

Synthesis and Study of Modified Polyaspartic Acid Coupled Phosphonate and Sulfonate Moieties As Green Oilfield Scale Inhibitors

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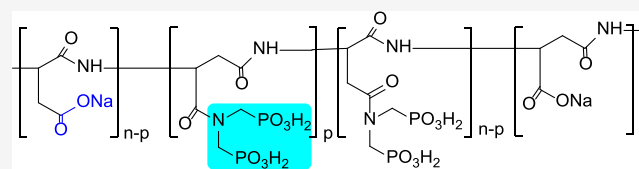
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ABSTRACT: The petroleum industry has strived for several years to explore environmentally friendly scale inhibitors with no acute environmental impact. Well-known industrial biodegradable polyaspartic acid is widely used as a potent scale inhibitor (SI) against various inorganic scales in industrial circulating cooling water and topside petroleum applications. However, polyaspartic acid showed weak thermal stability at the petroleum reservoir temperatures. Here, we attempt to develop a new class of polyaspartic acid for squeeze treatment applications under harsh conditions. In this project, a series of modified polyaspartic acid, including pendant anionic functional moieties (phosphonate and sulfonate) were synthesized and investigated as new SIs to inhibit the calcium carbonate (calcite, CaCO_3) and barium sulfate (barite, BaSO_4) scales under oilfield conditions. These classes were synthesized via aminolysis of polysuccinimide with nucleophilic amine reagents under alkaline conditions. The products are polyaspartic acid-capped aminomethylene phosphonic acid (SI-2), polyaspartic acid-capped bisphosphonic acid (SI-3), polyaspartic acid-capped aminomethanesulfonic acid (SI-4), and polyaspartic acid-capped aminoethanesulfonic acid (SI-5), as well as in-house synthesized polyaspartic acid (SI-1). The scale inhibition activities of these compounds against carbonate and sulfate scales were determined using the dynamic scale loop test at 100 °C and 80 bar. Furthermore, the long-term thermal aging and calcium tolerance experiments were also investigated. It was found that polyaspartic acid-capped aminomethylene phosphonic acid (SI-2) gave outstanding calcite scale inhibition performance and showed excellent thermal stability at 130 °C for 7 days compared to SI-1 and other modified SIs (SI-3–SI-5). This phosphonated polymer also exhibited superior calcium tolerance performance with Ca^{2+} ions up to 100 ppm, and moderate performance in the range of 1000–10 000 ppm calcium ions. This project highlights the success of designing and developing a new environmentally friendly calcite SI-based polyaspartic acid under harsh oilfield conditions.



1. INTRODUCTION

Inorganic scaling deposition is a critical problem in hydrocarbon production. Due to the intolerance of oilfield waters, inorganic scales can easily precipitate in the oil and gas wells. These scales lead to formation damage and reduction of hydrocarbon production.^{1,2} Oilfield scale forms on any surface in the petroleum reservoir.³ The commonest types of oilfield scales are calcium carbonate and sulfates of group 2 elements, for example, strontium (celestite, SrSO_4), calcium (gypsum, CaSO_4), and barium (barite, BaSO_4).^{4,5} Barite and calcite scales are considered to be the extreme scaling in oilfield applications.⁶ So, it is imperative to tackle the problem of scale deposition wisely and quickly in order to increase the total revenue from the petroleum reservoir.

Several techniques have been developed for inhibiting and remediating the scale formation.^{7,8} Scale inhibitors (SIs) are considered the ideal method for preventing the oilfield scale. SIs are water-based chemicals that prevent crystallization, nucleation, and precipitation of inorganic deposits.^{9,10} Polymeric and/or nonpolymeric-based SIs play a vital role in the oilfield scale inhibition. It was reported that most

conventional SIs for both scales (calcite and barite) are organic-chemical-based phosphonates ($-\text{PO}_3\text{H}_2$), sulfonate ($-\text{SO}_3\text{H}$), and carboxylate ($-\text{COOH}$) groups.^{11–13}

Phosphonate and sulfonate-based SIs are commonly applied for downhole and topside oilfield scale management. Phosphonate chemicals show excellent scale inhibition performance, particularly in squeeze treatments.^{14,15} They afforded remarkable retention and adsorption properties onto the formation rock and are easily monitored and detected.¹⁶ In addition, polymer-based sulfonates have attracted significant attention as superior SIs in extremely high salinity reservoirs.^{17,18} It was also found that introducing a few sulfonate moieties in the polymer structure improves its

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thermal stability, leading to a prolonged scale inhibition performance under harsh oilfield conditions.¹⁹

However, most commercial SIs have certain disadvantages, such as being intolerant to the production system and having poor biodegradation activities.⁴ Therefore, many commercial SIs are to be prohibited for offshore deployment in several oilfields (for example, the U.K. and Scandinavia). There is a clear need to move toward environmentally friendly SIs to match the offshore regulations (The Oslo and Paris Commission, OSPARCOM) for oilfield chemicals.^{20,21}

Environmentally friendly SIs (green SIs) must fulfill the required criteria, as follows: (1) biodegradation test (BOD₂₈ > 60%, OECD 306 procedure), (2) toxicity test (LC₅₀ and/or EC₅₀ > 10 mg/L), and (3) bioaccumulation test (log *P*_{OW} < 3).^{4,21} Numerous attempts have been investigated to afford improved green oilfield SIs.^{22–25} Various natural and synthetic polymers have been developed for oilfield scale inhibition under different conditions.^{4,15,22} Recently, we have synthesized a series of modified polycarbonate and polyetheramine-bearing phosphonate groups as new green oilfield SIs.^{26,27} Figure 1 shows some green SI-capped phosphonates developed by our research group.

