

Environmentally Friendly Phosphonated Polyetheramine Scale Inhibitors—Excellent Calcium Compatibility for Oilfield Applications

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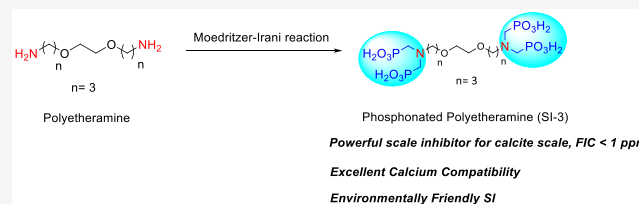
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ABSTRACT: Scaling is one of the most frequently stated problems in the oil industry, and scale inhibitors (SIs) are applied to prevent its formation. Organophosphonates are well-known types of SIs, particularly useful for squeeze treatments, which can be found as both non-polymeric and polymeric molecules. However, the performance of phosphonate-based SIs is often limited by poor compatibility with calcium ions. In addition, many phosphonated SIs exhibit poor seawater biodegradation. Therefore, there is still a need to develop effective SIs with reliable calcium compatibility, thermal stability, and environmental acceptability. A series of linear and branched phosphonated polyetheramines were synthesized. The final products were evaluated for their calcium carbonate (calcite) and barium sulfate (barite) scale inhibition performance using a high-pressure dynamic tube blocking rig at 80 bar and 100 °C. This study showed that the best phosphonated polyetheramines had excellent performance on both barite and calcite scale formation compared to some common commercial phosphonated SIs. In addition, all of the synthesized SIs showed superior compatibility with calcium ions and good thermal stability at 130 °C. The linear phosphonated polyetheramines gave the best seawater biodegradability, with BOD28 up to 47% by the OECD 306 procedure.



1. INTRODUCTION

The upstream oil industry considers inorganic scaling as a critical flow assurance problem; scale formation occurs when inorganic salts deposit from the aqueous phase due to the supersaturation of salts.^{1,2} The deposition of the mineral salts will cause damages through the production system and, therefore, loss of well productivity. Scaling can occur on almost any surface so that, once a scale layer is first formed, it will proceed to grow thicker unless treated.^{3,4} The most common types of inorganic scale in the oil and gas industry are calcium carbonate (calcite and aragonite) and sulfate salts of calcium (gypsum), strontium (celestite), and barium (barite).²

Several techniques are applied in the oilfield to overcome the problem of inorganic scale formation. The use of scale inhibitors (SIs) is the most popular and useful scale control method.⁵ SIs work by inhibiting either nucleation and/or crystal growth of the inorganic scale.²

Commercial SIs for carbonate and sulfate scaling are generally polymeric, e.g., polyphosphonates, polycrylates, polymaleates, polysulfonates, and copolymers, while some are non-polymeric molecules with only a few phosphonate groups ($-\text{PO}_3\text{H}_2$).^{2,6}

Phosphonated chemicals are a major class of SIs used for oilfield scale control. Placing phosphonate groups in the SI can be helpful to detect and determine its concentration of the SI in the produced water. Phosphonates also adsorb strongly to formation rocks, affording long squeeze lifetimes, decreasing the downtime needed for well management.⁷ In addition, SI attached aminomethylenephosphonate groups ($-\text{N}-\text{CH}_2-$

PO_3H_2) play key roles in the oilfield scale inhibition performance. The $-\text{N}-\text{CH}_2-\text{PO}_3\text{H}_2$ group presumably enhances the metal-binding capabilities of the molecule via both the amine and phosphonate interactions, which will improve the chelating potential of the SI.^{8–11} However, most of the commercial phosphonate SIs, such as diethylenetriaminepentakis(methylenephosphonic acid) (DTPMP) and aminotris(methylenephosphonic acid) (ATMP), gave poor biodegradability activities. In addition, most phosphonate SIs show poor compatibility with calcium ions, leading to precipitation and deposition of a Ca^{2+} -SI complex.¹²

To minimize the overall impact of offshore chemicals on the marine environment, the Oslo and Paris Commission (OSPAR) has proposed a harmonized mandatory control procedure for the use of oilfield chemicals in the North Sea.¹³ Several classes of biodegradable polymers have been developed and deployed in oilfields, but few of them have good thermal stability for downhole squeezing. There are several ongoing attempts to develop more biodegradable and biocompatible SIs. It has been shown that chemical substances containing

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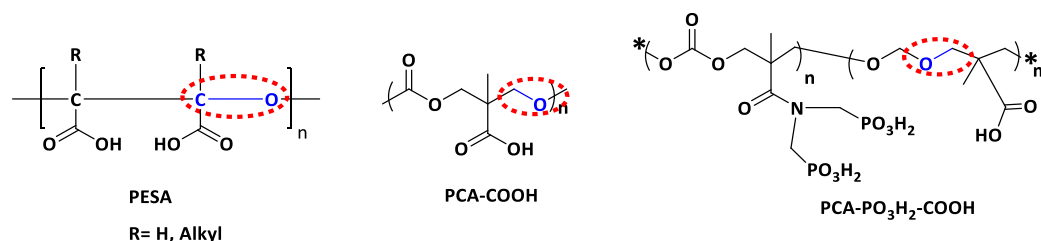


Figure 1. Examples of oilfield polymeric SIs containing backbone ether linkages.

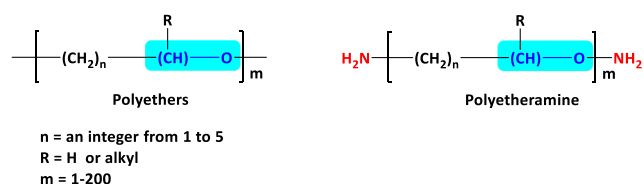


Figure 2. General structures of aliphatic polyether (left) and polyether amines (right), including ether linkage in the main chain.

heteroatom linkages in the main chain, such as ether and/or ester groups, displayed improvement on their biodegradation properties.¹⁴ For instance, Figure 1 shows the chemical structure of polyepoxysuccinic acid (PESA), which has been investigated as a green scale and corrosion inhibitor for the oil industry.¹⁵ Recently, our group has developed a new class of modified aliphatic polycarbonates (PCA-COOH and PCA-PO₃H₂-COOH) as environmentally friendly oilfield SIs for carbonate and sulfate scales (Figure 1).¹⁶ Also, Wang et al. have synthesized a series of 2-phosphono-butane-1,2,4-tricarboxylic acid (PBTPCA)-modified hyperbranched polyethers as biodegradable corrosion and scale inhibitors.¹⁷ Furthermore, Liu et al. have reported a polyether copolymer as an environmentally friendly scale and corrosion inhibitor.¹⁸

Polyethers are polymers that contain the C–O–C linkage, as shown in Figure 2. PEAs gained importance for biological and industrial applications during the last decades due to their unique physical, chemical, and biodegradation properties.^{19–21} The most common PEAs encountered in medical and industrial applications are polyethylene glycol diamine (PEG-amine) and polypropylene glycol diamine (PPG-amine).²² Another class of polyethers with several ether bonds (–C–O–C) in the backbone are polyether amines. This class has attracted attention, as they can include a variety of molecular weights, amine functionalities, and repeating unit features.²³ A range of polyetheramines are commercially available, including monoamines, diamines, and triamines with primary amino groups linked to the end of a polyether backbone. The general structures are presented in Figure 2.

