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Influence of polymer bases on the synergistic effects obtained from mixtures of additives in the petroleum industry: Performance and residue formation

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Abstract

Undesirable residue formation and lower performance can be observed during the use of polymer-based chemical additives in the petroleum industry when such compounds are mixed during a number of operations, such as oil production. In this work a demulsifier, a flocculant and a scale inhibitor and their respective polymeric bases were tested. These were evaluated through specific performance tests for each additive and a solubility test to assess residue formation. By correlating the performance of commercial additives and the respective polymeric bases, we can conclude that the polymeric base is responsible for the positive synergistic effects on demulsifier performance in the presence of other additives and for the negative synergistic effects on scale-inhibiting performance, also in the presence of other additives. Moreover, we found that the polymeric base can be responsible for the residue formation from the scale inhibitor and flocculant mixture, although it is not be responsible for the residue formation of the flocculant alone.

Keywords: Synergy; Performance tests; Polymer additives; Demulsifier; Flocculant; Scale inhibitor

1. Introduction

Chemical additives, especially polymeric additives, are widely used in the oil industry in a large number of operations, such as drilling, production, transportation and treatment. Such additives are used to correct operational problems as well as in the operation itself. Problems such as inorganic deposition, emulsion build-up and corrosion are very common during such operations and are solved through the addition of varied chemical additives at different concentrations (Hudgins, 1994; Davies et al., 1996, 1997).

Commercial additive formulations can contain more than one kind of active component, also known as base. Normally, each base has a particular effect on each kind of oil to be treated, and solvents are added to the formulation, such as aromatic compounds and alcohols, working as co-additives and/or to render the formulation less viscous and pumpable, so as to allow injection in line (Grace, 1992).

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Since usually petroleum is produced together with water and gas, so-called demulsifiers are added to destabilize the water-in-oil (W/O) emulsions. Such emulsions can form depending on the petroleum composition and on the turbulent flow regimen associated with the production technique. Such products aim at promoting the separation and removal of water from the oil, and at the same time preventing the separated water from containing a high residual oil content, which could cause the formation of oil-in-water (O/W) emulsion (Paulis et al., 1993).

During oil production, it is usual to co-produce a portion of the water employed for injection. As a consequence, huge volumes of water are generated, which in offshore operations have to be discarded in the sea. Such water, called produced water, is an oil-in-water (O/W) emulsion normally treated using flocculating agents that can be adsorbed on the interface of the oil drops so as to promote the neutralization of charges and/or the formation of inter-particle bridges (Feder et al., 2004; Fernandes et al., 2005).

The presence of water in petroleum production leads to corrosion and formation of salt deposits (scales). When this occurs, corrosion and scale inhibitors are used in order to prevent corrosion of pipes as well as scale formation, either through deposits on surfaces or through formation of scaling crystals, such as calcium carbonates and barium, strontium and calcium sulfates (Hasson et al., 1997; Drela et al., 1998; He et al., 1999; Dyer and Graham, 2002).

Synergistic effects can occur when chemical additives are used in admixtures in the petroleum industry. Such effects can enhance or diminish the performance of each additive and/or can cause undesirable residue. The knowledge of these kinds of effects permits (1) optimizing the amount of each additive added, (2) preventing damages and (3) reducing residue disposal.

The identification of the constituents of the formulations responsible for the synergistic effects leads to reformulation of such additives, aiming at minimizing any undesirable effect.

The aim of this work is to evaluate the influence of the polymeric-bases on the synergistic effects that occur when some additives (demulsifiers, flocculating agents and scale inhibitors) are used in admixtures in the petroleum industry.

2. Experimental section

2.1. Materials

Commercial demulsifier, flocculating agent and scale inhibitor additives, supplied by PETROBRAS, as well as their respective polymer bases, block copolymer of poly(ethylene oxide-*b*-propylene oxide)—COP1 (Dow Química, Brazil), cationic polyacrylamide–PAMC (CYTEC) and poly(sodium acrylate)–PAS (Oxiteno, Brazil) were used. Another block copolymer of poly (ethylene oxide-*b*-propylene oxide) — COP2 (Dow Química, Brazil) was used in order to compare its efficiency to the COP1; these two polyoxides differ in terms of arrangement of their blocks. Petroleum of medium API grade and oily water from the Campos Basin were also used in the study.

2.2. Methods

We characterized the commercial additives by Fourier Transform Infrared spectrometry (FTIR) and the polymeric bases by size exclusion chromatography (SEC), hydrogen nuclear magnetic resonance (^{1}H-RMN), besides FTIR. For each additive, we ran specific performance tests, that is, demulsification, flocculation and scale inhibition tests. We conducted these tests with the commercial additives individually and in binary and ternary mixtures, and also with the polymeric bases individually and in binary and ternary mixtures. Besides this, we performed residue formation tests for these same systems.

2.2.1. Characterization

2.2.1.1. Fourier transform infrared spectroscopy (FTIR). We performed FTIR on a Perkin Elmer 1720x spectrometer, taking measurements from 4000 to 400 cm^{-1}, with 2 cm^{-1} resolution. Each measurement was an average of 20 scans. For commercial additives (demulsifier, flocculant and scale inhibitor) and polymeric bases (COP1, COP2 and PAS), which are liquid samples, we performed qualitative analyses on AgBr cell. For polymeric base PAMC, which is a solid sample, we mixed it with KBr powder.

2.2.1.2. Size exclusion chromatography (SEC). We used SEC to determine the average molar mass of the polymeric bases, COP1 and COP2. The experiments were performed on styrene-divinylbenzene copolymer columns (10^4–10^3–500–100 Å), using tetrahydrofuran as a solvent and polystyrene as standards, in a Waters 600E. The detection system was refraction index. PAS and PAMC are water-soluble samples and we did not have water-soluble columns available. Thus, we considered the molar mass provided by the suppliers.

2.2.1.3. Hydrogen nuclear magnetic resonance (^{1}H NMR). We carried out ^{1}H NMR spectroscopy in a