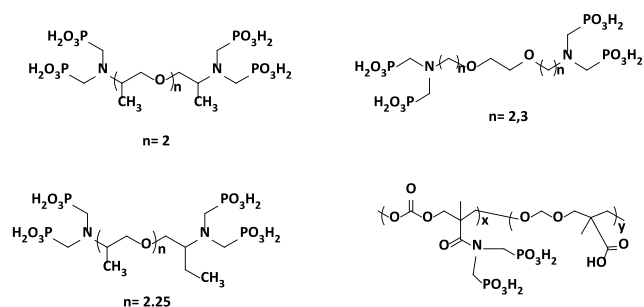


Figure 1. Schematic representation of modified polyethers containing phosphonate groups as green oilfield scale inhibitors developed by our group.^{26,27}

Polyamide-based SIs have attracted significant attention as a result of their powerful performance for biocompatibility and biodegradability.²⁸ It is well-known that polyaspartic-acid-based amide linkage is widely used as green SI in industrial circulating cooling water and topside petroleum applications. Many research groups have synthesized and investigated antiscaling evaluation of modified polyaspartic acid for industrial cooling water systems at low temperatures.^{29–35} The main problem of polyaspartic acid derivatives is being not thermally stable under harsh reservoir conditions, affording short squeeze lifetimes. Polyaspartic acid can be applied in squeeze applications at only 85 °C.³⁶ A possible reason for the lack of efficient activity of polyaspartic acid is the hydrolysis process at elevated temperatures.

In a continuation of our attempt to develop potential environmentally friendly SIs, particularly for high pressure high temperature (HPHT) petroleum reservoirs, we have synthesized polyaspartic acid incorporating carboxylate, sulfonate, and/or phosphonate moieties. Moreover, we studied the dynamic scale inhibition efficiency for the synthesized in-house polyaspartic acid (SI-1), polyaspartic acid-capped aminomethylene phosphonic acid (SI-2), polyaspartic acid-capped bisphosphonic acid (SI-3), polyaspartic acid-capped aminomethanesulfonic acid (SI-4), and polyaspartic acid-

capped aminoethanesulfonic acid (SI-5). All synthesized polymers were tested for calcium carbonate and barium sulfate scales based on the Heidrun oilfield, Norway. The inhibition efficiency of all synthesized SIs was determined using a high-pressure dynamic loop protocol at 80 bar and 100 °C. We have also studied the thermal stability of synthesized polymers under anaerobic conditions (130 °C and 7 days), as well as their calcium compatibility.

2. EXPERIMENTAL SECTION

2.1. Materials and Characterization. Chemicals and organic solvents were purchased from Sigma-Aldrich (Merck), Thermo Fisher Scientific, VWR, and Tokyo Chemical Industry Co., Ltd. Polysuccinimide was obtained from NanoChem Solutions, Inc. 1-Aminoethylidene bisphosphonic acid was prepared based on the literature.³⁷ The structures of the synthesized polyaspartic acid derivatives were characterized by Fourier-transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopy. IR spectra were obtained with the Agilent Cary 630 FTIR Spectrometer with ATR. ¹H NMR and ¹³P NMR spectra were recorded on a 400 MHz Bruker NMR spectrometer in deuterium oxide (D₂O) and deuterated dimethyl sulfoxide (DMSO-*d*₆).

2.2. Synthesis of Green Oilfield SIs. **2.2.1. Synthesis of Polyaspartic Acid (SI-1).** In a two-neck round flask linked to an additional funnel and a magnetic stirring bar was added the polysuccinimide (2.0 g) in distilled water (20 mL). An aqueous solution of 10% sodium hydroxide (NaOH) was added dropwise to the mixture until it turned homogeneous. The mixture was carried out at 60 °C for 24 h and then poured into ethanol (20 mL), providing a brown solid. The obtained solid was collected by filtration and dried under a vacuum for 12 h, giving polyaspartic acid (SI-1). The synthesis route of polyaspartic acid is presented in Figure 2, route A.

IR ν_{\max} (cm⁻¹): 3300 (NH), 1568 (CO), 1385 (CN). ¹H NMR (D₂O, 400 MHz): δ 4.36–4.60 (br, 1H, $-\underline{\text{C}}\text{H}-\text{CH}_2-\text{CONH}$), 2.46–2.70 (br, 2H, $-\text{CH}-\underline{\text{C}}\text{H}_2-\text{CONH}$).

2.2.2. Synthesis of Polyaspartic Acid-Capped Aminomethylene Phosphonic Acid (SI-2). In a two-neck round flask linked to an additional funnel and a magnetic stirring bar were added the polysuccinimide (0.47 g) and imino-bis(methyl phosphonic acid) (1.00 g) in distilled water (10 mL). The obtained solution was heated at 60 °C for 6 h. Subsequently, an aqueous solution of 10% NaOH was added dropwise to the suspension mixture until it turned homogeneous. The solution was stirred with vigorous stirring at 60 °C for 24 h and then poured into absolute ethanol (25 mL), giving a brown precipitate. The solid was concentrated by filtration and dried under a vacuum for 12 h. A total of 1.21 g of polyaspartic-acid-capped aminomethylene phosphonic acid (SI-2) was obtained, as shown in Figure 2, route B.

IR ν_{\max} (cm⁻¹): 3203 (NH), 1588 (CO), 1403 (CN), 1078, 967 (PO₃). ¹H NMR (D₂O, 400 MHz): δ 4.56–4.35 (br, 1H, $-\underline{\text{C}}\text{H}-\text{CH}_2-\text{CONH}$), 2.97–2.95 (d, 2H X 2, $-\underline{\text{C}}\text{H}_2-\text{PO}_3\text{H}_2$), 2.44–2.68 (br, 2H, $-\text{CH}-\underline{\text{C}}\text{H}_2-\text{CONH}$). ³¹P NMR (D₂O, 162.00 MHz): δ 7.88.