Chen et al. have reported a series of polyamino polyether methylene phosphonates (PAPEMPs) as SIs for calcium

carbonate scale in water systems.²⁴ The results showed that PAPEMP possesses high calcium tolerance and gave excellent inhibition of calcite scale, even at an elevated pH of 8.5–9.5, high dissolved solids content, and high saturation levels of calcium brines. However, although several companies have made this class of polymeric SIs commercially available, there are no reported studies in the open literature related to downhole, low pH oilfield applications for calcite or barite scale inhibition, as well as thermal stability or seawater biodegradation.

In this work, we report the synthesis of a series of phosphonated polyetheramines with different molecular weights via the Moedritzer–Irani reaction and their application as oilfield scale inhibitors (SIs). Five SIs (SI-1, SI-2, SI-3, SI-4, and SI-5) have been successfully prepared and evaluated for calcite and barite scale inhibition and compared to several commercial SIs using a high-pressure dynamic tube blocking rig at approximately 80 bar and 100 °C. The aqueous fluids (50:50 mix of formation and seawater–water) used in this work are based on the Heidrun oilfield, North Sea, Norway. We also report the seawater biodegradability, thermal stability, and calcium compatibility of the new SIs.

2. EXPERIMENTAL SECTION

2.1. Chemicals. All chemicals and solvents used for synthesis were purchased from VWR, Nippon Chemical Industrial Co., Ltd., Tokyo Chemical Industry Co., Ltd., and Sigma-Aldrich (Merck). The sodium salts of diethylenetriaminepentakis(methylenephosphonic acid) (DTPMP) and aminotris(methylenephosphonic acid) (ATMP) were supplied by Solvay. A series of polyether amines (Jeffamines) were obtained from Huntsman Corp. Polyaminomethylenephosphonate (PAPEMP) was supplied from Italmatch Chemicals S.p.A. Italy.

2.2. Characterization of Scale Inhibitors. The structures of target compounds were confirmed by nuclear magnetic resonance (NMR) spectroscopy. The NMR spectra were recorded on a 400 MHz Bruker NMR spectrometer in deuterium oxide (D₂O) with two drops of sodium deuterioxide solution. ¹H NMR and ³¹P NMR chemical shifts were obtained in D₂O.

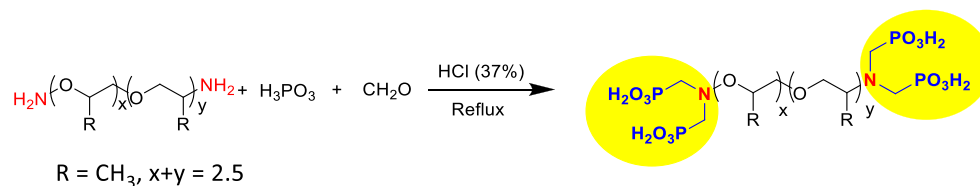


Figure 3. Synthesis of phosphonated polyetheramine derivatives.

Table 1. Antiscalcing Names and Chemical Structure of Phosphonated Polyetheramines

Scale Inhibitor	Chemical structure
Phosphonated Polyetheramine (SI-1)	<p style="text-align: center;">n=2</p>
Phosphonated Polyetheramine (SI-2)	<p style="text-align: center;">n=2</p>
Phosphonated Polyetheramine (SI-3)	<p style="text-align: center;">n=3</p>
Phosphonated Polyetheramine (SI-4)	<p style="text-align: center;">x+y+z = 5-6</p>
Phosphonated Polyetheramine (SI-5)	<p style="text-align: center;">n=2.25</p>

2.3. Synthesis of Scale Inhibitors (SIs). General Procedure for the Synthesis of Linear and Branched Phosphonated Polyetheramines via the Moedritzer–Irani Reaction. Five polyetheramines were synthesized using the Moedritzer–Irani reaction.²⁵ Figure 3 shows the general synthesis route of modified polyetheramine scale inhibitors. In addition, Table 1 provides the chemical structures of all phosphonated polyetheramine SIs. For example, the synthesis of phosphonated amine-terminated polyoxypropylene (Figure 3, R = CH₃, x + y = 2.5) is described herein as follows:

Polyetheramine (Figure 3, R = CH₃, x + y = 2.5) (2 g, 8.6 mmol) was added to a 250 mL two-neck glass flask fitted with a reflux condenser, a magnetic stirrer, and a thermometer. Phosphorous acid (H₃PO₃, 3.4 g, 34.7 mmol) dissolved in water (10 mL) was then charged to the flask dropwise, followed by the addition of HCl 37% (3.4 g, 34.7 mmol). The

flask was kept in an ice bath due to the exothermic nature of the reaction. Next, the reaction mixture was heated up to 60 °C while nitrogen (N₂) was injected into the system using a N₂-filled balloon. At 60 °C, aqueous formaldehyde 37% (HCHO, 2.8 g, 34.7 mmol) was added dropwise over 30 min. Then, the temperature of the mixture was increased to 110 °C and refluxed for 72 h. The reaction mixture was then cooled to room temperature. The solvent of the liquid phase was removed in vacuo, and the residue was washed with diethyl ether. Volatiles were removed under reduced pressure to afford phosphonated polyetheramine (SI-1) as a thick oil. All of the desired phosphonates were confirmed by using ³¹P NMR spectroscopy.

