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High molar mass polyethers as defoamers of heavy crude oil

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ABSTRACT

The presence of foam in the petroleum industry causes many problems in gas-liquid separators and its complete elimination, by employing a silicon-free defoamer agent, poses a significant challenge. In this research, a series of high molar masses polyethers was synthesized using different epoxide monomers (1,2-propylene oxide PO, 1,2-butylene oxide BO, 1,2-hexylene oxide HO and 1,2-dodecylene oxide DDO), varying their molar masses from 10,000 to 120,000 g/mol. The synthesis was performed by anionic ring-opening polymerization (AROP) using as initiation system an ammonium salt and triisobutylaluminum as complexing agent and monomer activator. All polymers were characterized by ¹H NMR, SEC and TGA, experimentally evaluated as defoamer agents of gasified heavy crude oil (13.08 °API) and compared to a silicon based defoamer. Results revealed that PBO and PHO with molar masses above 80,000 g/mol show high activity as foam suppressors, similar to that of commercial silicon based defoamer agents.

1. Introduction

A great deal of effort is spent in the petroleum industry to prevent the formation of foam or to destroy it. Such foams can reduce oil production capacity, damage equipment and cause poor oil-gas separation, leading to large overheads [1]. Depending on the nature of the crude oil and the type of separation scheme used, foaming problems can curtail crude oil production and even cause unwanted and unexpected process shutdowns [2]. Poindexter et al., studied how foam is generated from a series of crude oils depending on their composition and physical properties such as density, bulk viscosity, surface tension and asphaltene and resin contents [3]. Recently Blázquez et al. has developed a new methodology for the characterization of foam stability by modeling crude oil defoam kinetics, finding a correlation between the stability of the foam and a parameter that is function of both the viscosity and the composition of the crude oil [4].

There are many methods used for controlling foaming, such as breaking the foam by mechanical devices, removing the foaming agents, using process units designed to avoid their generation or to break them or, finally, spreading water over the foam [5]. However, the most common and robust method to control the foam is to add anti-foaming or defoaming agents. Many commercial products are used, such as organic silicone and fluorosilicone compounds, phosphate esters, metallic soaps of fatty acids, sulfonated compounds, glycols ethers and alcohols [2]. By far, the most commonly used products are silicone-based products, particularly polydimethylsiloxane (PDMS) or

fluorosilicone based products for the most severe cases [1]. The injection of silicone additives has been used for many years to control the foam of crude oil in gravitational separators. Despite the excellent efficiency of these additives, petroleum companies wish to reduce the quantity of applied silicone or even avoid their use altogether in separation processes because these types of defoamer can lead to the deposition of silica at the surfaces of catalysts used during the hydro-treatment step of petroleum refining, thus reducing their efficiency.

Non-silicone-based defoamer agents are increasingly desired for petroleum processing, this in spite of their lower efficiency relative to that of silicones-based defoamers [6]. Among the silicon-free compounds evaluated as defoamer agents of crude oil, polyether-based antifoamers, specifically poly(ethylene oxide)-poly(propylene oxide) (PEO-PPO) block copolymers, are mainly proposed. Rezende et al., evaluated the efficiency of commercial polyether-based defoamer agents, (PEO-PPO), with average molar masses between 2400 and 8000 g/mol, and also silicones grafted with PEO and PPO chains (polyether silicones) with average molar masses between 3000 and 20,000 g/mol, in two degasified medium crude oil samples with different compositions. The test showed that polyether grafted silicones exhibited the best performance as defoamer agents, while polyether-based defoamer showed lower (or even null) performance [7]. A possible explanation of this low efficiency of the polyethers is their molar masses, lower than that of the silicon based antifoams. Indeed, it has been reported that the efficiency of polyethers and other polymers as agents for petroleum conditioning depends strongly on the correct

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choice of an adequate molar mass [8–11].

The ether block copolymers used nowadays as defoamer agents are synthesized by anionic ring-opening polymerization (AROP), employing alkali metal alkoxides and hydroxides as reaction initiators [12]. However, this kind of polymerization is often disturbed by the occurrence of side reactions, such as transfer to monomers for substituted epoxides, which hinder the achievement of high molar masses (> 15,000 g/mol), despite good control of the propagation step of polymerization [13–14]. In contrast, it has been reported that the anionic polymerization of propylene oxide, initiated by alkali metal alkoxides in combination with trialkylaluminum, allows the synthesis of poly(propylene oxide)s with much greater molar masses, capable of reaching above 20,000 g/mol [15]. Considering as a hypothesis that improved defoaming of petroleum can be achieved using polyethers with a greater chain length, a series of high molar mass polyethers, over 100,000 g/mol, was prepared. The initiation system used was a combination of an ammonium salt and triisobutylaluminum, following a previous study, in which the homopolymerization of epoxides containing various aliphatic side chains (1,2-propylene oxide (PO), 1,2-butylene oxide (BO), 1,2-hexylene oxide (HO) and 1,2-dodecylene oxide (DDO)) and moderate molar masses (up to 35,000 g/mol) was reported [16].

This kind of high molar mass polyether was synthesized and, for the first time, evaluated as a defoamer agent of gasified heavy crude oil, employing a method implemented in the laboratory to mimic the conditions in gas-oil separators [17]. The evaluation method is based on the rapid depressurization of the system, similar to that observed at the inlet of the gas-liquid separators used in the petroleum industry. The sample of gasified petroleum was taken just at this zone, stored and sealed in a metallic cylinder container under real pressure conditions and with the natural gasses dissolved in the heavy crude oil.