2.2.3. Synthesis of Polyaspartic Acid-Capped Bisphosphonic Acid (SI-3). In a two-neck round flask linked to an additional funnel and a magnetic stirring bar were added the polysuccinimide (0.47 g) and 1-aminoethylidene bisphosphonic acid (1.00 g) in distilled water (10 mL). The obtained solution was heated at 60 °C for 6 h. Subsequently, an aqueous solution of 10% NaOH was added dropwise to the suspension

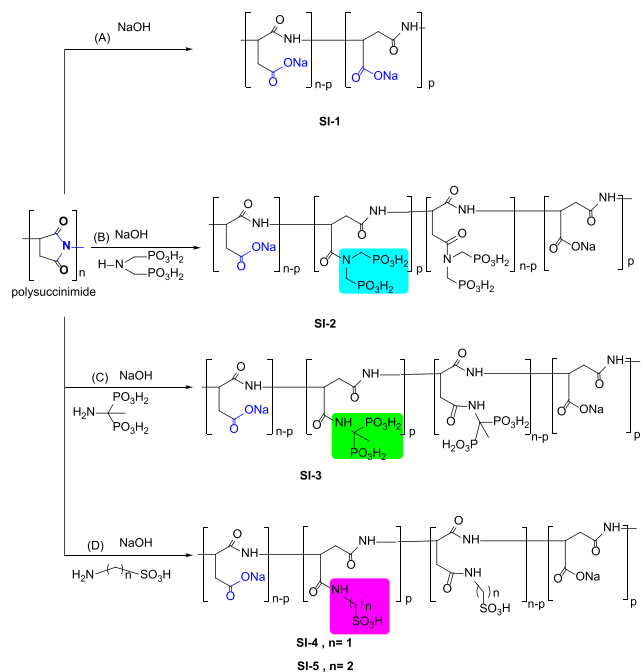


Figure 2. (A) Synthesis of polyaspartic acid (SI-1), (B) modified polyaspartic acid with aminomethylene phosphonic acid (SI-2), (C) modified polyaspartic acid with bisphosphonic acid (SI-3), and (D) modified polyaspartic acid with methane and ethanesulfonic acid (SI-4 and SI-5, respectively).

mixture until it turned homogeneous. The solution was stirred with vigorous stirring at 60 °C for 24 h and then poured into absolute ethanol (25 mL), giving a brown precipitate. The solid was concentrated by filtration and dried under a vacuum for 12 h. A total of 1.15 g of polyaspartic-acid-capped bisphosphonic acid (SI-3) was obtained (Figure 2, route C).

IR ν_{\max} (cm⁻¹): 3200 (NH), 1573 (CO), 1393 (CN), 1055, 947 (PO₃). ¹H NMR (D₂O, 400 MHz): δ 4.59–4.29 (br, 1H,

–CH–CH₂–CONH), 2.68–2.44 (br, 2H, –CH–CH₂–CONH), 1.35 (t, 3H, –CH₃–C(PO₃H₂)₂). ³¹P NMR (D₂O, 162.00 MHz): δ 18.66.

2.2.4. Synthesis of Polyaspartic-Acid-Capped Aminoalkanesulfonic Acid (Alkane = Methane and Ethane Labeled SI-4 and SI-5, Respectively). In a two-neck round flask linked to an additional funnel and a magnetic stirring bar were added the polysuccinimide (1 mol equiv) and N-sulfoalkane amines 1–2 (1 mol equiv) in deionized water (10 mL). The obtained solution was heated at 60 °C for 6 h. Subsequently, an aqueous solution of 10% NaOH was added dropwise to the suspension mixture until it turned homogeneous. The solution was stirred with vigorous stirring at 60 °C for 24 h and then poured into absolute ethanol (25 mL), giving brown precipitates. The solids were concentrated by filtration and dried under a vacuum for 12 h. A total of 2.52 and 2.69 g of polyaspartic-acid-capped aminoalkanesulfonic acid (alkane = methane and ethane named SI-4 and SI-5, respectively) were obtained (Figure 2, route D).

2.2.4.1. Polyaspartic-Acid-Capped Aminomethanesulfonic Acid (SI-4). IR ν_{\max} (cm⁻¹): 3300 (NH), 1585 (CO), 1395 (CN), 1173 (SO₃). ¹H NMR (D₂O, 400 MHz): δ 4.64–4.30 (br, 1H, –CH–CH₂–CONH), 3.97 (s, 2H, –CH₂–SO₃H), 2.70–2.44 (br, 2H, –CH–CH₂–CONH).

2.2.4.2. Polyaspartic-Acid-Capped Aminoethanesulfonic Acid (SI-5). IR ν_{\max} (cm⁻¹): 3380 (NH), 1575 (CO), 1389 (CN), 1176 (SO₃). ¹H NMR (D₂O, 400 MHz): δ 4.58–4.39 (br, 1H, –CH–CH₂–CONH), 3.48 (br, 2H, –CH₂CH₂–SO₃H), 3.09–3.03 (br, 2H, –CH₂CH₂–SO₃H), 2.77–2.55 (br, 2H, –CH–CH₂–CONH).

2.3. High-Pressure Dynamic Tube Blocking Test Protocol. The high-pressure dynamic tube blocking test is a commonly used laboratory protocol that evaluates the inhibition efficiency of SIs against various inorganic scales. The dynamic scale rig (DSR) has a versatile design that can be manipulated up to 300 bar (4300 psi) and 200 °C, depending on the application field. In this study, a high-pressure dynamic