2.4. High-Pressure Dynamic Tube Blocking Test Methods. A schematic representation of the high-pressure dynamic tube blocking rig (scale rig) is shown in Figure 4. The

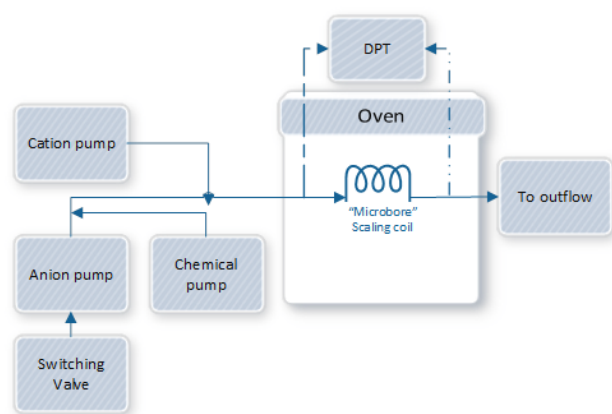


Figure 4. Schematic diagram of the dynamic tube blocking equipment for SI testing.

Table 2. Water Composition Used in This Study

ion	Heidrun formation water (ppm)	seawater (ppm)	50/50 mixed brine (ppm)
Na ⁺	19,510	10,890	15,200
Ca ²⁺	1020	428	724
Mg ²⁺	265	1368	816.5
K ⁺	545	460	502.5
Ba ²⁺	285	0	142.5
Sr ²⁺	145	0	72.5
SO ₄ ²⁻	0	2960	1480
HCO ₃ ⁻	880	120	500

heart of the rig has three pumps that are capable of pumping fluids at a rate of 10 mL/min through a 316 micro bore coil. This coil is placed in an oven. The coil is 3 m long and has an inner diameter of 1 mm. Records of the differential in pressure across the coil so as to measure the rate of scaling and the initiation are made. The results are collected on a computer, and the results are transferred to an Excel file. Excel is used to plot the data. The tube blocking rig is designed to withstand temperatures of up to 200 °C and pressures of 300 bar (ca. 4200 psi). The experimental results from high-pressure dynamic tube blocking tests provide a reasonable estimate of

the minimum inhibitor concentration (MIC) for the SIs. The equipment was adjusted to run four different stages of the testing automatically as follows:

1. A blank test without added SI.
2. A series of 1 h tests with the scale inhibitor at decreasing concentrations.
3. A repeated test automatically beginning with the SI concentration one before the concentration that led to scale formation.
4. Another blank test without SI.

Dynamic tube blocking tests to monitor SI performance were carried out on an automated rig (built by Scaled Solutions Ltd., Scotland, U.K.) at 100 °C and 80 bar, as described previously by our research group.^{26–30} As shown in Figure 4, the first pump is used to inject brine 1, which includes all of the cations required, and the second pump is used to inject brine 2, which includes the scaling anions, as presented in Table 2. The coil cleaning solutions are also injected by anion pump. The chemical pump is injected with SI solution. The software can be set to monitor the SI concentration automatically.

In this study, the SI concentration was regulated to decrease in increments every hour. The starting concentration was at most 100 ppm and was decreased to 50, 20, 10, 5, 2, and 1 ppm and finally without SI to make sure we always got scale formation.

For evaluating the inhibition capability of the in-house synthesized SIs for both calcite and barite scales, the starting concentration of the injected SI was 100 ppm for the first tests. Occasionally, there were random failures, and thus, the rapid scale was taken at the point when the differential pressure increased to 0.5 bar (7 psi) and above. This is called the “fail inhibitor concentration” (FIC) of the SI and not the minimum inhibitor concentration (MIC). FIC must not be confused with MIC, the latter being the lowest concentration that completely inhibits scale formation. The formed scale in the coil was cleaned between each of the four stages using 5 wt % tetrasodium ethylenediaminetetraacetate solution (Na₄EDTA) that had a pH between 12 and 13. After scale removal, the distilled water was injected for 10 min with a flow rate of 9.99 mL/min.

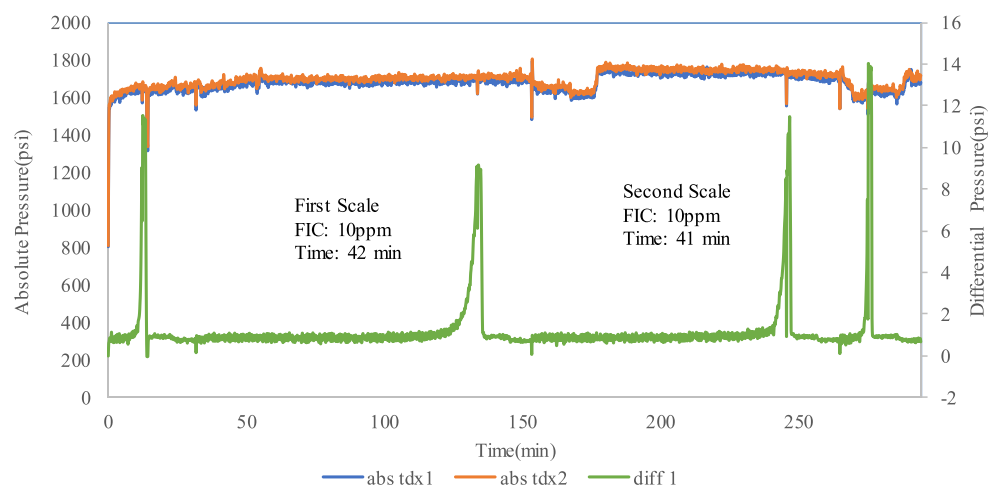


Figure 5. Example of logging data for a scale inhibitor test for determination of FIC and time values for high-pressure dynamic tube blocking experiments of ATMP for barite scale.

The graph in Figure 5 shows the four stages of a tube blocking experiment. Both calcite and barite scaling tests produce similar graphs. The information on the graph is from the absolute pressure in any of the sides of scaling and the differential pressure across the coil. If no scale has been formed, the differential pressure is 1 psi at a flow rate of 9.99 mL/min. Figure 5 also shows an example of the determination of FIC and scaling times, in this case for ATMP and barite scaling. In the first blank test with no SI, the differential pressure rises above 10 psi after 14 min. In this stage, the coil was cleaned using the cleaning solution (Na_4EDTA) and water, which caused a drop in differential pressure to 1 psi. The first stage of the experiment began with injection of 20 ppm of ATMP. No scale was formed at this concentration. The test carried on by injecting 10 ppm of ATMP. During this hour of injection, the pressure difference increased until at 42 min at 10 ppm enough scale was formed to cause a 9 psi pressure difference at which point the injection stopped. Thus, 10 ppm is the FIC and 42 min is the time at that concentration. The process of cleaning the coil by Na_4EDTA and distilled water was then conducted automatically. In order to confirm the repeatability of the tests, the whole procedure was repeated. In this stage, the FIC was observed at 10 ppm after 41 min. The test was finished by another blank test. The scale was formed after 13 min in the second blank test, confirming good reproducibility.

