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Rheological properties and viscosity reduction of South China Sea crude oil

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ABSTRACT

The rheological properties of South China Sea (SCS) crude oil were studied. A group of synthetic long-chain polymers, including octadecyl acrylate-maleic anhydride bidodecyl amide copolymer (VR-D), octadecyl acrylate-maleic anhydride bioctadecyl amide copolymer (VR-O) and octadecyl acrylate-maleic anhydride phenly amide copolymer (VR-A), were employed to serve as viscosity reducers (VRs). Their performance was evaluated by both experimental and computational methodologies. The results suggest that the SCS crude oil has low wax content yet high resin and asphaltene contents, which lead to high viscosity through formation of association structures. Additionally, the SCS crude oil appears to be a pseudoplastic fluid showing linear shear stress-shear rate dependence at low temperature. Interestingly, it gradually evolves into a Newtonian fluid with exponential relationship between shear stress and shear rate at higher temperature. Synthetic VRs demonstrate desirable and effective performance on improvement of the rheological properties of SCS crude oil. Upon the introduction of 1000 ppm VR-O, which is synthesized by using octadecylamine in the aminolysis reaction, the viscosity of SCS crude oil is decreased by 44.2% at 15 °C and 40.2% at 40 °C. The computational study suggests significant energy level increase and shear stress decrease for VR-containing crude oil systems.

1. Introduction

The increasing demand of petroleum results in an increasing exploitation and production of crude oil resources, among which the heavy oil resources in the world are at least twice as many as those of conventional light crude oil. Heavy and extra-heavy crude oil refining poses enormous challenges in the pipeline transportation of petroleum liquids. One critical issue is their high viscosity and low fluidity, which are governed by their fundamental physical and chemical properties such as oil compositions (i.e., saturates, aromatics, resins and asphaltenes, traces of sulfur, nitrogen, chlorine and metal compounds), and the complicated interactions among different oil species [1–4]. Generally, waxes, paraffins with high melting points, are mainly responsible for the low-temperature flow issues of waxy crude oils. In addition, high resin and asphaltene contents also lead to undesirable rheological properties and reduced mobility, causing precipitation, emulsification, high viscosity, equipment corrosion and coking deactivation of catalysts in numerous processes of the petroleum industry [5–7]. Therefore, knowing the fundamental properties of resins and asphaltenes is very important for evaluating and predicting their impacts on crude oils refining and process design and optimization.

Resins and asphaltenes can be separated from petroleum sources. Their structures have been studied by both experimental characterization techniques [8–11] and theoretical calculations [12,13]. Typically, resin and asphaltene molecules tend to form association structures, which lead to crude oils with very high viscosity [14–16]. The major forces governing the resin and asphaltene aggregates formation are very complicated, including charge transfer, electrostatic interaction, van der Waals force, the acid-base interaction, hydrogen bonding, π–π interaction and coordination interaction [17–20].

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It has been reported that polymers, graphene, graphene oxide (GO) and reduced GO could reduce the viscosity of fluids [21–25]. To reduce the viscosity and to improve the fluidity of crude oils and heavy petroleum fractions, one approach is to break or disperse the asphaltene-resin-involved association aggregates using various additives, such as synthetic viscosity reducers (VRs) [26,27], lighter blending components [28], electric or magnetic fields [29,30], heterogeneous catalysts [31,32], and nanoparticles [33]. A spectrum of polymers has also been synthesized to improve the fluidity [34–37]. These methods exert significant impact on the complex aggregates, lowering the viscosity and yield stress of crude oil and enabling much easier flow and transportation.

It is fundamentally crucial and practically necessary to investigate the physical and chemical properties of crude oil, which govern its application in the petroleum industry. Huge oil reserves were found in the South China Sea (SCS), which greatly boosts the research on this unique oil source. In this work, we focused on the rheological behaviors and viscosity reduction of SCS crude oil. The properties of SCS crude oil sample, especially its rheological properties, were thoroughly characterized. Moreover, a series of nitrogen-containing long-chain polymers were synthesized and employed to serve as the VRs. Furthermore, the rheological property evolution of SCS crude oil upon VR introduction was evaluated via both experimental and computational methodologies.

2. Experimental

2.1. Materials

Crude oil obtained from the South China Sea oil field was used in this work. Other chemicals used were of analytical grade and were used as received without any further treatment. The chemicals and corresponding suppliers are listed below. Methanol and acrylic acid were obtained from Shanghai Titan Scientific Co., Ltd. (Shanghai, China). Toluene, sodium hydroxide, *p*-toluene sulfonic acid, *cis*-butenedioic anhydride and hydroquinone were provided by Shanghai Lingfeng Chemical Reagent Co., Ltd. (Shanghai, China). Benzoyl peroxide, vinyl acetate, dodecylamine, octadecylamine, aniline and dodecyl mercaptan were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). 1-Octadecanol was obtained from Yonghua Special Chemical Reagent Company (Taicang, Jiangsu).