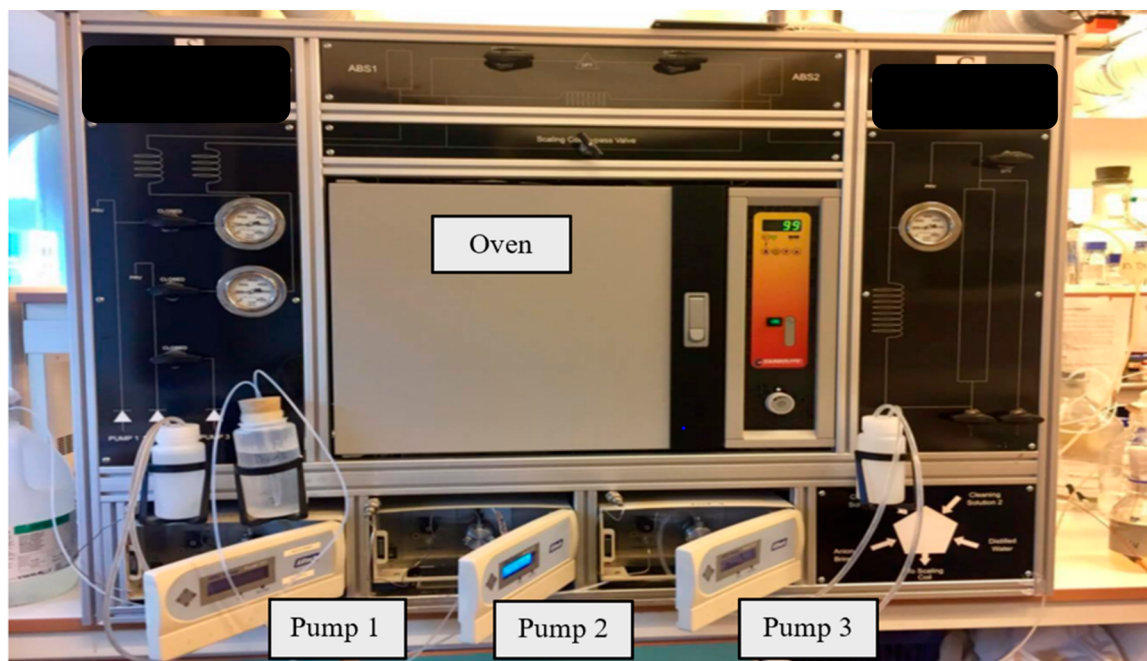


Figure 3. Schematic diagram of the dynamic scale rig (DSR).

tube blocking scale rig manufactured by Scaled Solutions Ltd. (U.K) was used to detect the inhibition activity of the in-house synthesized polyaspartic-acid-based SIs. The DSR includes three pumps. Each pump flushes up to 10.00 mL/min through a test coil made of 316 steel with 1.00 mm internal diameter and a length of 3.00 m. The coil is located inside an oven at 100 °C. The pressure in the tubing system is set to 80 bar. This procedure was carried out several times in our published articles.^{25–27,38}

Figure 3 shows the schematic diagram of the DSR. From left to right, the following features can be listed as follows:

1. Pump 1: pumping brine 1 (B1) of scaling cations. It resembles formation water, and the flow rate remains constant throughout the entire test (5.00 mL/min).
2. Pump 2: pumping brine 2 (B2) of scaling anions. It simulates the injection seawater. In addition, pump 2 flushes cleaning solutions containing a tetrasodium ethylenediamine-tetraacetate solution (Na₄EDTA 5 wt %, pH = 12–13) and deionized water, respectively.
3. Pump 3: pumping the SI solution. This solution was always prepared from the 1000 ppm of SI in 500 mL of deionized water. The pH should be measured and adjusted to 4–6 in order to simulate field conditions.

The compositions of brines B1 and B2 used throughout this project are used according to the formation water from Heidrun oilfield, North Sea, Norway. The detailed composition of the brines is summarized in Table 1. We used a 1:1

Table 1. Oilfield Water Chemical Compositions

ion	Heidrun formation water (ppm)	seawater (ppm)	50/50 mixed brine (ppm)
Na ⁺	19 500	10 900	15 200
Ca ²⁺	1020	428	724
Mg ²⁺	265	1368	816
K ⁺	545	460	502
Ba ²⁺	285	0	142
Sr ²⁺	145	0	72
SO ₄ ²⁻	0	2960	1480
HCO ₃ ⁻	880	120	500

volume mixture solution of produced water and synthetic seawater to form the barium sulfate inorganic scale by applying all ions (except bicarbonate ions) in Table 1. All salts were mixed and stirred for 1 h, affording a completely soluble mixture solution. Then, each brine solution was degassed for 15 min utilizing a water-jet vacuum pump. This step is of relevant importance as dissolved gases and bubbles within the tubing system might lead to a pump to stop mixture solutions flushing. Usually, all injected brines were freshly prepared for each experiment. Due to the stochastic nature of the nucleation process, it is rare to get precisely the same inhibition time values for each test.

The main reason for conducting a tube blocking experiment is to detect the minimum inhibitor concentration (MIC) and fail inhibitor concentration (FIC). FIC is defined as the inhibitor concentration at which the chemical loses its potential to prevent inorganic scale and where the differential pressure is exceeded over 9 psi. While the MIC is the inhibitor concentration tested before the FIC, at which the SI was effective at inhibiting scale formation. Due to practical and economic reasons, it has been determined that an ideal MIC should be between 1 and 50 ppm, but a more practical range is

from 1 to 10 ppm. The DSR is linked to a computer including the LabView 8.0 program that automatically monitors the SI concentration pumped into the system and the flow rates from each pump. Time and pressure drop due to scale formation were recorded. The following procedure of SI testing consists of four automated stages for each test.

1. A first blank test, where B1 + B2 are pumped into the tubing at a flow rate of 5.00 mL/min each, without pumping any SI.
2. First scale test, where a series of programmed SI concentrations are injected for 1 h each or until the inorganic scale is deposited along with both brine solutions.
3. Repeated scale test (also called second scale test), where B1 + B2 are pumped into the system together with the SI concentration. This step guarantees that the reproducibility of the experiment is acceptable. A difference of ±5 min between first and second scale tests is tolerable.
4. A second blank test, where only both brines are flushed at a flow rate of 5.00 mL/min each without added SI.

For the new synthesized SIs, we always start the SI concentration at 100 ppm and follow by 50, 20, 10, 5, 2, and 1 ppm. The test time for each experiment is 1 h for each concentration until the inorganic scale is detected in the microbore coil. When the deposit is formed at the FIC, it is automatically detected by the system. An abrupt increase of pressure to 0.5 bar (7 psi) indicates that the limit of differential pressure has been reached. The coil is then saturated with scale deposit, and it proceeds to clean automatically with 5 wt % Na₄EDTA solution and then deionized water. The flow rate for both solutions is 9.99 mL/min for 10 min. Then, the system is ready for the next experiment. The obtained results are exported to Microsoft Excel in order to build the plots.

