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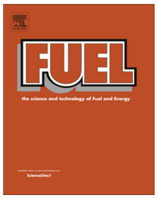

Theoretical and experimental insights into the control of calcium sulfate scales by using random copolymers based on itaconic acid

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HIGHLIGHTS

- Control of $CaSO_4$ scales by a new itaconic acid–sodium vinyl sulfonate copolymer.
- Theoretical–experimental research of the supramolecular assembly copolymer-$CaSO_4$.
- Evaluation of a industrial prospective of copolymer in incompatible water systems.

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ABSTRACT

A new itaconic acid (IA)–sodium vinyl sulfonate (VS) copolymer is proposed to control the formation of calcium sulfate scales. The supramolecular interacting system IA–VS copolymer-calcium sulfate scales was characterized by means of scanning electronic microscopy, X-ray powder diffraction analysis, Fourier transform infrared spectroscopy, differential thermal analysis, density parameters, X-ray fluorescence and atomic absorption spectroscopy, as well as molecular modeling through density functional theory. Industrial potential of the IA–VS copolymer and its operation in an incompatible water system having scaling calcium salts are also evaluated. Results show that the IA–VS copolymer is able to control growing of inorganic mineral scales through the formation of supramolecular complexes, which are soluble in aqueous solution and can induce morphological changes into the precipitated material.

1. Introduction

Inorganic scales formation taking place in the oil reservoirs, drilling systems, production systems and surface equipment is a major operational problem that impacts negatively in the production stride of the oil industry [1–3]. Specifically, calcium sulfate ($CaSO_4$) and calcium carbonate ($CaCO_3$) are the most common mineral scales encountered [4], and they generate formation damage and obstruction of production pipe-lines leading to a reduction of the oil production rate and consequently to significant economic losses [5–8]. Those mineral scales present inverse solubility, which means that as the system temperature increases its solubility decreases. Specially, in carbonated reservoirs with extreme conditions of high temperature and high salinity, scale formation represents huge and critical technological challenges to be solved [7–9].

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Typically, in oil reservoirs with low or intermediate temperatures the mineral scale problems have been solved using scale inhibitors of the phosphonate type [5,9–11]. However, when temperatures are higher than 150 °C, this class of chemical products shows a poor performance or even fails, mainly due to thermal decomposition of the phosphonate chemical group [7,12]. For this reason, the development of new chemicals with antiscale properties acting at high temperature, and the corresponding deep understanding of the chemical mechanism by which they control mineral scale problems, are a worldwide objective [7–9,11].

Recently, it has been reported a new group of polymeric scale inhibitors which have the characteristic of being sulfonated-carboxylic acid copolymers that prevent calcite scale formation under oil reservoir conditions at high temperature (177 °C) and with brine with low calcium concentration (100 mg L^{-1}) [7]. Likewise, our research and technological development team has developed a new type of random copolymers derived from itaconic acid or its isomers and alkenyl sodium sulfonates, which have the attribute of preventing sulfate and carbonate scale formations under reservoir conditions at high temperature (163 °C) and brine with high calcium concentration (1,500 mg L^{-1}) [8].

As a contribution to the efforts to attack the negative impact that the calcium sulfate scaling has in different industrial processes, in the present work it is determined the capability of a new itaconic acid (IA)–sodium vinyl sulfonate (VS) copolymer to control calcium sulfate scale formation at high temperatures (even until 195 °C). Likewise, through theoretical and experimental studies, it is proposed the supramolecular complexes formation as the key chemical mechanism behind the showed excellent performance for this new antiscaling IA–VS copolymer.

2. Experimental methodology

2.1. Synthesis

A IA–VS random copolymer (Fig. 1) was synthesized from analytically-pure-grade Aldrich IA and VS, according to a method previously reported [8]. Distilled water was used in all studies.

2.2. Standard precipitation of $CaSO_4$ and $CaCO_3$ systems

All precipitation experiments were carried out in duplicate and followed the Standard NACE TM0374-2007 [13]. All chemical scales inhibitor dosages given below were considered on a 50% of the active basis obtained from the synthesis of the IA–VS copolymer. J.T. Baker analytical reagents were used throughout and distilled water was employed. Calcium sulfate was precipitated from supersaturated solutions prepared by mixing $CaCl_2{\cdot}2H_2O$ and Na_2SO_4 analytical reagents, as described below. All Ca^{2+} ions concentration remaining in the solutions were determined by means of Perkin–Elmer atomic absorption spectrophotometers, 5000 and AA300 models.

