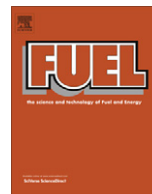




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Demulsifying super-heavy crude oil with bifunctionalized block copolymers

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ABSTRACT

One of the main problems that petroleum industry must face is the growing difficulty to extract both water and salts present in heavy crude oils. High viscosity, and enormous contents of resins and asphaltenes contribute to stabilize the water droplets dispersed in crude oil, making petroleum demulsification harder and the development of new dehydrating agents necessary. A series of copolymers consisting on a central block polypropylene oxide (PPO), and two side block of ethylene oxide (EO) were synthesized. These copolymers were afterwards submitted to a functionalization process, in order to graft some secondary amines to EO segments, to increase their interactions with the aqueous phase dispersed in the petroleum. The average molecular weight of the functionalized copolymers was adjusted according to the weight-average molecular weight (M_w) of the sample of super-heavy crude oil. The water removals from the petroleum sample were evaluated by bottle testing, mainly varying the kind of functional group and copolymer content. It was observed that these novel demulsifying agents have a better performance than traditional compounds, such as non-functionalized block copolymers and commercial formulations commonly used to remove water from super-heavy crude oil. The existence of maximal water separation at a certain concentration of the functionalized copolymers was observed, and explained in terms of a saturation of the water/oil interphase with polymeric chains.

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1. Introduction

Crude oil is a complex hydrocarbon mixture comprising maltenes and asphaltenes; besides due to their molecular characteristics, oil and water are immiscible, but when oil is produced, the simultaneous production of water is unavoidable. Once production begins, both oil and water are transported through pipes, to storage tanks. The energy used during the extraction and transport generates turbulence promoting the mixing of both phases, resulting into binary and ternary kinds of emulsion, such as: water/oil (w/o), oil/water (o/w), water/oil/water (w/o/w), and oil/water/oil (o/w/o) respectively. These emulsions can be very stable and their formation is favored by compounds naturally present in the oil acting as emulsifiers such as asphaltenes, naphthenic acids, heterocyclic nitrogen compounds, oxidized hydrocarbons, resins and clay emulsifiers. The stability of these emulsions mainly depends on the composition of crude oil. Crude oil emulsions differ in their composition from one deposit to another [1].

The water emulsified in oil contains inorganic salts; mostly sodium, magnesium, calcium chlorides, carbonates and sulfates; and iron sulfides and oxides, if all of them are not removed they can cause various problems in subsequent refining processes.

For export purposes, crude oil must contain 0.5% water as maximum value, and comply with a lower salt content than 50 mg L^{-1} , so the breaking of water-crude oil emulsion is thus a substantial process step in oil production.

The removal of water is carried out for technical reasons; in order to reduce corrosion damages, to prevent the expensive transportation of water, and to abate salt content.

Initially crude desalting, which remove salts and other contaminants from crude oil was mainly done as a preventive action to diminish corrosion costs. However, in recent years, desalination technology has become more important, it also helps to avoid heat exchanger fouling, and to prevent catalysts deactivation used in later stages of the refining process [2].

Therefore, from the economic point of view it is imperative and important to separate water from oil, completely and quickly as possible in the same production site, in order to prevent the emulsion aging and becomes more difficult their rupture [3]. To achieve this goal, physical and chemical methods have been used, both independently and sequentially [1].

Traditionally, the breakdown of water in oil emulsion is achieved with the addition of small amounts of demulsifier (tens of ppm, up to 1000 ppm) to crude oil stored in tanks of separation, just before being pumped. Demulsifiers are expected to perform different functions during the water removal, for example, altering the rheological properties of the interfacial layer, destabilizing the

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oil layer endogenous emulsifier, and displacing them there, producing finally to phase separation [4].

Commercial demulsifiers are a mixture of several components with different polymer structures, as well as a wide range of molecular weights. Demulsifiers most used today in the oil industry are resins alkyl-phenol formaldehyde, copolymers of polypropylene oxide – polyethylene oxide, alkoxyated amines, alkoxyated epoxy resins types and mixtures of them [5–14], emulsifiers are expected to perform different functions during the water removal, such as emulsion breakage, acceleration of the water drops coalescence, water clarification, and definition of oil–water interphases. Usually, polymers and/or surfactants used as commercial demulsifiers carry out only one of these functions; consequently, different active matters must be combined in a formulation for a good demulsification achievement.

Some examples of polymeric demulsifiers are listed below; US Patent 4568737 discloses hybrid dendrimers of polyamidoamines, polyesters, and polyethers, however their preparation is very complicated resulting into very expensive and rarely used [15]. US Patent 2008/0153931 refers to the application of non-dendrimeric, highly functional, and hyper branched polymers as demulsifiers of crude oil emulsion with a water content of 55 vol.% [16]. WO2009/097061 patent reveals the treating of emulsions of crude oils with an API gravity comprised 20–30, using some demulsifier containing at least 70% per weight of ethylene oxide 3-hydroxypropylene oxide, or a mixture [17]. US Patent 2006/0036057 shows the treating of crude oil emulsion, with 15 API gravity, with phosphoric ester demulsifier composition achieved by reacting one or more alkylphenol–formaldehyde resin alkoxyates, from 0.001 to an approximate 1.0 M equivalent of one or more phosphorous compounds [18]. WO2007/115980 claims that alkoxyated orthoesters cause the separation of water contained in an emulsion. These products were evaluated in the North Sea and the Middle East crude oil and synthetic brine, obtaining separation between 30% and 100% [1].