2.4. Formation Water and Seawater Tolerance Tests.

Oilfield formation water usually contains a high amount of calcium ions. The primary objective of the tolerance test is to confirm the compatibility of injected SIs with seawater (SW) and formation water (FW), particularly for high calcium brines under high temperatures. SIs must be tolerant with the brine compositions to avoid SI–Ca complex precipitation, causing formation damage.^{1,2} A calcium compatibility test is also vital for squeeze treatment applications in the reservoir wells. There is a clear need to enhance the inhibition performance and prolong the SI squeeze lifetimes. To verify whether our synthesized SIs form this complex precipitation, a set of SIs and Ca²⁺ ions concentrations were added into a synthetic seawater brine mixture.

The calcium compatibility testing works as follows:

1. Four concentrations of SI (100, 1000, 10 000, and 50 000 ppm) were added in 20 mL of distilled water in 20 mL jars.
2. Four different concentrations of Ca²⁺ ions of 10, 100, 1000, and 10 000 ppm were mixed with synthetic seawater (3.00% of NaCl) and then poured into corresponding glass vessels. The pH of the mixture solution was ranged from 4.0 to 4.5. The jars were shaken very well, and the appearance of the mixture was checked at room temperature. All jars were then placed in an oven at 80 °C.
3. The appearance of the solution was detected and reported after 30 min and 1, 4, and 24 h by our visual observation to check for cloudiness and/or deposition of tested SI with calcium ions. This protocol was repeated for all synthetic SIs to check their Ca²⁺ tolerances.

2.5. Thermal Aging Test. The hydrothermal stability test aims to approve that the SI is stable at elevated temperatures in

the petroleum reservoir. A long-term thermal aging test is needed to check the probability of deploying the new SIs for squeeze applications. The thermal aging test of the synthesized SIs is described herein as follows: A 5 wt % solution of SI in distilled water (pH = 4–4.5) was mixed in a 20 mL sealed tube, and then the mixture was flushed with nitrogen gas for 1 h in order to minimize the oxygen in the solution. Next, the SI solution was heated at 130 °C for 7 days. The obtained solution was then screened for antiscaling activities compared to the untreated SI using a DSR.

3. RESULTS AND DISCUSSION

3.1. Chemistry. We have synthesized in-house polyaspartic acid (SI-1) via the alkaline hydrolysis of polysuccinimide (Figure 2, route A), as reported previously in the literature.^{29–35} To characterize the obtained polyaspartic acid (SI-1), FTIR and NMR spectroscopy techniques were used. FTIR spectra of SI-1 displayed a broad absorption peak at 3300 cm⁻¹ attributed to the N–H bond stretching vibration, the band at 1706 cm⁻¹ revealed the C=O of carboxyl, and the absorption band at 1568 revealed the stretching vibration of the C=O bond of the amide moiety. In addition, the obtained peak at 1385 represents the C–N stretching vibration in the amide group. Furthermore, ¹H NMR spectra of SI-1 in D₂O displayed broad peaks in the range of δ 4.36–4.60 ppm attributed to –CH–, while the other broad peaks at δ 2.46–2.70 ppm corresponded to –CH₂–.

All modified polyaspartic acid derivatives in this project were prepared via aminolysis of polysuccinimide with nucleophilic amine reagents under alkaline conditions.^{29–35} For example, the ring-opening polymerization of polysuccinimide via aminolysis with imino-bis(methyl phosphonic acid) afforded modified polyaspartic-acid-capped aminomethylene phosphonic acid SI-2 (Figure 2, route B). FTIR and NMR (¹H and ¹³P NMR) spectroscopy were also utilized to elucidate the obtained compound. The FTIR spectrum of SI-2 displayed strong absorption bands at 1078 and 967 cm⁻¹, indicating the presence of a phosphonate group (–PO₃–) into the polyaspartic acid molecular chain. In addition, ¹H NMR shows a distinct doublet signal at δ 2.97–2.95 ppm attributed to –CH₂–PO₃H₂–. It was also found that the chemical shift of the phosphonate moiety of SI-2 revealed a singlet peak at δ 7.88 ppm. Thus, the modified polyaspartic-acid-capped –N–CH₂–PO₃H₂ has been synthesized successfully. Moreover, polyaspartic-acid-capped bisphosphonic acid (SI-3) was prepared via aminolysis of polysuccinimide with 1-aminoethylidene bisphosphonic acid and then characterized using the same spectroscopic techniques. ³¹P NMR of bisphosphonates (H₂O₃P–C–PO₃H₂) into the side chain of SI-3 displayed a significant peak at δ 18.66 ppm. Two other polyaspartic acid derivatives have been modified with sulfonate moieties via an aminolysis procedure giving SI-4 and SI-5.

3.2. Scale Inhibition Performance. A dynamic tube blocking test has been used to evaluate the inhibition efficiency of all modified polyaspartic acid compounds (SI-2–SI-5) against carbonate and sulfate inorganic deposits compared to the unfunctionalized polyaspartic acid (SI-1). The scale inhibition performance experiments of all synthesized SIs were performed at 100 °C and 80 bar. The pH of all tested SIs was adjusted to 4–6 in a 1000 ppm aqueous medium to match the pH of the well reservoir. All obtained results were replicated twice in order to check the reproducibility of the SI test.

