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Synthesis, structure-activity relationship and evaluation of new non-polymeric chemical additives based on naphthoquinone derivatives as wax precipitation inhibitors and pour point depressants to petroleum

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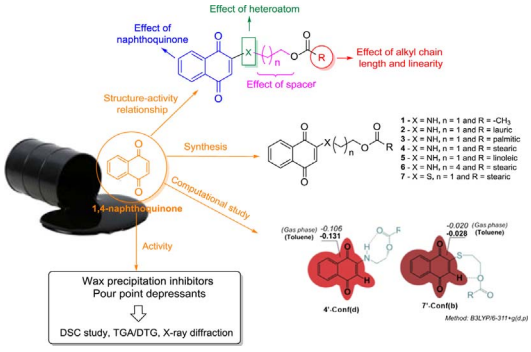
GRAPHICAL ABSTRACT



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ABSTRACT

Wax deposition is one of the major flow problems for petroleum transportation and production. In this context, the development of more efficient methods to remediate paraffin precipitation has received great attention within the oil industries. In the present study, eight new long-chain esters were prepared in less than four synthetic steps and in high yields (84–97%). Seven of them contain naphthoquinone nuclei, and one presents a cyclohexyl group. The new molecules were tested as non-polymer wax precipitation inhibitors and pour point depressants. Calorimetric experiments were employed to identify the effect of four pre-determined chemical groups within the molecules and to set out the best components for maximized inhibition: (i) the length of alkyl chain in the ester group, (ii) the length of the alkyl chain separating the polar nuclei and the ester group, (iii) the heteroatom bonded to the polar nuclei, and (iv) the importance of the naphthoquinone nuclei. After determination of the pour point and wax appearance temperature (WAT) of Brazilian oils by differential scanning calorimetry (DSC), the highest efficiency was observed for naphthoquinone esters derived from stearic and palmitic acids when containing two methylene groups as a separator and nitrogen as the heteroatom. These new additives present better results than the commercially available polymer-based inhibitors in all tested samples, even when applied at smaller concentrations, compared to many other polymer-based inhibitors reported in the literature. The importance of the naphthoquinone moiety as the polar portion of the inhibitor was confirmed when it was replaced by a cyclohexyl group. Molecular modeling and X-ray diffraction studies were also carried

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out to rationalize the relationship between structure and activity and the action mechanism of these new chemical additives.

1. Introduction

Petroleum is composed of a complex mixture of compounds originating after the deposition and decomposition of organic matter. This mixture is primarily formed from microorganisms and phytoplanktonic algae, which together with inorganic sediments define the oil constituents.

Crude oil is completely fluid at high pressure and temperature, which are the conditions present in rock formations. When the oil undergoes reduced temperature or pressure, however, the wax molecules become less soluble and can form crystals, which separate from the oil phase, precipitating and packing on pipeline walls. Blockages caused by precipitation of wax withhold the oil flow, leading to interruptions in the production line, operational safety issues, and increased costs and consequently causing various problems in the transfer operations [1–6]. In cases where fluidity problems are related to the deposition of paraffin, it is necessary to study and understand the deposition process that occurs when the paraffins are present in the crude oils [5,7–10].

The new challenge to be faced in the future is the production of oil that originated from pre-salt areas. The oil extracted from these areas contains paraffins of high molar mass that present differentiated behavior when subjected to temperature variations. This behavior impacts the results of the pour point, a property used in the allocation and commercialization of oils. Several methods have been proposed to manage, prevent, and remediate wax deposition. The wax-mitigating techniques currently used include mechanical (pigging), chemical, and thermal (hot water or oil) methods. Among these techniques, the use of chemicals is typically recommended due to their lower cost compared to other methods for the prevention of wax deposition.

At least three types of chemicals can be used, including solvents, dispersants, and wax crystal modifiers or paraffin deposition inhibitors [11–21].

Paraffin deposition inhibitors are capable of retarding the crystallization of paraffinic compounds by the formation of smaller crystals and/or by preventing the growth of crystalline networks [22]. Previous work has shown that the greater the similarity between the non-polar part of the additives and the paraffins present in the oil, the larger their ability to fix to the paraffinic hydrocarbons becomes, creating barriers for the growth of crystals [23].

The general structure of inhibitors is composed of non-polar alkyl portions (wax-like). This aliphatic functionalization must interact with the crystals, providing nucleation or co-crystallization sites. The other component present in the modifier compound should have polar characteristics for blockage of excessive crystal growth, which alters and interferes with the crystallization process [24,25]. According to the literature, most of the inhibitors are formed by polymers/copolymers containing the ester function derived from a fatty acid [7,17,25–44].