The supersaturated solutions were prepared from separate glass bottles, one containing 10 mL of $CaCl_2{\cdot}2H_2O$ solution (11.10 g L^{-1} as Ca^{2+}) and the other 10 mL of Na_2SO_4 solution (10.66 g L^{-1} as SO_4^{2-}). Then, the bottles were kept at room temperature for 5 h to stabilize their temperature. After that time, these solutions were mixed in a glass tube of 20 mL capacity immersed in a temperature-controlled bath. The precipitation of the calcium sulfate supersaturated solutions were monitored, after this was heated for 24 h at 70 °C, by analyzing aliquots of the filtered solutions using 11-μm pore-size filters to measure the Ca^{2+} concentration through atomic absorption spectroscopy (AAS).

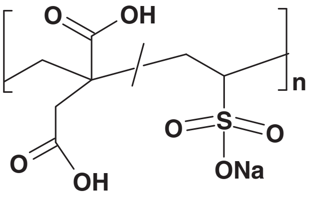

Fig. 1. Scheme of the itaconic acid and sodium vinyl sulfonate random copolymer.

In another series of experiments performed under the same above described conditions, precipitations of calcium sulfate solutions were carried out adding, to the $CaCl_2$ solutions before mixing with Na_2SO_4 solutions, IA–VS copolymer at 0.02 and 0.04 wt%, which are the concentrations that lead to the best reported efficiency of the antiscaling agent [8]. The inhibitor efficiency was measured by using Eq. (1),

$$\text{Inhibition}\% = \frac{[Ca^{2+}]_{\text{in sample after precipitation}} - [Ca^{2+}]_{\text{in blank after precipitation}}}{[Ca^{2+}]_{\text{in blank before precipitation}} - [Ca^{2+}]_{\text{in blank after precipitation}}} \times 100 \quad (1)$$

where $[Ca^{2+}]$ is the concentration of Ca^{2+} ions. The after-precipitation sample and after-precipitation blank are the filtrates obtained after that calcium sulfate supersaturated solutions, containing and not containing scale inhibitor, respectively, were heated for 24 h at 70 °C. In turn, the before-precipitation blank refers to the sample at the beginning of the experiment.

Once the IA–VS copolymer inhibited the precipitation of $CaSO_4$ crystals, it was investigated the effect of the chemical over $CaSO_4$ crystals previously precipitated from supersaturated solutions containing $CaCl_2{\cdot}2H_2O$ (22.20 g L^{-1}) and Na_2SO_4 (21.32 g L^{-1}). The morphologies of precipitated calcium sulfate were analyzed by scanning electron microscope (SEM), Fourier transform infrared (FTIR) spectra and X-ray diffraction (XRD) analysis techniques.

Calcium–carbonate precipitation experiments were carried out using solutions of $CaCl_2{\cdot}2H_2O$ (12.15 g L^{-1}), $NaHCO_3$ (7.36 g L^{-1}) and $MgCl_2{\cdot}6H_2O$ (3.68 g L^{-1}) also in accordance with the Standard NACE TM-0374-2007 [13]. The morphologies of calcium carbonate crystals were tested also by SEM, FTIR spectra and XRD analysis methods.

2.3. Precipitation of $CaSO_4$ and Sr^{2+}

In order to analyze the antiscale operation of IA–VS copolymer under the presence of two different divalent cations, it was further added with 498 mg L^{-1} of $SrCl_2$ to the final solution of $CaSO_4$ precipitation tests in the sake of having a molar ratio of $Ca^{2+}/Sr^{2+} \sim 12$, *i.e.*, greater than unity as that (~39.54) occurred in the water system resulting from the mixing between congenital water (CW) and seawater (SW) (Table 1) in a volume relationship CW:SW of 1:3. The formed scales were analyzed by SEM, and the amount of calcium dispersed, both with and without the addition of IA–VS random copolymer to the $CaCl_2{\cdot}2H_2O$ solution at 0.02 wt%, was analyzed by AAS.

2.4. Precipitation of $CaSO_4$ under high pressure and high temperature

Calcium sulfate was precipitated from supersaturated solutions as described above from a mixing of $CaCl_2{\cdot}2H_2O$ (11.1 g L^{-1}) and Na_2SO_4 (10.66 g L^{-1}) solutions, which were placed in a glass batch reactor preserving a 1–1 volume relationship. Different experiments were carried out at 145 psi of pressure during 24 h at each of the 120, 150, and 195 °C temperatures. At the end of experiments, Ca^{2+} concentrations were analyzed in aliquots of the remaining filtered solution using 11-μm pore-size filters by