Tables 2 and 3 tabulated the obtained experimental results from the DSR for calcite and barite scales, respectively. It was

Table 2. Summary of Calcium Carbonate Scale Inhibition Experiments Providing FIC and Scaling Time Values^a

SI ^b	1st blank	1st scale test		2nd scale test		2nd blank
	time (min)	conc. (ppm)	time (min)	conc. (ppm)	time (min)	time (min)
SI-1	15	5	6	5	5	14
SI-2	14	2	19	2	20	15
SI-3	13	2	32	2	32	15
SI-4	15	5	12	5	12	13
SI-5	14	5	35	5	40	13
SI-1 ^c	15	20	23	20	21	16
SI-2 ^c	16	2	21	2	20	16
SI-3 ^c	15	5	31	5	28	15
SI-4 ^c	12	100	21	100	18	14
SI-5 ^c	12	100	22	100	21	13

^aThe pH of synthesized SIs has been applied at 4–6 in 1000 ppm aqueous medium. ^bThe accuracy for all numerical values was ± 5 min. ^cAll synthesized polyaspartic acid-based SIs (SI-1 to SI-5) were evaluated against calcium carbonate scaling after heating at 130 °C for 7 days.

Table 3. Summary of Barium Sulfate Scale Inhibition Experiments Providing FIC and scaling time Values^a

SI ^b	1st blank	1st scale test		2nd scale test		2nd blank
	time (min)	conc. (ppm)	time (min)	conc. (ppm)	time (min)	time (min)
SI-1	11	50	47	50	47	10
SI-2	11	20	4	20	4	11
SI-3	11	20	11	20	13	11
SI-4	10	20	8	20	10	10
SI-5	11	20	16	20	18	10
SI-1 ^c	11	100	29	100	25	11
SI-2 ^c	10	100	25	100	23	11
SI-3 ^c	11	100	35	100	30	11
SI-4 ^c	10	100	12	100	15	12
SI-5 ^c	12	100	15	100	17	12

^aThe pH of synthesized SIs has been applied at 4–6 in 1000 ppm aqueous medium. ^bThe accuracy for all numerical values was ± 5 min. ^cAll synthesized polyaspartic acid-based SIs (SI-1 to SI-5) were evaluated against barium sulfate scaling after heating at 130 °C for 7 days.

reported that polyaspartic acid afforded good scale and corrosion inhibition performance for cooling water system applications.^{29–35} For the oilfield calcite scaling, SI-1 gave very good inhibition activity with an FIC of 5 ppm after 6 and 5 min for both runs, respectively (Table 2).

For the new modified polyaspartic-acid-based SIs, the polyaspartic-acid-capped aminomethylene phosphonic acid (SI-2) showed excellent scale inhibition efficiency at 2 ppm, as shown in Figure 4. This plot affords the required information for detecting an FIC and scaling times. In the first blank stage with no SI, rapid scaling formed after 14 min. The microbore coil was then cleaned using the mixture solution (Na₄EDTA) and distilled water, dropping the differential pressure to 1 psi. In the second process (known as the first scale test), the experiment was performed by

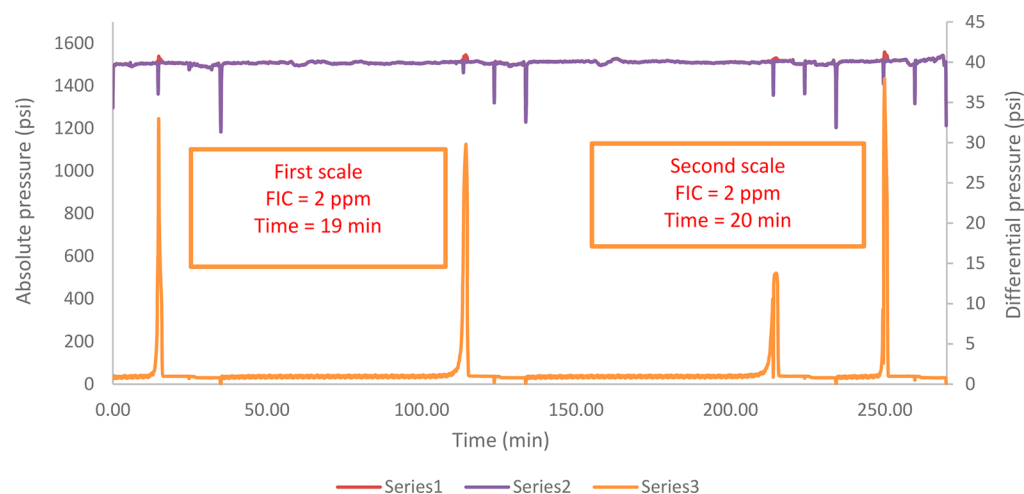


Figure 4. Schematic diagram displaying the four stages of SI-2 for carbonate scale in the scale dynamic loop (pressure vs time).

flushing 5 ppm of SI-2. Interestingly, no scale was detected, and then the experiment moved on to the next programmed concentration of 2 ppm. It was found that the calcite scaling was formed after 19 min at this SI concentration. Then, cleaning the tubing was performed automatically using Na₄EDTA and water solutions. The test was then moved on to the third stage (known as the second scale test) to approve the repeatability of the tests. The FIC was detected at 2 ppm after 20 min (Table 2). Finally, the experiment was finished with a repeated blank experiment (fourth stage), providing scale formation after 15 min. On the basis of the above results, the dynamic scale inhibition test provided excellent reproducibility of the experiments.

More recently, the low toxicity level of bisphosphonates (BPs) motivated us to synthesize and study a set of novel and commercial bone-targeting drug-bearing bisphosphonates as oilfield SIs.³⁹ The results showed that most synthesized bisphosphonate-based SIs gave outstanding carbonate inhibition activity under harsh oilfield conditions. These results motivated us to functionalize the polyaspartic acid with BP groups, affording SI-3 (Figure 2, route C). The dynamic loop test for SI-3 also revealed excellent inhibition properties with an FIC of 2 ppm after 32 min for both experiments (Figure 5 and Table 2).