2. Experimental

2.1. Materials

Toluene (98%, J.T. Baker) was purified by employing polystryllithium seeds. These seeds react with the water molecules present as traces in the unpurified toluene sample; subsequently this solvent was distilled under reduced pressure and then stored in graduated glass tubes also under reduced pressure. PO (1,2-propylene oxide, 99%, Sigma-Aldrich), BO (1,2-butylene oxide, 99%, Sigma-Aldrich) and HO (1,2-hexylene oxide, 97% Sigma-Aldrich), were purified over CaH₂. The calcium hydride reacts with the water molecules present in the unpurified monomers, later the monomer was distilled and stored under reduced pressure at 20 °C in graduated glass tubes until use in a glass flask equipped with poly(tetrafluoroethylene) (PTFE) stopcocks. DDO (1,2-dodecylene oxide, 90%, ABCR) was washed three times with dry toluene. The toluene was evaporated under reduced pressure. Tetraoctylammonium bromide (NOct₄Br, 98%, Sigma-Aldrich) was dissolved in dried toluene and stored in graduated glass tubes fitted with PTFE stopcocks. Triisobutylaluminum (i-Bu₃Al, 1 mol/L in toluene, Sigma-Aldrich) was used without further purification.

Heavy crude oil was sampled from an oil field located in the Gulf of Mexico and kept in pressurized 4 L metal recipients.

2.2. Polymerization procedures

Polyethers were synthesized by anionic ring-opening polymerization, using as monomers propylene oxide, butylene oxide, hexylene oxide and dodecylene oxide. All polymerizations were initiated at –30 °C and let go up to 20 °C under anhydrous conditions in a glass reactor equipped with a magnetic stirrer and fitted with PTFE stopcocks. All the reagents were purified. Reactions were achieved using an ammonium salt as an initiator and triisobutylaluminum as complexing agent and activator, both dissolved in organic solvents.

The synthesis of poly(propylene oxide) with a theoretical molar mass of 30,000 g/mol, is depicted as example. A reactor was flamed under reduced pressure and cooled prior to the introduction of toluene (10 mL) and PO (1.2 mL, 17.2 mmol) through connected glass tubes. Next, a toluene solution of NOct₄Br (0.12 mL, 0.033 mmol, C = 0.276 mol/L) followed by i-Bu₃Al solution in toluene (0.05 mL, C = 1 mol/L) were added via a syringe under an argon atmosphere. Polymerizations initially proceed at –30 °C, followed by a period of 5 h at room temperature and finally stopped by the addition of ethanol. The reaction yield (100%) was determined gravimetrically after complete drying of the polymer under reduced pressure at 50 °C. All the syntheses were carried out following this same polymerization procedure, just varying the monomer/initiator ratio in order to adjust the polyethers average molar mass.

Silicone, polydimethylsiloxane (PDMS), was evaluated as received from the supplier and dissolved in xylene solvent at 7.50 wt% concentration.

2.3. Polymer characterization

¹H (400.2 MHz) and ¹³C (100.6 MHz) NMR measurements were performed on a Bruker Avance 400 spectrometer, in CDCl₃, at room temperature. Polymer molar masses were determined by size exclusion chromatography (SEC) using tetrahydrofuran (THF) as eluent. Measurements were performed on a PL GPC50 integrated system with RI and UV detectors and three TSK columns: G4000HXL (particles of 5 μm, pore size of 200 Å and exclusion limit of 400,000 g/mol), G3000HXL (particles of 5 μm, pore size of 75 Å and exclusion limit of 60,000 g/mol), and G2000HXL (particles of 5 μm, pore size of 20 Å and exclusion limit of 10,000 g/mol) at an elution rate of 1 mL/min. Polystyrenes were used as standards.

Thermal degradation measurements were carried out using a TA Instrument Thermal Analysis TGA Q50 V6.7. All samples were scanned from 25 °C to 500 °C, at heating rates of 10 °C/min under N₂ atmosphere.

2.4. Physical characterization of petroleum

The sample of heavy crude oil was subject to a series of characterizations in order to determine their main physical features. API gravity was determined following the ASTM-D-287-12b method. Salt and water contents in the crude oil were determined, according to the ASTM-D 3230-06 and ASTM-D 4006-07 procedures, respectively. Kinematic viscosity was measured following the ASTM-D 445 method. In the case of the pour point, this was evaluated according to the ASTM-D 97 procedure. SARA (saturated, aromatics, resins and asphaltenes) composition was obtained by the precipitation of asphaltene with n-heptane, while maltenes were separated through the HPLC method with a Water Spherisorb NH₂ column 10 μm (20 × 250 mm) preparative [18].

2.5. Method for the evaluation of defoaming agents

The gasified heavy crude oil employed in the evaluation of the defoamer agents was contained in a 4 L metal cylinder of stainless steel; oil samples were taken from the well at sampling conditions of 76.5 °C and a pressure of 5.88 bar.

Polyethers and a commercial silicone additive were evaluated as foam inhibitors in “living” heavy crude oil using an apparatus to measure the collapsed foam developed in our facilities in order to mimic the process conditions of gas-oil separators [17]. The metallic cylinder containing the crude oil was placed in a vertical position and supported by a metallic rack. From its top, the metallic cylinder was provided with a nitrogen gas supply line. At the bottom, an outlet line was fitted where the defoamers was fed and covered with heating jackets (Fig. 1). The foaming process was induced by preheating the steel metal cylinder at an outside temperature in the range from 40 to

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