In this paper, we select to use model fluids linked to production from the Heidrun oilfield, Norway. Table 2 presents the water composition of produced fluids from the Heidrun platform in the Norwegian Sea. We used a 50/50 volume mixture of formation water and synthetic seawater to give barite scaling (BaSO_4). The inorganic salts in Table 2 are mixed and stirred to ensure the salts are completely dissolved. They were then degassed for precisely 15 min using a vacuum pump to ensure the dissolved gas is removed. Bubbles in the water phase can cause the pump to stop because they prevent the brine from flowing through the line. We used a similar procedure to prepare Na_4EDTA solution.

2.5. Compatibility Test. The produced water contains divalent cations, which will affect the inhibition efficiency of many SIs. The barium sulfate saturation ratio (SR) of the brine mixture and the presence of divalent cations Ca^{2+} and Mg^{2+} are the main factors that affect the inhibition efficiency of phosphonate-based barite scale inhibitors.^{31,32}

Compatibility tests are necessary to check that the scale inhibitor does not precipitate when combined with formation brines, causing formation damage. In order to examine the compatibility of SIs with calcium ions, solutions with different calcium ion contents were mixed with various inhibitor concentrations to evaluate if precipitation occurs. SIs of 100, 1000, 10,000, and 50,000 ppm were dissolved in 20 mL of deionized water in 50 mL glass bottles. Then, 30,000 ppm sodium chloride (3.0 wt %) and calcium ions in doses from 10 to 10,000 ppm were added. The pH of the solution was adjusted in the range of 4.0–4.5. The bottles were shaken until everything was dissolved and the solution looked clear. The containers were placed in the oven at 80 °C; the test time was generally 24 h. The turbidity and/or precipitation of SIs complexed with calcium ion in the synthetic brine solution were checked after 30 min, 1 h, 4 h, and 24 h.

2.6. Thermal Stability Test. Thermal aging tests are required to ensure that the inhibitor is stable at the high-temperature reservoirs for the anticipated squeeze lifetime. The

inhibitor solution is aged in a static bottle, and then, its scale inhibition performance is compared with a nonaged sample.²

A 2.5 wt % additive solution in deionized water is purged with nitrogen for 1 h and placed in a pressure tube. It is then nitrogen-sparged to minimize the residual oxygen in the tube before heating at 130 °C for 1 week. The aged solution is then examined for its sulfate and carbonate inhibition performance in the dynamic scale loop test.

2.7. The OECD 306 Seawater Biodegradability Screening Test. The Organisation for Economic Development and Co-operation (OECD) has established and approved a series of international standardized procedures (ISO) for the biodegradability test. The authorities have developed quality criteria (GLP, EN 45000, ISO 9000), which are applied to interpret the degree of biodegradation.³³

OECD 306 is a biodegradation procedure that specifically provides how chemical substances biodegrade in seawater. This is a critical parameter for the screening of the ecological behavior of chemicals. The OECD 306 biodegradation testing works as follows:

1. Biodegradability testing measures the complex biochemical process that happens when microorganisms consume a given type of compound. However complicated, the test results measure relatively simple markers of the biodegradation process.
2. A chemical compound's ability to biodegrade depends on the amount of carbon available for microbial consumption.
3. Regulations require biodegradability claims to be associated with aerobic biodegradation, which generally measures oxygen consumption, carbon dioxide (CO_2) production, and the condition of inorganic carbon intermediates.³⁴

In this work, a method based on OECD 306 guidelines is used to determine the marine biodegradability of the SIs, which is an efficient method for screening new SIs in-house and has been utilized by many previous studies in this research field.^{26–30} For each SI, the biological oxygen demand (BOD) was measured using the OxiTop Control manometric system (WTW, Germany) over a 28-day period. By comparing the measured BOD and the calculated theoretical oxygen demand (ThOD) values, the percentage of biodegradability can be calculated. Seawater was used as the test medium, without added inoculum. To ensure nonlimiting conditions for microbial activity and growth, nutrients were added.

To accomplish this test, test flasks containing seawater, nutrients, and the test chemical (SI) are needed. Three different types of control flasks are used as follows: (1) one blank with nutrient amended seawater only, to indicate contamination during the experiment; (2) negative controls with autoclaved seawater, nutrients, and the test compounds at 69 mg/L final concentration; (3) positive controls with nutrient amended seawater and an easily biodegradable substrate, sodium benzoate, at 100 mg/L final concentration. The positive and negative controls are used to minimize the influence of false positives and negatives.

The seawater used in the test (20 L) was collected at NORCE Norwegian Research Centre AS in Mekjarvik (near Stavanger, Norway). At the sampling day, the seawater had a temperature of 12 °C. The collected seawater was stored in a dark room at 20 °C overnight. The next day, seawater (297 mL) was distributed into 510 mL volume amber bottles, and

the nutrient solution was added. The OxiTop control setup was prepared according to recommendations of the manufacturer, and bottles with measuring heads were incubated for 3 h at 20 °C prior to the start of the experiment. After the 3 h incubation, 1.8 mL of a 1.0% (w/w) solution (in distilled water) of each test compound was added to the test and negative control flasks, while 1.0 mL of a 30 g/L sodium benzoate solution was added to the positive control flask. The bottles were capped with measuring heads and placed on magnetic stirrers in the incubator cabinet, and the measuring heads were started immediately.

Oxygen consumption data were recorded over a 28 day period, while all flasks were incubated in the dark at 20 °C. After 28 days, data and results were collected. ThOD of each scale inhibitor was calculated as described in the OECD 306 guidelines, taking into account complete nitrification. Blank oxygen consumption values (BOD values representing background respiration in seawater) were deducted from the BOD of each test compound prior to determining percent biodegradability according to the OECD 306 guidelines.