We have recently reported that modified sulfonic acid compounds (e.g., taurine-capped phosphonates) showed excellent inhibition activity for the carbonate scale.⁴⁰ In this project, the modified polyaspartic acid with sulfonate groups (SI-4 and SI-5) gave similar calcite inhibition efficiency to SI-1, as presented in Figure 5. SI-4 gave a scale inhibition activity

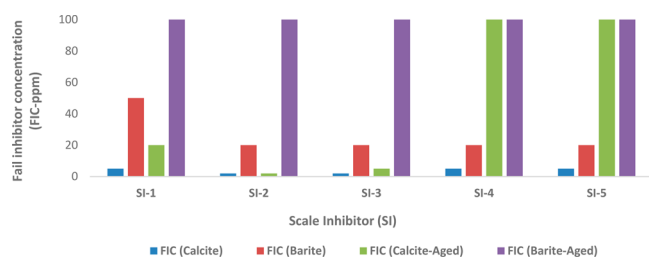


Figure 5. Summary of FIC results for synthesized polyaspartic acid derivatives for calcite and barite scales, both before and after aging at 130 °C.

at an FIC of 5 ppm for each run. In addition, the FIC of SI-5 (polyaspartic acid-capped taurine) was 5 ppm after 35 and 40 min in the first and repeated experiments, respectively.

For the oilfield barite scaling, SI-1 gave a moderate performance with an FIC at 50 ppm after 47 min for both tests, as shown in Figure 5 and Table 3. The phosphonated polyaspartic acid SI-2 demonstrated better performance compared to SI-1, failing at 20 ppm after 4 min in both experiments. The other phosphonated polyaspartic acid SI-3 also gave good barite inhibition efficiency. The FIC was detected at 20 ppm after 11 and 13 min for each run, respectively (Table 3).

Furthermore, the sulfonated polyaspartic acid displayed reasonable inhibition efficiency against oilfield barite scaling. SI-4 revealed an FIC of 20 ppm after 8 and 10 min in both tests, respectively. In addition, the FIC of SI-5 was also displayed at 20 ppm, while the delay time is slightly longer in the range of 16–18 min (Figure 5, and Table 3).

Clearly, the carboxylated polyaspartic acid SI-1 showed very good calcite inhibition performance and moderate barite inhibition activities according to the oilfield conditions. This suggests that pendant carboxylate groups on the side chain of SI-1 gave limited barite scaling inhibition performance. Interestingly, the two modified polyaspartic acids with amino methylenephosphonates (SI-2) and bisphosphonates (SI-3) exhibited excellent calcite inhibition efficiency. They also afforded a very good barite inhibition performance. Our obtained inhibition results have matched the concept of adding multiple phosphonate moieties in the inhibitor backbone in order to improve the scaling inhibition activities.^{41,42} Furthermore, the modified polyaspartic incorporating amino-methanesulfonic acid SI-4 and aminoethanesulfonic acid (also known as taurine) SI-5 afforded similar carbonate scale inhibition activity to SI-1. Moreover, SI-5 displayed improved scale inhibition properties against sulfate scaling in comparison with SI-1. It was also observed that the number of carbon atoms in the sulphonated capping agents does not have a significant role in improving the scaling inhibition properties. In addition, we have investigated that the repeatability of all dynamic tube blocking experiments gave similar results, leading to the accuracy and precision of our testing protocol.

3.3. Long-Term Thermal Stability Test. As stated earlier, polyaspartic acid showed poor scale inhibition performance at elevated temperatures. The possible reason for the lack of its

inhibition performance may be due to the hydrolysis process of the amide linkage. Thus, polyaspartic acid is more beneficial for topside oilfield applications but not for downhole squeeze treatment. In continuation of our research, the group focused on developing environmentally friendly oilfield scale inhibitors for HPHT applications (squeeze treatment).^{25–27,39,40} We have carried out laboratory thermal aging experiments for all synthesized polyaspartic acid derivatives at 130 °C for 7 days under an anaerobic medium. The dynamic tube-blocking experiment was then performed for all aged SIs against carbonate and sulfate scales in comparison with the unaged sample, as presented in Tables 2 and 3.

For the carbonate scale, the aged polyaspartic acid SI-1 lost its inhibition activities, dropping from an FIC of 5 to 20 ppm. Contrarily, SI-2 was thermally stable under these harsh conditions, giving an FIC of 2 ppm after 21 and 20 min for each experiment, as shown in Figure 6 and Table 2. In

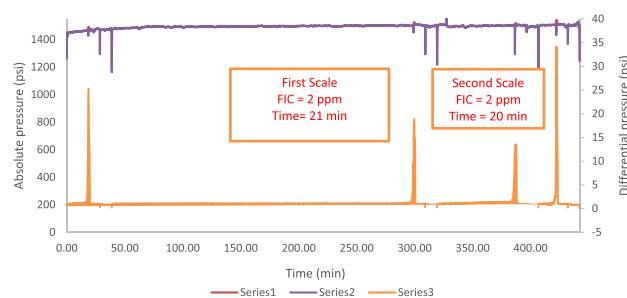


Figure 6. Schematic diagram affording the carbonate dynamic results for the aged SI-2 for carbonate scale at 130 °C in the scale dynamic loop (pressure vs time).

addition, the FIC of SI-3 went from 2 to 5 ppm for both runs. The delay time of the aged SI-3 at 5 ppm was slightly longer than the unaged SI-1 of 31–28 min. This shows that the SI-3 still has very impressive scale inhibition properties under harsh oilfield conditions, and it can be a good candidate as an SI for squeeze treatment applications. Moreover, SI-4 and SI-5 showed poor thermal stability performance at 130 °C. For example, SI-4 failed at 100 ppm in the first and repeated runs (Figure 5).

Furthermore, it was investigated that SI-1 and all modified polyaspartic acid compounds SI-2–SI-5 were not thermally stable at 130 °C for the sulfate scale, affording an FIC of 100 ppm for both tests. For example, SI-3 displayed an FIC of 100 ppm after 35 and 30 for both experiments (Table 3 and Figure 5).