2.2. Synthesis of viscosity reducers (VRs)

2.2.1. Esterification reaction

Esterification reaction of 1-octadecanol (OD) and acrylic acid (AA) was carried out in a three-necked flask reactor under constant magnetic stirring at 125 °C for 8 h (Scheme 1). The reaction temperature was accurately controlled by using an oil-bath heater, in which toluene (T), *p*-toluene sulfonic acid (SA) and hydroquinone (HQ) were used as solvent, catalyst and polymerization inhibitor, respectively. Specifically, the starting mixture had a molar composition of n(OD): n(AA): n(T) = 1: 1.3: 2.3. The corresponding mass ratios, m(SA)/m(OD+AA) and m(HQ)/m(OD+AA), were 0.007 and 0.01, respectively. Subsequently, the resulting product, octadecyl acrylate, was washed with sodium hydroxide aqueous solution (5 wt%) and thereafter deionized water followed by vacuum drying at 50 °C for 4 h.

2.2.2. Polymerization reaction

Vinyl acetate (VA), *cis*-butenedioic anhydride (BDA) and synthesized octadecyl acrylate (ODA) in the esterification reaction were used as monomers for copolymerization, which was performed in a three-necked flask heated in an oil-bath under N_2 environment (80 mL min^{-1}). The reaction is detailed in Scheme 2. Toluene (T), benzoyl peroxide (BPO) and dodecyl mercaptan (DM) were used as solvent, polymerization initiator and chain-transfer agent, respectively. The starting mixture had a molar composition of n(VA): n(BDA): n(ODA): n(T) = 1: 1: 4: 12. Both benzoyl peroxide and dodecyl mercaptan account for 3% of the total mass of reactants (VA, BDA and ODA). The polymerization reaction was maintained to be under 100 °C under constant mechanical stirring for 6 h. Subsequently, the polymerization product mixture was transferred into a beaker containing methanol to stop the reaction and to enable precipitation of the copolymer. Finally, the solid product was separated through filtration and dried under vacuum at 50 °C for 4 h.

2.2.3. Aminolysis reaction

Three VRs were synthesized through aminolysis reaction. The synthesized polymer reacted with dodecylamine (D), octadecylamine (O) and aniline (A), forming three groups of VRs labeled as VR-D, VR-O and VR-A, respectively (see Scheme 3). The aminolysis reactions was conducted in a three-necked flask containing toluene solvent, which was kept at 90 °C for 6 h under N_2 flow (80 mL min^{-1}). Upon aminolysis, the synthesized products were separated through filtration and dried under vacuum for 4 h.

2.3. Analyses and measurements

2.3.1. Characterizations

A series of crude oil characteristics, including water content, wax content, SARA (referring to Saturates, Aromatics, Resins and Asphaltenes, respectively) distribution, API gravity and freezing point, were determined using Chinese National Standard Test Method (CNSTM), Chinese Petroleum Standard Test Method (CPSTM) and ASTM standard test method.

The wax content of crude oil was determined according to the method recommended by Baudilio et al. [38]. Approximately 2 g of SCS crude oil was dissolved in 40 mL of *n*-pentane followed by addition of 120 mL acetone. Subsequently, this mixture was cooled to −20 °C and kept for 24 h. Further, the solid phase was separated through filtration. The wax product was obtained by redissolvation of the solid phase in *n*-hexane followed by solvent removal.

The SARA distribution was determined by using ASTM D2007-93 standard test method. Firstly, asphaltenes and resins were isolated through precipitation in *n*-hexane solvent with a solvent to crude oil ratio of 30 by volume. Upon cooling to −30°C, asphaltenes were separated via filtration. The obtained solid asphaltenes were further washed with *n*-heptane and dried under vacuum. Subsequently, the liquid phase (maltene fraction) was separated into saturated hydrocarbons, aromatics, and resins by applying a standard chromatographic process. Specifically, the chromatographic separation was carried out using a glass column packed with alumina (100–200 mesh, Sinopharm, China). Trichloromethane, *n*-hexane and toluene were employed to recover resins, saturates, and aromatics at a Soxhlet apparatus, respectively. The contents of SARA can be calculated according to the amount recovered [39].

The water content of all samples was analyzed according to the CNSTM GB/T 8929-2006. The API gravity of each sample was estimated from its specific gravity value measured at 40 °C using a pycnometer based on CNSTM GB/T 1884-2000. The freezing point was determined by using a SYP1008-III freezing point analyzer (Shanghai Petroleum Instruments Company, Shanghai, China) according to CPSTM SY/T 0541-2009. The test tube containing sample was cooled at 0.5–1.0 K min^{-1}. Each measurement was repeated for 2–3 times to ensure reproducibility.

2.3.2. Rheology tests

All rheology tests were performed using a MCR-52 rotary rheometer (Anton Paar, Physica, Austria) equipped with a stainless