16	18	20	22	24	26
300	9.2	17.1	26.4	37.4	60.5	77.6	87.2	90.3	94.5	94.8	93.3	94.7	94.3
600	8.5	15.9	20.7	35.5	54.6	70.9	80.6	89.2	93.8	93	93.5	93.5	93.8
900	7.6	12.1	13.7	21.3	37.8	48.2	67.8	78.9	83.7	83.5	94.6	82.9	83.6
1,200	4.5	6.7	7.3	8.7	12.9	18.7	35.9	50.5	65.8	70.2	70.6	70.1	71.5

Morphology study of CaCO_3 and CaSO_4 after SVIS-AA treatment

SEM of CaCO_3 and CaSO_4

The morphologies of CaCO_3 and CaSO_4 were characterized by SEM before and after the treatment by SVIS-AA, and the

results are shown in Figure 5. It can be seen that (a) the morphologies of CaCO_3 without SVIS-AA copolymer (a) showed a cubic structure with layers, and the surfaces were compact and smooth (a). After SVIS-AA copolymer was added into the test solution, the morphologies of CaCO_3 precipitate changed to a smooth sphere structure (b). Specifically, the crystal form of the former showed the

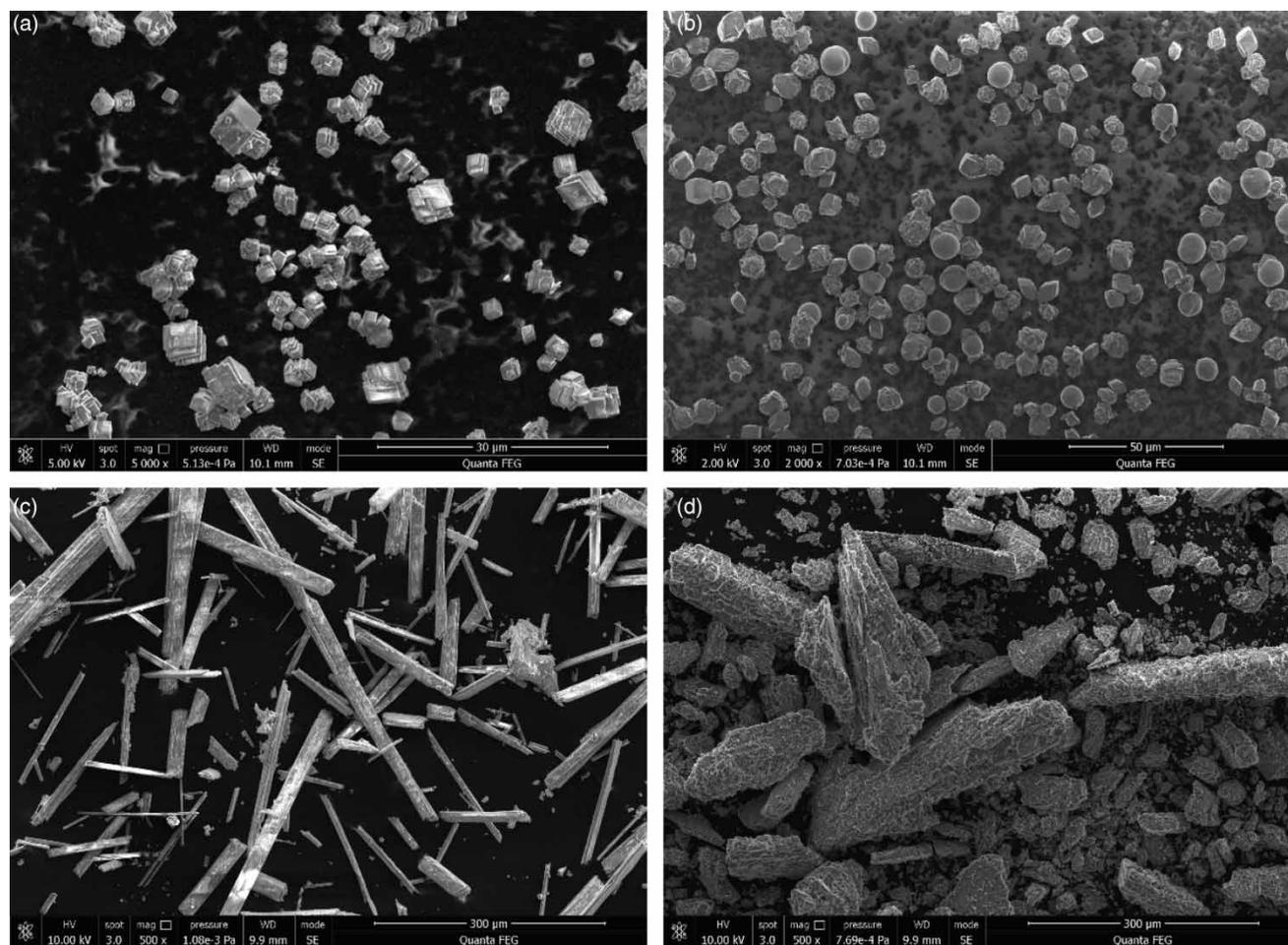


Figure 5 | SEM photographs of (a) CaCO_3 without SVIS-AA copolymer, (b) after SVIS-AA treatment and (c) CaSO_4 without SVIS-AA copolymer, (d) after SVIS-AA treatment.

characteristics of calcite, while the latter was more like vaterite (Ling et al. 2012).

In Figure 5, it is clear that in the absence of SVIS-AA copolymer, the morphologies of CaSO_4 were rod shape with sharp edges (c). However, after the treatment of SVIS-AA copolymer, the morphologies of CaSO_4 were defective rod shape with a rough surface (d). In a word, the morphologies of both CaCO_3 and CaSO_4 changed a lot with the treatment of SVIS-AA copolymer.

XRD analysis of CaCO_3 and CaSO_4