3. RESULTS AND DISCUSSION

3.1. Chemistry. A series of polyetheramines with different molecular weights (148, 176, 230, 403, and 568) were

Table 3. Blank Tests and Fail Inhibitor Concentration (FIC) Values for Commercial and New Scale Inhibitors (SIs) for Barite Scale

SI (1000 ppm)	barite scale					
	first blank	first scale test		second scale test		second blank
	time (min)	conc. (ppm)	time (min)	conc. (ppm)	time (min)	time (min)
PAPEMP	12	20	28	20	24	10
ATMP	11	10	42	10	41	11
DTPMP	10	5	5	5	9	10
SI-1	10	10	9	10	9	10
SI-2	10	5	20	5	27	10
SI-3	12	2	10	2	14	10
SI-4	10	10	21	10	29	10
SI-5	10	20	26	20	30	11
SI-3 ^a	10	10	31	10	35	10
SI-4 ^a	10	20	37	20	37	10

^aSI-1 and SI-4 were tested for barite scale after thermal aging at 130 °C for 7 days.

phosphonated in-house using the Moedritzer–Irani reaction.²⁵ Linear and branched polyetheramine attached aminomethylenephosphonates have been developed by the reaction of polyetheramine with phosphorous acid, formaldehyde, and hydrochloric acid in water as a benign solvent under refluxing to afford phosphonated polyetheramines (Figure 3). To characterize the target chemicals and to verify the reactions, NMR spectroscopy was used. ³¹P NMR spectroscopy is a powerful common procedure for confirming the phosphorus-containing compounds. For example, the chemical shift (δ) of the phosphonate functional group ($-\text{PO}_3\text{H}_2$) of phosphonated polyetheramine (SI-1) displayed a singlet signal at δ 22.00 ppm. Four other polyetheramine derivatives have been functionalized with aminomethylenephosphonate groups via the Moedritzer–Irani reaction giving SI-2, SI-3, SI-4, and SI-5. The ³¹P NMR chemical shifts of all synthesized SIs linked to

phosphonate groups were observed around δ 22–23 ppm, as presented in Table 1.

3.2. High-Pressure Dynamic Tube Blocking Test. An investigation of the barite and calcite scale inhibition potential of the new SIs was performed in a high-pressure dynamic tube blocking rig at 100 °C and 80 bar. In all experiments, consistent results were obtained from the first and second SI tests. There is an undeniable relationship between pH and scale inhibition, which is due to the protonation of the SI. For the barite scale, previous studies found that a rise in the pH of the crystal growth medium over a pH limit of 4–9 gives an enhancement in inhibitor performance. In contrast, the poor inhibitor performance is exhibited at pH < 4.27.³⁵ Therefore, in this study, the pH of the SIs prepared in the 1000 ppm solution was adjusted to 4–6 in order to be at typical oil and gas reservoir pH.

Table 3 shows the barite scale inhibition results for the in-house synthesized SIs and several commercial SIs for comparative purposes. Table 3 shows the results for two blank tests (with no injection of SI) and also two SI tests under the same conditions. For the barite scale tests, the scale formation time for blank tests is 10–12 min. For the commercial phosphonate SIs, DTPMP and ATMP show good inhibition performance with FIC values of 5 and 10 ppm, respectively. The weakest barite scale inhibition belongs to PAPEMP, which failed at 20 ppm after 28 min.

In contrast, all five of the new SIs gave good to excellent barite scale inhibition compared to the commercial SIs. Among the new SIs, SI-2 and SI-3 are the chemicals that were synthesized from the linear polyetheramines. The difference between SI-2 and SI-3 is the length of their chain and, therefore, their molecular weight. Table 3 shows that SI-3 gave the best barite scale inhibition results by failing at 2 ppm, after 10 and 14 min in the first and second tests, respectively.

Figure 6 shows a graphical plot obtained for the barite scale tube blocking test using SI-3, also summarized in Table 3. In the first test with inhibitor, we obtained a FIC value of 2 ppm after 10 min and in the second test at 2 ppm and after 14 min. This was a better result than all of the commercial phosphonates but also shows good test reproducibility, which was a consistent observation throughout the study. SI-2 showed weaker inhibition performance with a FIC value of 5 ppm after 20 and 27 min in the first and second tests, respectively (Figure 7). SI-1 and SI-4 both failed at the same concentration of 10 ppm. The weakest scale inhibition result for the sulfate test was obtained from testing SI-5, in which the scale was formed at 20 ppm.

The experimental data for commercial and synthesized SIs for calcite scale inhibition are summarized in Table 4. In general, most SIs showed lower FIC values for calcite scale compared to barite scale, except ATMP and DTPMP. ATMP and DTPMP SIs failed at 20 and 10 ppm, respectively. PAPEMP showed an excellent inhibition performance for carbonate scale with a FIC value just inside the 1 ppm 1 h window. As explained in our previously published articles, ATMP and DTPMP are not very compatible with Ca^{2+} ions.²⁶

The results from the calcite scale test for the in-house SIs are given in Table 4. All of the synthesized SIs were observed to give excellent calcite scale inhibition. In particular, SI-3 gave no carbonate scaling even after 1 h at the lowest concentration of 1 ppm, as shown in Figure 8. Also, the calcite scale test for SI-2 gave an excellent result, failing at 1 ppm after 58 min (Figure 9) in both tests. SI-1 showed the weakest result with FIC of 5

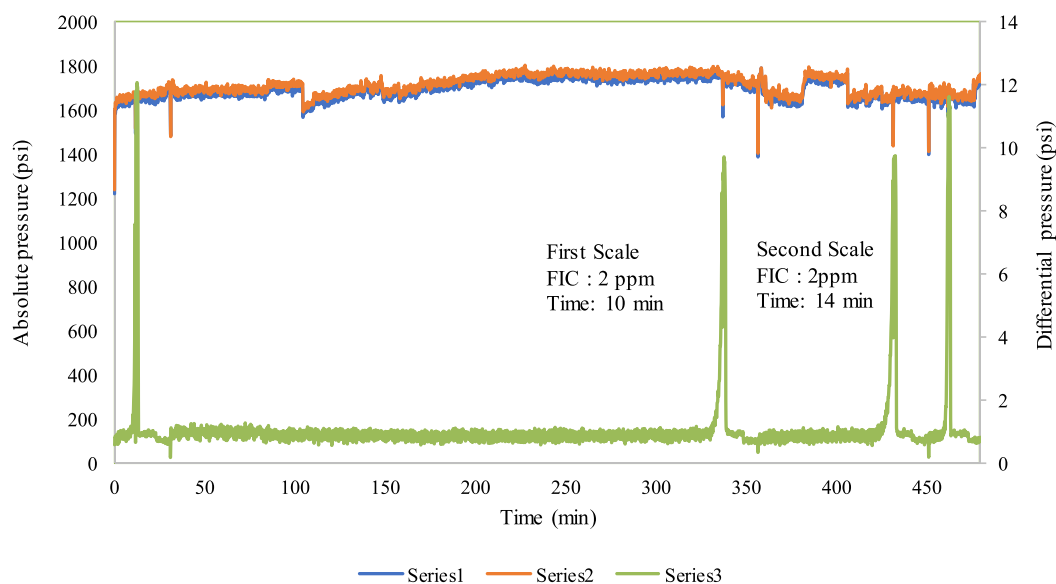


Figure 6. FIC and time values from high-pressure dynamic tube blocking experiments of SI-3 for barite scale.

