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The effect of hydrogen bonds between flow improvers with asphaltene for heavy crude oil

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ABSTRACT

A series of chemical products with characteristic groups in molecular structures were synthesized as novel flow improvers (FIs) for heavy asphaltenic crude oil. The rheological measurement results showed that the FI-5 could behave the better performance in improving fluidity of heavy oil than FI-2 due to the former could form stronger hydrogen bonds with asphaltene in oil, which was confirmed through Fourier transform infrared spectroscopy (FTIR) and energy of simulating studies. Furthermore, X-ray diffraction (XRD) analysis results demonstrated that two products altered asphaltene structure at different degree through hydrogen bonding interaction, and the aggregation-dispersion effect of FIs on asphaltene were respectively obtained through scanning electron microscope (SEM), which beneficially weakened the stable structure of asphaltene in the heavy crude oil system. Hence, the mechanisms were tried to propose that could explain the phenomenon in rheological measurement why FI-2 was not as good as FI-5 in improving fluidity of heavy oil. Results also indicated that the asphaltene content and aggregation structure in oils were vital parameters for its viscosity.

1. Introduction

The heavy crude oil is gaining unprecedented attention by reason of the increasing oil demand, and the increasing urgency also can be attributed to the reduction of conventional oil [1]. However, some studies indicated that the high viscosity of crude oil was inseparable with containing asphaltene that intensely affected the flow performance of heavy oil [2–10], which also seriously limited the oilfield production. So the way was proposed that used chemical products for adding into the crude oil to inhibit such heavy organic compounds as asphaltene precipitation and aggregation in oil system, this was beneficial to reduce viscosity of heavy crude oil, especially in the North China oil fields with abundant extra heavy oil resources [11,12], During past time, the many chemical products were mainly studied for waxy oils [13–16], but these compounds have poor effect for asphaltenic oils, because asphaltene is the core of wax crystal growth [17].

There are diverse studies indicated that asphaltene tended to self-association and entanglement to form concentrated system, this caused the viscosity of oil sharply increases as rise of asphaltene content [4,18–20]. The asphaltene aggregation can be attributed to hydrogen bonding between functional groups and other charge transfer interactions [21–23], and polar moiety of chemical compounds and asphaltene molecules can form the stronger hydrogen bonds by breaking the original hydrogen bonding [24], but also the long alkyl chain of products can inhibit aggregation of asphaltene because of forming solvable layer [25]. So the viscosity reduction of heavy oils can be achieved by the interaction of flow improvers and asphaltene to disperse or break these aggregates. However, due to the structure of numerous non-hydrocarbon compounds is not the same in different samples of oil, so the multiple different structures of asphaltene of composing these compounds were proposed [26–33]. Thus, it is necessary to select novel flow improvers with characteristic functional groups to aim asphaltene in heavy oil of Xinjiang, China.

In this work, on the basis of these premises, a series of flow improvers with functional groups capable of hydrogen bonding with asphaltene were developed. After viscosity reduction efficiency evaluation, two high quality flow improvers (FI-2 and FI-5) that differ only in hydroxyl groups were respectively characterized. The mechanism will be proposed by comparing difference of two flow improvers with asphaltene that can understand how the flow improvers improved the fluidity of heavy oil system.

2. Experimental section

2.1. Materials

The monomers of styrene (ST), lauryl acrylate (LA), acrylamide (AC) and N-methylol acrylamide (NMA) were respectively used as

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reactants, the 2,2′-Azodiisobutyronitrile as a initiator, which all were of analytical grade from Aladdin reagent (Shanghai) co., Ltd. Chemical agents of toluene, n-heptane and anhydrous ethanol (> 95%) for crude oil component separation were all chemical grade purchased from Chengdu Kelong Chemical Co., Ltd.

2.2. Crude oil component separation

The heavy crude oil from Xinjiang of China was elucidated in this paper. Its components were strictly isolated and quantified in accordance with NB/SH/T 0509-2010. Meanwhile, the asphaltene in same species of crude oil was prepared through using the way in the article [34]. The weight-average molecule weight of asphaltene was 754.14 g·mol^{-1} according to GPC test, it was close to the weight of theoretical model. Its oxygen main existence in the form of hydroxyl groups could be proved according to the infrared spectroscopy analysis of asphaltene. The content of C, H, N and S elements in asphaltene were evaluated through elemental analyzer, 84.9%, 7.15%, 1.5% and 4.0%, respectively, which were close to the contents of the similar elements in theoretical model. So, the asphaltene average structure in this paper used for the theoretical model was proposed by López-Chávez [35], because their similarities were verified by analyzing the results of the infrared spectrum, X-ray diffraction (XRD), GPC test and elemental analysis, which was showed in Fig. 1.