The XRD spectra of CaCO_3 are shown in Figure 6(a) and 6(b). A crystal may contain multiple types of crystal forms. A crystal form generally contains multiple characteristic diffraction peaks. Different characteristic diffraction peaks correspond to different diffraction angles (2θ). Calcium carbonate exists mainly in three crystal forms: calcite, aragonite and vaterite. In spectrum (a), CaCO_3 mainly existed in the

form of calcite owing to the diffraction peaks at 23.14° , 29.48° , 35.99° , 47.62° , and 48.60° according to relevant literature (Chen et al. 2015; Menzri et al. 2017; Wang et al. 2017). In spectrum (b), the diffraction peaks at 23.89° , 27.21° , 32.82° , 43.96° and 49.15° correspond to vaterite, and the diffraction peak at 29.49° corresponds to calcite. Compared with spectrum (a), the diffraction peaks of calcite have mostly disappeared, and CaCO_3 mainly existed in the form of vaterite. Therefore, it shows the trend that the crystal form of CaCO_3 changed from calcite into vaterite in the presence of SVIS-AA copolymer (dosage of SVIS-AA copolymer, 15 mg L^{-1}).

The XRD spectra of CaSO_4 are presented in Figure 6(c) and 6(d). Calcium sulfate exists mainly in three crystal forms: CaSO_4 , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$. In spectrum (c), the diffraction peaks at 11.73° and 23.48° correspond to $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The diffraction peaks at 14.84° , 25.80° , 29.82° and 49.47° correspond to $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ according to relevant literature (Ling et al. 2012;