Recently the characterization of Mexican crude oils [19–21], and the analysis of their emulsions have started [22], as well as the application of a novel kind of demulsifier for heavy crude oils, based on block copolymers bifunctionalized with amines [23]. It was also established that the main parameters controlling the destabilization of the water–oil interface, during the crude oil dehydration process, are the average molecular weight and polydispersity of the polymers used as demulsifiers [24]. This paper, now presents the application of this novel type of copolymers for water removal in a super-heavy Mexican crude oil.

2. Materials, characterization and methods

Propylene oxide (PO) 99%, ethylene oxide (EO) 99%, phosphoric acid 85%, ethanol, methanol and hexane; all of Sigma Aldrich. Pellets of anhydrous KOH 99% (Fermont), and ethylene glycol 99% (JT Baker), tetrahydrofuran (THF) anhydrous 99.8% (Mallinckrodt), were used with no further purification.

Four samples of four formulations of commercial block copolymers (EO–OP–EO) were supplied by the technical department of chemical products of the Mexican institute of petroleum. These formulations (CPF-1, CPF-2, CPF-3 and CPF-4, see Table 4) are commonly used to dehydrate heavy crude oils from the Gulf of Mexico. The main features of the block copolymers which are employed in the formulations mentioned above are given in Table 5.

Fourier Transform Infrared Spectroscopy (FTIR): The synthesized copolymers were characterized by FTIR with a Bruker Tensor 27 spectrometer.

Nuclear Magnetic Resonance (NMR) Spectroscopy: The ^1H and ^{13}C spectra were obtained from 150 mg of each of the samples

dissolved in CDCl_3 . The NMR experiments were performed in a Varian NMR spectrometer model Mercury-BB at 200 MHz. The chemical shifts were referenced to tetramethylsilane (TMS) (^1H , $\delta = 0.0$ ppm, and ^{13}C , $\delta = 0.0$ ppm).

Size Exclusion Chromatography (SEC): The molecular weight distribution of the synthesized polymers was determined by SEC, using an Agilent 1100 series chromatograph consisting on a 5 μm column of PLgel, and employing THF as eluent. The flow rate was 1 $\text{mL}\cdot\text{min}^{-1}$ at 303 K (determined with the refraction index detector attached to the equipment). The synthesized polyethers were dissolved in THF at a concentration of 1.5 $\text{mg}\cdot\text{mL}^{-1}$. The average molecular weights (M_n and M_w) and the polydispersity index (I) were calculated from the SEC data. Calibration was made with a polystyrene standards kit. The average molecular weights and polydispersity index of a series of PPO standards purchased from polymer laboratories™ ($M_n = 580, 1270, 2960, 7200, 21,000, 50,400, 113,300, 325,000$ and $696,500$ $\text{g}\cdot\text{mol}^{-1}$) were determined by SEC to check that the calibration with PS is appropriate.

Thermogravimetric analysis (TGA): Possible chemical degradations were determined by thermogravimetric analysis measurements (TGA, TA-instruments TGA 2950, heating rate 5 $^\circ\text{C}\cdot\text{min}^{-1}$).

2.1. Crude oil characterization

Physical testings: Specific gravity was measured according to the ASTM D-287 method [25], kinematic viscosity was determined according to ASTM D-445 [26], values of number average molecular weight (M_n) were obtained directly from measurements of freezing point depression of decane-saturated benzene solutions by employing a petroleum cryoscope (Cryette No.1 Model 5009) [19], sulfur was determined conforming to the ASTM D-4294 [27], wax content was measured according to the UOP-46 norm and the asphaltene content was obtained according to the ASTM D-2007 method [28].

Samples of Mexican crudes oils were fractionated in saturated, aromatics and resins, after deasphalting (SARA) by means of the HPLC method with a Water Spherisorb® NH_2 Column 10 μm (20 \times 250 mm) Preparative, using the following solvent sequences: n-heptane for the saturated and aromatic fractions and chloroform for the resins [19].

Osmometry: SARA fractions dissolved in toluene were characterized with a Model Wescan 232 vapor pressure osmometer (VPO). This osmometer has a detection limit of 5×10^{-6} mol/L when used with toluene. 1, 2-Diphenylethanedione was employed to calibrate the instrument, and a polymer standard was used to check the calibration. Additional details of the technique are given elsewhere [19]. The weight-average molecular weight of the crude oil was obtained averaging the osmometry molecular weight of each SARA fraction ($M_w = \sum w_i \cdot M_i$).

2.2. Demulsification evaluation by bottle testing

The crude oil for testing was poured into a series of graduated bottles with inserted and covers. In each bottle the crude oil was added up to the 100 mL mark. All the bottles were placed in a water bath with temperature controlled at 358 K for a period of 30 min. An aliquot of the different block copolymers dissolved in xylene was subsequently introduced in each bottle, except one (the blank) which was dosed with xylene only; all the bottles were shaken during 2 min at the rate of 2 blows per second. After mixing, block copolymers were placed again in the thermalized bath and the rupture of the emulsion oil water was read during the time of the evaluation [23]. The bottle testing results were confirmed by the Karl Fisher method ASTM-E 203-08 and an average residual content of water of 2% was determined.

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