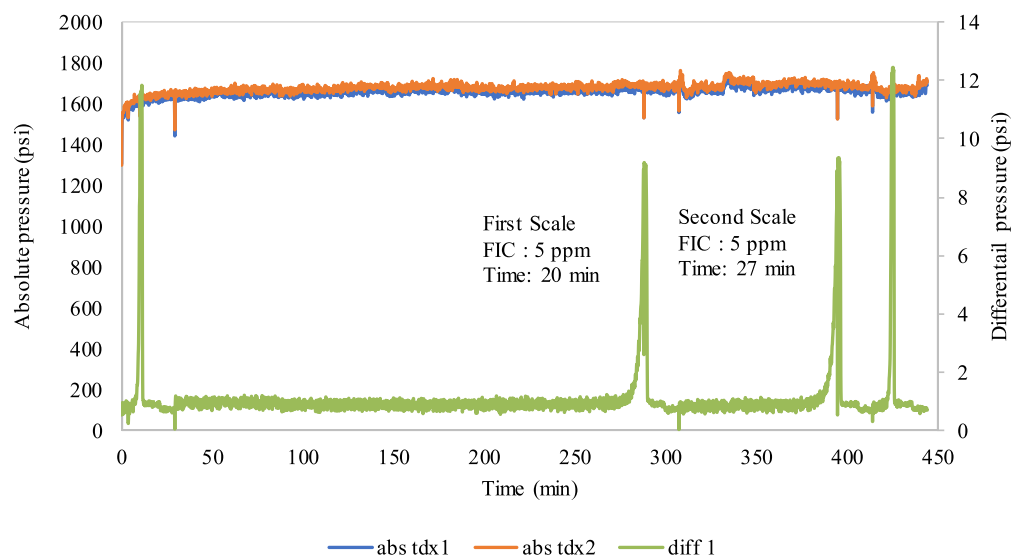


Figure 7. FIC and time values from high-pressure dynamic tube blocking experiments of SI-2 for barite scale.

ppm, but this is still better than two of the commercial phosphonates, ATMP and DTPMP.

In summary, these results show that all of the tested SIs gave lower FIC values against calcite scale formation than the barite scale, except for DTPMP and ATMP. Low compatibility of the two commercial phosphonates with divalent metal ions might be the reason for the poor performance of DTPMP and ATMP for carbonate scale, as explained previously.^{8–11,26}

The results from the in-house synthesized SIs suggest that the phosphonated linear polyetheramines are better SIs than the phosphonated branched polyetheramines. The two best products SI-3 and SI-2 are synthesized from linear polyetheramines with different molecular weights (176 and 148, respectively) and containing two ether linkages in the main backbone. As mentioned in the previous studies, the distances between the aminomethylenephosphonate groups play a key role in the oilfield scale inhibition performance.²⁶ Thus, SI-3 with longer distances between aminomethylenephosphonate

groups has a better inhibition performance than SI-2, as shown in Tables 3 and 4.

3.3. Thermal Stability Test. Long-term thermal aging tests were carried out for the best linear and branched phosphonated polyetheramine SIs. The specific objective of this experiment is to investigate the thermal stability of the SIs at a fairly high reservoir temperature for squeeze application.³⁶ 5 wt % solutions of linear phosphonated polyetheramine (SI-3) and branched phosphonated polyetheramine (SI-4) were thermally aged at 130 °C for 1 week under anaerobic conditions. The aged SIs were retested in dynamic tube blocking scale inhibition tests for barite and calcite scaling. The experimental results are presented in Tables 3 and 4 for both the untreated and thermally aged samples.

SI-3 showed weaker performance after aging, changing from a FIC of 2 to 10 ppm for barite scaling (Figure 10). However, thermal aging had less of an effect on its inhibition ability for calcite scale. In the preaging test, no scale was formed when SI-3 was injected at its lowest concentration of 1 ppm, but after

Table 4. Fail Inhibitor Concentration (FIC) Values for Commercial and New Scale Inhibitors (SIs) for Calcite Scale

SI (1000 ppm)	calcite scale					
	first blank	first scale test		second scale test		second blank
	time (min)	conc. (ppm)	time (min)	conc. (ppm)	time (min)	time (min)
PESA	10	2	6	2	1	10
PAPEMP	10	1	4	1	15	11
ATMP	11	20	26	20	26	12
DTPMP	10	10	20	10	20	12
SI-1	10	5	4	5	6	10
SI-2	12	1	58	1	58	14
SI-3	10	<1 ^a		<1 ^a		10
SI-4	12	2	20	2	20	12
SI-5	17	2	8	2	10	15
SI-3 ^b	10	1	20	1	20	14
SI-4 ^b	11	2	17	2	17	10

^aNo scale was formed during the test. ^bSI-1 and SI-4 were tested for calcite scale after thermal aging at 130 °C for 7 days.

the aging test, the calcite scale was formed at a FIC value of 1 ppm and after 20 min (Figure 11). This is still a very impressive performance. Thermal degradation may have been even less if the SI is aged on the reservoir rock.³⁷

A possible reason for the loss of inhibition performance of SI-3 and SI-4 may be due to the hydrolysis. We speculate that the backbone of polyether may not be stable to the thermal aging process used, leading to hydrolysis of the ether linkage to give alcohol derivatives.