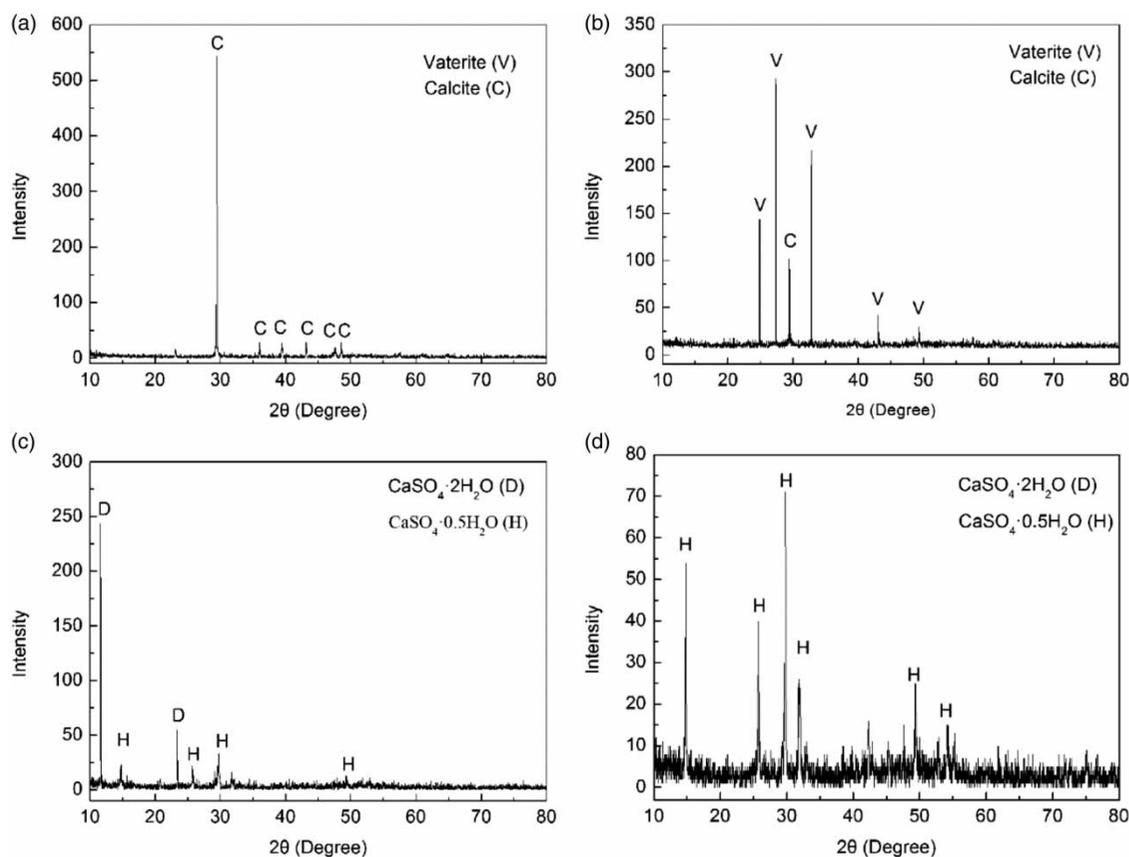


Figure 6 | XRD photographs of (a) CaCO_3 without SVIS-AA copolymer, (b) after SVIS-AA treatment and (c) CaSO_4 without SVIS-AA copolymer, (d) after SVIS-AA treatment.

Zhao *et al.* 2016). In spectrum (d), the diffraction peaks at 14.84°, 25.84°, 29.82°, 32.01°, 42.38° and 49.42° correspond to CaSO₄·0.5H₂O. The diffraction peaks of CaSO₄·2H₂O disappeared and the intensity of the diffraction peaks of CaSO₄·0.5H₂O were significantly enhanced. It shows the trend that the crystal form of CaSO₄ changed from the crystal phase mixture of CaSO₄·2H₂O and CaSO₄·0.5H₂O into CaSO₄·0.5H₂O.

Mechanism of calcium scale inhibition

SVIS-AA copolymer contains a large number of carboxyl and sulfonic groups, which are the structural basis of the copolymer to inhibit scale. Carboxyl and sulfonic groups could recognize and encapsulate Ca²⁺ in the solution of scale, and form water-soluble complexes (Ling *et al.* 2012; Wang *et al.* 2014). Furthermore, carboxyl and sulfonic groups could adsorb on the surface of CaCO₃ and CaSO₄ crystals, which would distort and damage the crystal structure. In addition, sulfonic groups can improve the water solubility of SVIS-AA copolymer and avoid the formation of polymer salt. Based on the above reasons, SVIS-AA copolymer possesses an excellent ability to control scale.

CONCLUSIONS

A phosphorus-free scale inhibitor was successfully synthesized. The structure of the product was characterized by FT-IR, ¹H NMR and ¹³C NMR. It showed better scale inhibition efficiency against CaCO₃ and CaSO₄ than PAA in the same conditions. Meanwhile, SVIS-AA copolymer could maintain excellent scale inhibition efficiency in high temperature and high hardness environments. Finally, the SEM and XRD study of CaCO₃ and CaSO₄ indicated that SVIS-AA copolymer could change the morphologies of particles.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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