



Synthesis of unexplored aminophosphonic acid and evaluation as scale inhibitor for industrial water applications

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ABSTRACT

A new aminophosphonic acid was synthesized by condensation of 4,4'-(propane-2,2-diylbis(4,1-phenylene) bis(oxy)dianiline), phosphorous acid and formaldehyde, according to the Moedritzer-Irani reaction. The structure of the inhibitor was analyzed by ¹H and ³¹P NMR, FT-IR, mass spectrometry and thermogravimetry.

The new inhibitor presented high efficiency in a static condition on the model imitating water composition with respect to CaCO₃ and CaSO₄ deposits. The crystal formation of CaCO₃ and CaSO₄ was investigated by scanning electronic microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). The inhibitor obviously affected the procedure of crystal growth. The morphology of the CaCO₃ crystals, in the absence of inhibitor, showed a predominant content of rhombohedral crystals (calcite), whereas in the presence of inhibitor we could observe a mixture of calcite with acicular crystals (aragonite) and a small content of spherical crystals (vaterite). Concerning CaSO₄ crystals, thin needles with a smooth surface were observed in the absence of the inhibitor, which became thicker with many crystal defects in the presence of the inhibitor.

Consequently, the new aminophosphonic acid described here can be used as a potential scale inhibitor.

1. Introduction

The precipitation of insoluble or slightly soluble salts in steam generators, boilers, cooling towers, pipes and other equipment used in water-intensive processes is a serious problem. Deposits of alkaline earth ions in the form of carbonates and sulphates is of particular concern, since these salts usually have a solubility that decreases with increasing temperature (inverse solubility) [1]. Can and Üner [2] showed that the formation of salts begins at a temperature of 30–35 °C and their deposit increases with that of temperature. In addition, this process is intensified with the evaporation of water. It was previously described that many brines found in oil-bearing strata of offshore reservoirs contain high concentrations of alkaline-earth-metal ions (Ba²⁺, Ca²⁺, Sr²⁺ and Mg²⁺) [3]. During secondary oil recovery, seawater containing SO₄²⁻ is injected into the reservoir to maintain pressure. When the water reaches the oil well, a solid precipitate is formed, which blocks production tubing and can cause damage to the

reservoir itself. This problem is widely spread in the oil industry. In Kazakhstan, mineralized water in oil fields reaches 20–80% [4]. In some cases, mineralization reaches 220–250 g/L, which leads to high levels of salt deposits [5]. An expensive solution to this problem is to decrease the sulphate concentration in the seawater by reverse osmosis prior to injection. A far cheaper alternative is the use of chemicals. These chemicals either prevent the mineral scale from forming, or alter the precipitate to such an extent that the scale no longer presents a problem [6–9]. The main conventional mechanisms for inhibiting scaling are chelation, dispersion, crystal distortion, and threshold action [10–12].

Inorganic polyphosphates, primarily tri-polyphosphate and sodium hexa-metaphosphate (SHMP), have been widely used as scale inhibitors. It is assumed that the active mechanism of SHMP as an inhibitor is due to its adsorption onto the surface of CaCO₃ microcrystals, which hinders their growth and agglomeration. The main significant disadvantage of inorganic polyphosphates is their low thermal stability,

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leading to a loss of inhibitory properties, a propensity to hydrolyse into orthophosphates with the formation of insoluble calcium salts and a low efficiency with respect to CaSO_4 . Entering productive horizons with fresh water, SHMP activates the development of sulphate-reducing bacteria. As a result, there is a tendency to limit the use of polyphosphates [13].

Nowadays, synthetic water additives are used that prevent scaling, such as phosphonates, phosphonocarboxylates, organic sulphonates and phosphonated polymers, which are very efficient at preventing scaling [14].

Close attention is paid to inhibitors based on chelating agent. They are divided into two types depending on the mechanism of action [15]:

1. Inhibitors based on carboxyl-containing moieties that can bind to calcium ions prevent the formation of precipitates of sulphates or carbonates when they are used in a stoichiometric ratio.
2. Inhibitors based on phosphonic groups have a “threshold” effect and act as chelatants. In a sub-stoichiometric ratio they are able to inhibit the growth of crystals of precipitating salts. These inhibitors also have a crystal destruction effect in the case of the formation of crystal nuclei. They are able to alter the shape of the embryonic crystal and slow down its growth.

The principle attention currently being paid worldwide is to scale inhibitors based on phosphorus-containing chelating agent [16]. The main companies developing such molecules are “Monsanto Co” (Dequest), “Nalco” (Visco), in the USA; “Mirriko” (Descum-2) in Russia; “Manuchar NV” in Belgium; “Roemex Limited” in the UK.

Some reagents present drawbacks when they are used in oil and gas fields. Certain scaling inhibitors are thermally unstable [17,18]. The concentration of most inhibitors is quite elevated (10–20 mg/L) [19], which causes extremely high costs, so the use of these reagents is not always economically justified [20–22].

In the present work, we describe the synthesis of a newly identified organophosphorus scale inhibitor and its efficiency for carbonate and calcium sulphate deposits under static conditions in model solutions.

2. Experimental section

2.1. Material and methods

Phosphorous acid > 98% (Alfa Aesar, Karlsruhe, Germany) and formaldehyde solution 37 wt.% in H_2O (Sigma-Aldrich) were used. Other chemicals were purchased from Sigma-Aldrich and Alfa Aesar and were used as received without additional purification.