3.4. Calcium Compatibility Test. One of the main factors to consider in squeeze treatment is the compatibility of the SI with calcium ions, particularly for phosphonate-based SIs compared with polycarboxylate or polysulfonate SIs.^{2,12,26} A series of compatibility tests were conducted at 80 °C to achieve a solid understanding of the compatibility of the in-house synthesized SIs with calcium ions. SI-2 and SI-3 gave the best scale inhibition performances for barite and calcite scales, and therefore, we decided to monitor the calcium tolerance of these SIs. The range for the SI concentration was from 100 to 50,000 ppm, and the calcium ion concentration varied from 100 to 10,000 ppm in the presence of 30,000 ppm of NaCl. It

was found that the phosphonated polyetheramines SI-2 and SI-3 showed an excellent compatibility performance with all concentrations up to 10,000 ppm of Ca²⁺ ions over the 24 h test period. We have illustrated the most extreme matrix investigated in Table 5. A possible explanation is the polyether linkage in the SI backbones which can chelate with calcium ions.

Table 5. Compatibility Test in 10,000 ppm of Ca²⁺ and 30000 ppm (3.0 wt %) of NaCl for SI-2 or SI-3

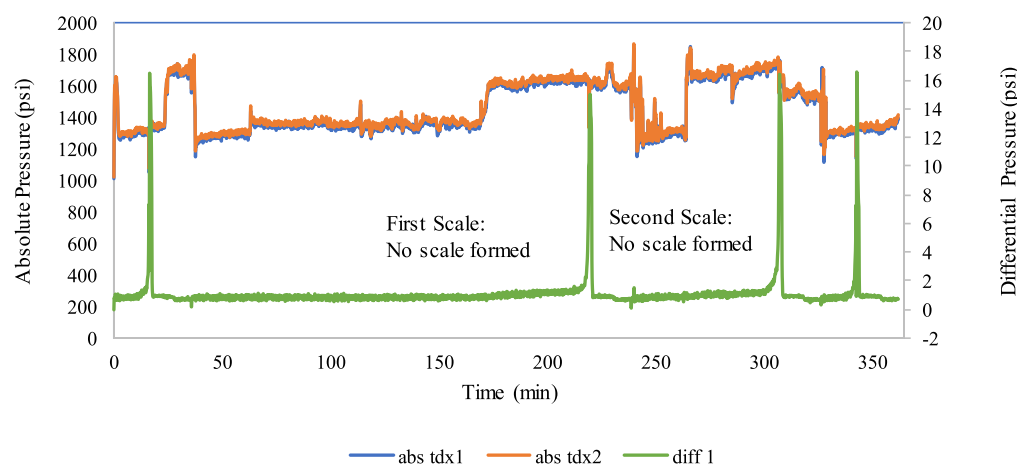
dose (ppm)	appearance				
	at mixing	30 min	1 h	4 h	24 h
100	clear	clear	clear	clear	clear
1000	clear	clear	clear	clear	clear
10000	clear	clear	clear	clear	clear
50000	clear	clear	clear	clear	clear

Table 6. Biodegradability Activity Measured by the OECD 306 Procedure over 28 Days

chemical	% BOD28 by OECD 306
seawater	0
sodium benzoate	90
DTPMP	15 ²⁶
ATMP	34 ²⁶
SI-1	13
SI-2	47
SI-3	24
SI-4	21
SI-5	18

3.5. Biodegradation Test. All synthesized linear and branched phosphonated polyetheramines SI-1, SI-2, SI-3, SI-4, and SI-5 were tested for their biodegradation activities using the OECD 306 protocol for biodegradability in seawater using the closed bottle method over 28 days.

A summary of the seawater biodegradation studies is given in Table 6. Tests are conducted in triplet and the average BOD28 given. The data including previous studies in our laboratory using the same test method showed a poor degradation of 15% in 28 days for DTPMP and moderate biodegradation of 34% for ATMP.²⁶ The reference chemical sodium benzoate degraded very well with no notable lag time,

**Figure 8.** FIC and time values from high-pressure dynamic tube blocking experiments of SI-3 for carbonate scale.

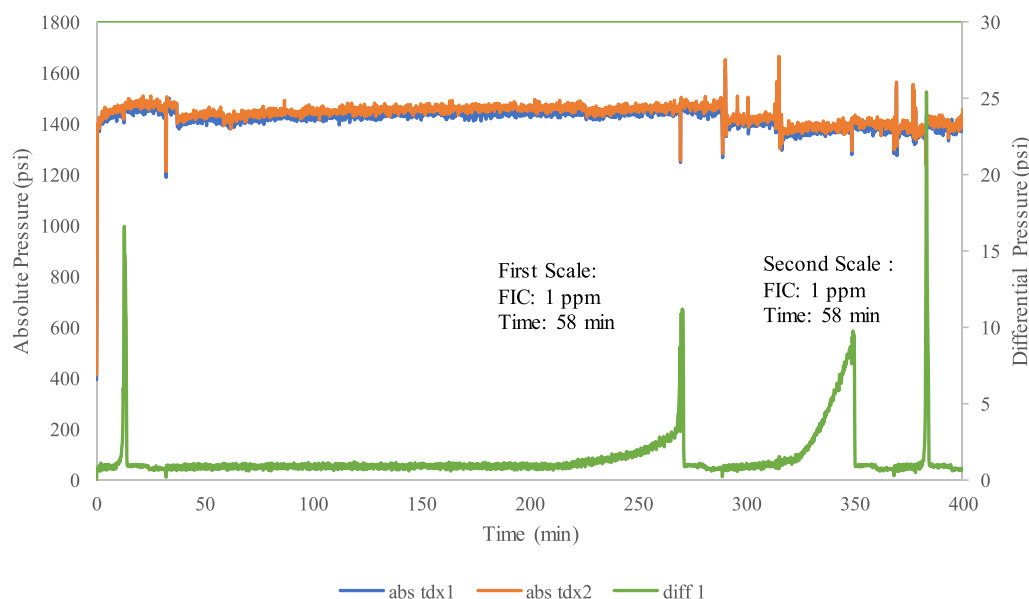


Figure 9. FIC and time values from high-pressure dynamic tube blocking experiments of SI-2 for carbonate scale.