In this work, eight new fatty esters were synthesized to study the structure-activity relationship and determine their respective efficiencies as wax deposition inhibitors and pour point depressants. For this, differential scanning calorimetry (DSC), pour point determination, X-ray diffraction and molecular modeling were utilized.

2. Material and methods

2.1. Materials

All chemicals are commercially available, and the following reagents were used: 2-hydroxy-1,4-naphthoquinone (97%), 1,4-naphthoquinone (97%), lauric acid (99%), palmitic acid (98%), stearic acid (98%), linolenic acid (99%), dicyclohexylcarbodiimide (99%), 4-dimethylaminopyridine (99%), 2-aminoethan-1-ol (99%), 2-aminoethane-1-thiol (99%), 5-aminopentan-1-ol (95%), acetic anhydride (98.5%), cyclohexanone (99.5%), sodium borohydride (95%), and triethylamine (99%). The reagents 2-aminethan-1-ol, cyclohexanone and triethylamine were used after purification by distillation. These reagents were stored in amber flasks sealed with paraffin while cooling and under an inert atmosphere of argon. All other reagents were used without previous treatment. The solvents used without pretreatment were distilled water, ethanol (anhydrous, 99.5%), ethyl ether (99.8%), ethyl acetate (99.5%) and methanol (98%). The solvents dichloromethane (99.5%) and hexane (99%) were used after fractional distillation.

Crude oil A and B studied in this work were obtained from Brazilian oil industries. The main characterization parameters are as follows: Oil A/B: BSW (v/v) = 1.0/4.4 (ASTM 4007-02); °API = 35.3/24.3 (ASTM D 7042); Density 20° (g/cm^3) = 0.8444/0.9047 (ASTM D 7042); Salinity NaCl (ppm) = 3185.2/63.1 (ASTM D 6470-99); Sulfur (%) = 0.0718/0.3565 (ASTM D 4294); Pour Point (°C) = 42/21 (ASTM D 5853); Wax content (%) = 75.58/54.40 (ASTM D2549-02).

2.2. Methods

2.2.1. Synthesis

Melting points were determined using a Fisatom model 430D, and infrared (IR) spectra were recorded on a Bomem FTLA2000-102-ABB spectrometer. The ^1H nuclear magnetic resonance (NMR) and ^{13}C NMR spectra were obtained on a Vary VNMRS spectrometer model 400 (400 MHz) with tetramethylsilane (TMS) as an internal standard. NMR analyses of the compounds were performed in deuterated chloroform (99.8%) with 1% (v/v) TMS and stabilized with silver foil (Cambridge Isotope Laboratories, Inc.). Mass spectra were recorded on an ultra-high resolution and accuracy mass spectrometer (model 9.4 T Solarix, Bruker Daltonics) operated in both ionization modes: positive and negative electrospray ionization with Fourier transform ion cyclotron resonance mass spectrometry. ESI(+) and ESI(−)-FT-ICR MS spectra were acquired with a resolving power of m/Δm50% ca. 500,000, in which Δm50% is the full peak width at a half-maximum peak height of *m/z* 400 and a mass accuracy < 1 ppm. This provided an unambiguous molecular formula assignment for singly charged molecular ions, such as $[M-H]^+$ or $[M+H]^-$ and DBE (double bound equivalents) values.

2.2.2. General procedure for Steglich esterification in the synthesis of compounds **2–8**

In a round bottom flask of dichloromethane (10 mL) under magnetic stirring, 1.0 mmol of fatty acid (except for palmitic acid – 2.0 mmol), dicyclohexylcarbodiimide (DCC) (1.2 mmol) and dimethylaminopyridine (DMAP) (0.2 mmol) was added until precipitation of dicyclohexylurea (DCU). Thereafter, 12, 13, 16, or 18 (1 mmol) was added, and the reaction was stirred at room temperature according to the reaction times described in Table 2 (results and discussion). The crude product was washed with a saturated $NaHCO_3$ solution and distilled water. After drying and evaporating the solvent under reduced pressure, a chromatographic column was made using silica as the stationary phase and a 20% EtOAc:hexane mixture as the eluent.

2.2.3. Pour point

The pour point of the samples was obtained according to ASTM D 5853 [45]. The same procedure was applied on oils A and B with 200 ppm of the synthesized inhibitors. This concentration was found as the optimal parameter for similar chemical inhibitors in previous work [17]. All presented results were obtained with triplicate tests.