Fourier-transformed infrared spectra (FTIR) were obtained with a Bruker Tensor II. NMR spectra (^1H and ^{31}P) were obtained on a Bruker Advance spectrometer at 300 Mhz. Mass spectra were recorded on LC-MS-2020 Shimadzu (electrospray ionization ESI+, 150–900). Reverse-phase-high-performance liquid chromatography (HPLC) was performed on Prostar HPLC (Varian). Analytical HPLC was carried out with a Pursuit 5-C18 column (2.5 μm , 4.6 \times 150 mm, Varian). Thermogravimetric analysis was realized on a LABSYS EVO TGA-DSC instrument up to 1600 °C. Micrographs and EDX spectra were obtained on a scanning electron microscope (SEM) JEOL JSM-6490LV instrument.

2.2. Synthesis of propane-2,2-phenylene-diylbis(4,1-phenylene bis (4,1 bis (azanediyl) bis (methylene) diphosphonic acid)

The synthesis of the inhibitor was carried out according to the

Moedritzer-Irani reaction [23,24].

A two-necked round bottom flask (100 mL) equipped with a magnetic stirrer and reflux was placed under azote with an additional funnel attached. 4,4'-propane-2,2-diylbis(4,1-phenylene)bis(oxy)dianiline (0.41 g, 1 mmol) was dissolved in hydrochloric acid (1.95 mL). Phosphorous acid (0.33 g, 40 mmol) was dissolved in water (2.2 mL). The two solutions were mixed together and the reaction mixture was stirred under reflux (temperature: 115 °C). After the mixture became a homogeneous phase (brown colour), formaldehyde (0.30 g, 100 mmol) was added dropwise over 1 h. The reaction mixture was stirred for 72 h. The process was monitored by thin layer chromatography (TLC) and ^{31}P NMR. The solution was cooled to room temperature and the solvent was removed on a rotary evaporator. To remove unreacted formaldehyde and phosphorous acid, ethyl alcohol containing 10% distilled water (\approx 100 mL) was added and the mixture was heated under reflux for 3 h. Hot filtration was performed to separate the liquid and solid phases. The product was extracted from the precipitate with boiling acetone. The resulting yellow oil was purified by column gel chromatography with Sephadex G-25 gel, which had been previously swollen in triethanolamine carbonate for about 8 h in the fridge. A solution of triethanolamine carbonate was used as the eluent. A yellow oily liquid was obtained and washed several times with methanol and evaporated [25,26].

^1H NMR (300 MHz, $\text{DMSO}-d_6$): δ ppm = 1.60 (br d, $\text{CH}_3\text{-C-CH}_3$), 3.22–3.41 (m, CH_2P), 6.78 (m, H-Ar), 6.95 (d, H-Ar), 7.13 (m, H-Ar), 7.24 (d, H-Ar), 7.37 (d, H-Ar).

^{31}P NMR (300 MHz, $\text{DMSO}-d_6$): δ ppm = 0.00 (peak of reference H_3PO_4), 2.59 (initial peak phosphonic acid) 22.13 (s, $\text{O} = \text{P}(\text{R})(\text{OH})_2$).

MS (electrospray ionization ESI $^+$): m/z calc. for $\text{C}_{29}\text{H}_{32}\text{N}_2\text{O}_8\text{P}_2$ [$\text{Mi} + \text{Na}$] $^{2+}$ 310.58, found 310.58.

2.3. Static tests for scale inhibition

The evaluation of the effectiveness of the scale inhibitor against calcium carbonate and calcium sulphate deposits under static conditions was carried out according to previously described methods [27–29]. The static laboratory method consists of precipitating CaCO_3 and CaSO_4 from water, i.e. heating with or without the presence of a scale inhibitor. In our work we used formation water of the chloride-calcium and sulphate-calcium type.

The salt composition that simulates carbonate deposits is $\text{Ca}^{2+} = 1100 \text{ mg/L}$, $\text{Mg}^{2+} = 380 \text{ mg/L}$, $\text{Na}^+ = 7500 \text{ mg/L}$, $\text{HCO}_3^- = 976 \text{ mg/L}$, $\text{Cl}^- = 14023 \text{ mg/L}$. Two solutions are required to imitate scale formation. Solution 1 contains calcium chloride 3046 mg/L and hexavalent magnesium chloride 3177 mg/L, while solution 2 is sodium chloride 18084 mg/L and sodium bicarbonate 1344 mg/L.

The effectiveness of scale inhibition was determined for concentrations of 10, 30, 50, 70, 100, 150 or 200 ppm of solution 1 in 50 mL. This was mixed with 50 mL of solution 2. Lids were placed on the flasks, the temperature was fixed at 75 °C for 5 h. Then the samples were filtered and the calcium ion content determined. 10 mL of filtrate were placed in the conical flasks and 40 mL of distilled water, 2.5 mL of 20% sodium hydroxide solution and 10–15 mg of a mixture of murexide and sodium chloride were added.

Secondly, the salt composition simulating sulphate (gypsum) deposits is $\text{Ca}^{2+} = 4911 \text{ mg/L}$, $\text{Mg}^{2+} = 148 \text{ mg/L}$, $\text{Na}^+ = 11623 \text{ mg/L}$, $\text{SO}_4^{2-} = 8792 \text{ mg/L}$, $\text{Cl}^- = 20291 \text{ mg/L}$. To prepare the imitation of scale formation in this case, two further solutions are needed. Solution 3 is calcium chloride 1360 mg/L, while solution 4 contains sodium chloride 18800 mg/L, hexahydrate magnesium chloride 1240 mg/L and sodium sulphate 13000 mg/L.

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