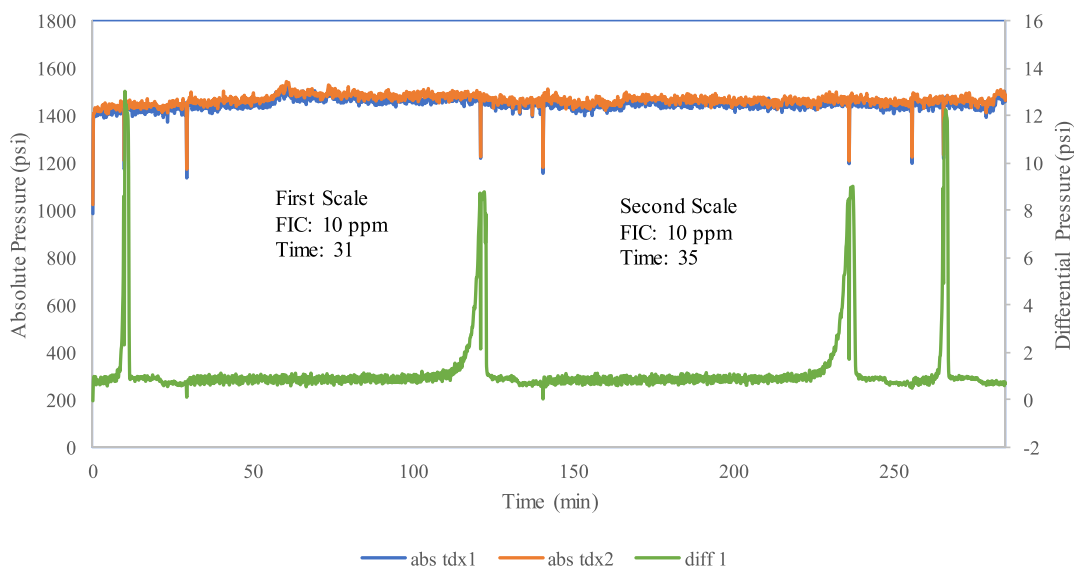


Figure 10. FIC and time values from high-pressure dynamic tube blocking experiments of aged SI-3 at 130 °C for 1 week for sulfate scale.

giving 28-day biodegradation of about 84–94% (average 90%), as described previously.²⁶ In-house phosphonated polyetheramines showed moderate to good biodegradation activity. The linear phosphonated polyetheramines SI-2 and SI-3, which showed the best inhibition performances, gave BOD28 values of 47 and 24%, respectively. With expected low bioaccumulation (due to high water solubility) and ecotoxicity, this would make these SIs environmentally acceptable in many offshore regions.

Interestingly, these were the two highest BOD28 values obtained for the new phosphonated polyetheramine SIs, and they both had ethoxylate polyether linkages, not propoxylate groups. In addition, the backbone structure of these polymers was neither branching and a tertiary carbon atom as in SI-4. It is known that branching in the chain structure has a role in determining the biodegradation rates and mechanism of alkoxyated products.^{38–41} Products with monobranched alkyl groups exhibited biodegradation rates slower than the linear

ones. Based on the above results, it appears that that the backbone of polyetheramines should be unbranched for best seawater biodegradation.

4. CONCLUSION

In this research project, we have synthesized and investigated a new class of phosphonated polyetheramines, both linear and branched, as potential oilfield SIs. All of the new products showed a high inhibition capability against both calcite and barite scale, often better than commercial phosphonated SIs. Linear phosphonated polyetheramines gave the best results compared to the branched molecules. For example, SI-3, synthesized from linear polyetheramine with a molecular weight of 176, showed excellent barite inhibition with a FIC value of 2 ppm and superior calcite scale inhibition in that no scale formed at the lowest injected concentration (1 ppm).

The two best inhibitors, SI-2 and SI-3, showed excellent compatibility with Ca^{2+} up to 10,000 ppm. Anaerobic thermal

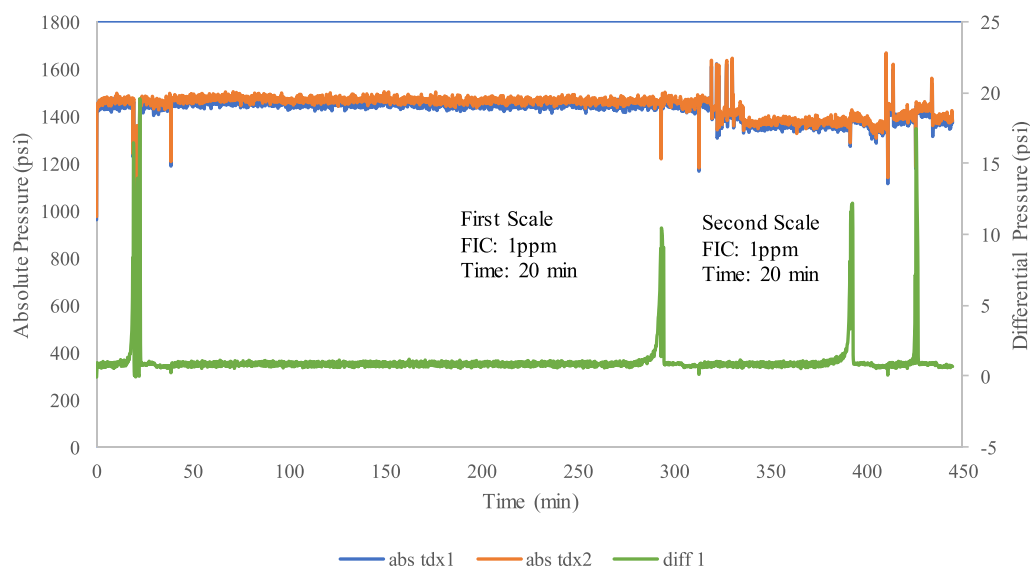


Figure 11. FIC and time values from high-pressure dynamic tube blocking experiments of aged SI-3 at 130 °C for 1 week for carbonate scale.

aging of the SIs for 1 week at 130 °C showed good thermal stability by giving just a small decline in scale inhibition performance. Linear phosphonated polyetheramines (SI-2 and SI-3) showed good to moderate seawater biodegradation by the OECD 306 test. SI-2 showed the highest biodegradation amounts of 47% in 28 days, while SI-3 gave reasonable biodegradation of 24% over 28 days.

Overall, the oilfield barite and calcite scale inhibition performance, calcium compatibility, thermal stability, and seawater biodegradation make linear phosphonated polyetheramines strong candidates as potential oilfield scale squeeze inhibitors. We are planning to study the SIs in more detail, including adsorption properties on formation rock using static adsorption tests, sand pack columns, and eventually core flooding. Due to the number of phosphonate groups in the backbone of SIs, we assume these SIs will afford efficient squeeze properties with longer squeeze lifetimes.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.0c01636>.

Table S1, chemical structure and spectra data of phosphonated polyetheramine SIs; Figure S1, the scale rig used for high-pressure tube blocking testing of SIs (PDF)

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Notes

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