3.4. Calcium Tolerance Tests. It is well-known that many commercial SIs are incompatible with formation/injection seawater under oilfield conditions. Thus, there is a clear need to check the compatibility between the SIs and calcium ions to avoid the formation damage in the petroleum reservoir, especially for squeeze treatment applications.^{1,2} A series of tolerance experiments were operated at 80 °C to detect the compatibility of all synthesized polyaspartic acid derivatives with calcium ions at different concentrations. The SI concentrations were operated in the range of 100 to 50 000 ppm, and the Ca²⁺ ion concentrations changed from 10 to 10 000 ppm, including 3.00% NaCl.

SI-1 provided excellent calcium tolerance performance with all calcium ion concentrations (10–10 000 ppm) throughout

the experiment period. This suggests that SI-1 is tolerant with very high Ca²⁺ ion concentrations and can be used for both topside injection and squeezing application into low-formation temperature petroleum reservoirs.

It was also investigated that the phosphonated polyaspartic-acid-bearing aminomethylene phosphonic acid SI-2 showed outstanding compatibility performance at all SI concentrations for 10 and 100 ppm calcium ions (Table 4). In addition, SI-2

Table 4. Summary of Tolerance Tests for SI-2 in 100 ppm of Ca²⁺ Ions at 80 °C

dose (ppm)	appearance				
	at mixing	30 min	1 h	4 h	24 h
100	clear	clear	clear	clear	clear
1000	clear	clear	clear	clear	clear
10000	clear	clear	clear	clear	clear
50 000	clear	clear	clear	clear	clear

gave excellent calcium tolerance performance at 100–1000 ppm of SI concentrations for 1000–10 000 ppm of Ca²⁺ ions throughout the 24 h experiment period (Tables 5 and 6).

Table 5. Summary of Tolerance Tests for SI-2 in 1000 ppm of Ca²⁺ Ions at 80 °C

dose (ppm)	appearance				
	after mixing	30 min	1 h	4 h	24 h
100	clear	clear	clear	clear	clear
1000	clear	clear	clear	clear	clear
10000	clear	clear	haze	haze	haze
50000	clear	haze	haze	haze	haze

However, 10 000–50 000 ppm SI-2 concentrations displayed cloudiness and precipitation with 1000–10 000 ppm of Ca²⁺ ions, as illustrated in Tables 5 and 6. These obtained results can propose SI-2 as an environmentally friendly SI for squeeze treatment application in moderate Ca²⁺ concentration gas wells.

The other phosphonated polyaspartic-acid-containing BPs SI-3 gave moderate to poor compatibility performance at all SI/Ca²⁺ concentrations. For example, precipitates were formed in the presence of all SI concentrations (100–50 000 ppm) and 10 000 ppm of Ca²⁺ ions throughout the test period. We have recently investigated whether hydroxybisphosphonate SIs are incompatible with high calcium ion concentrations under oilfield conditions.³⁹

Interestingly, the sulfonated polyaspartic acids SI-4 and SI-5 exhibited excellent tolerance performance at all SI and Ca²⁺ concentrations. It was reported that capping the SI with sulfonate functional groups can improve its calcium compatibility properties.⁴³

4. CONCLUSIONS AND OUTLOOK

In this project, we attempted to make a thermally stable class of biodegradable polyaspartic acids for oilfield scale management under harsh conditions. A series of modified polyaspartic-acid-bearing pendant anionic functional moieties (phosphonate and sulfonate) have been synthesized and investigated as green scale inhibitors, particularly for carbonate and sulfate oilfield scales. The main conclusions are listed as follows:

Table 6. Summary of Tolerance Tests for SI-2 in 10 000 ppm of Ca²⁺ Ions at 80 °C

dose (ppm)	appearance				
	after mixing	30 min	1 h	4 h	24 h
100	clear	clear	clear	clear	clear
1000	clear	clear	clear	clear	clear
10000	haze	haze	haze	precipitated	precipitated
50000	precipitated	precipitated	precipitated	precipitated	precipitated

1. The unfunctionalized polyaspartic acid (SI-1) gave a reasonable carbonate inhibition performance with an FIC of 5 ppm and moderate sulfate inhibition with an FIC value of 50 ppm. It was also observed that SI-1 afforded excellent calcium tolerance properties at all calcium ion and SI concentrations. However, SI-1 was not thermally stable at 130 °C under anaerobic conditions for both scales.

2. The phosphonated polyaspartic acid with aminomethylene phosphonic acid (SI-2) displayed excellent calcite inhibition activity with an FIC of 2 ppm for both runs and good barite inhibition efficiency at 20 ppm. SI-2 showed superior calcium tolerance performance at all SI concentrations for calcium ions in the range of 10–100 ppm and moderate tolerance performance for 1000 and 10 000 ppm of Ca²⁺ ions throughout the experiment period. Interestingly, the thermal aging test of SI-2 exhibited excellent thermal stability properties under harsh oilfield conditions. The FIC was 2 ppm for both runs against carbonate scaling. In addition, the aged SI-2 gave poor thermal stability performance for the barite scales.

3. The polyaspartic-acid-capped bisphosphonates (SI-3) showed excellent calcite inhibition performance (FIC = 2 ppm) and a reasonable barite inhibition effect (FIC = 20 ppm). This inhibitor shows a specific drawback with Ca²⁺ ions, affording a calcium–SI complex. SI-3 afforded good thermal stability against calcite scaling.

4. The sulfonated polyaspartic acid SI-4 and SI-5 displayed similar scale inhibition activity to SI-1 with an FIC value of 5 ppm against carbonate scaling. These classes were not thermally stable at 130 °C for calcite and barite scales, giving FIC values of 100 ppm.

Overall, the obtained results show that polyaspartic-acid-capped aminomethylene phosphonic acid (SI-2) can be proposed as a powerful calcite SI for squeeze application in the petroleum industry. We plan to explore SI-2 in further detail, containing adsorption/desorption activities onto the petroleum reservoir rock using static and dynamic adsorption experiments.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.1c01473>.

Tables S1–S12: Compatibility tests for polyaspartic acid based SIs (PDF)

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Notes

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