2.3. Preparation of products

The polymerization reactions were conducted in four-neck flask equipment with magnetic stirrer, reflux condenser and thermometer at 70 °C for 6 h as well as keeping stirring in nitrogen atmosphere, in where toluene as solvent. The molar ratio of monomers was listed in Table 1. Hereafter, the reaction mixture was cooled to room temperature and purified by precipitation in excess volume of methanol, and then products (i.e., random copolymers) were obtained via filtering and vacuum drying for 24 h.

Obviously, the viscosity reduction effect of flow improvers with Acrylamide in molecular were not better with N-methylol acrylamide for the case of same molar ratio in Table 1, which may relate to the possibility of the latter providing with hydroxyl groups.

2.4. Characterization

The chemical structures of flow improvers were respectively characterized by using the infrared (IR) spectrum and 1H-nuclear magnetic resonance (1H NMR) spectrum. The samples of the asphaltene untreated and treated with 800 ppm of flow improvers were respectively prepared by completely dissolving in toluene solvent and shaking for 2.0 h and then evaporating solvent. This way can fully promote the mutual effect of them and prevent solvent interference. All samples were respectively characterized in KBr pellet using a WQF-520 Fourier Transform Infrared Spectrometer at the wavenumber range of 500–4000 cm^{-1}. The procedures for sample preparation and characterization were mentioned in reference [36].

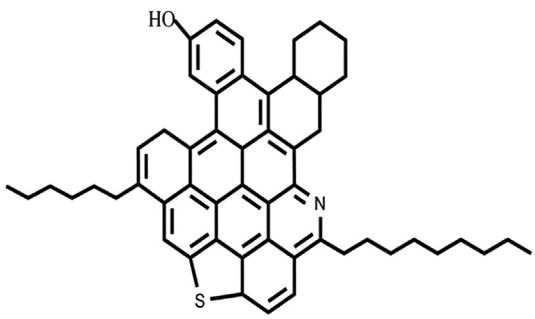

Fig. 1. Average structure of asphaltene sample proposed for modeling.

Table 1
Molar ratio and viscosity reduction effect of FIs for heavy crude oil.

Kind of FIs	Molar ratio of monomers	Dosage of FIs (ppm)	Viscosity reduction rate (%)
FI-1 (ST:LA:AC)	3:5:1	800	43.2
FI-2 (ST:LA:AC)	3:5:2	800	50.8
FI-3 (ST:LA:AC)	3:5:3	800	48.5
FI-4 (ST:LA:NMA)	3:5:1	800	49.6
FI-5 (ST:LA:NMA)	3:5:2	800	56.1
FI-6 (ST:LA:NMA)	3:5:3	800	51.3

2.5. Simulating studies

The mechanisms were evaluated by determination of the interaction energy between chemical compounds and asphaltenes with themselves and between chemical compounds and asphaltenes at a molecular scale through simulation method [36]. In this work, the energy of interaction pairs between asphaltenes and two flow improvers, respectively FI-2 and FI-5, were performed with density functional theory as implemented with DMol^3 code. The well-known GGA with the PBE functional was adopted for the exchange-correlation interaction. During structural relaxation, the convergence tolerances of energy, maximum force, and displacement were 1.0×10^{-5} Ha, 0.002 Ha/Å, and 0.005 Å, respectively. The interaction effect can be achieved through using an asphaltene average structure (Fig. 1) and a unit of FI-2 and FI-5 to replace themselves due to their repeat similarity of structure. The interaction strength among them could be obtained through comparing total energies that evaluated in line with formula 1:

$$\Delta E_{inter} = \Delta E_{dimer} - \sum_{i=1}^{n} \Delta E_{monomer,i}$$

where $\Delta E_{monomer}$ indicates the energy of monomeric interaction pairs and ΔE_{dimer} representatives the energy of dimeric species.

2.6. X-ray diffraction (XRD)

X-ray diffraction has been widely used to characterize the structural properties of asphaltenes. In this paper, X-ray diffraction (from the Dutch PANalytical company) was used to compare the structural information of asphaltenes and asphaltenes after treating with 800 ppm of FI-2 and FI-5, respectively. By this way, it can be obtained whether flow improvers interact with asphaltenes to affect asphaltenes structures. All analyses were carried out at a scanning rate of 1°/min, and over the scanning range of 5–80°.

2.7. Scanning electron microscope (SEM)

The samples of asphaltenes were dosed with 800 ppm of FI-2 and FI-5 in toluene solvent and fluctuated by using an ultrasonic water bath machine for 2.0 h in order to fully promote the mutual effect of them. And then test samples were obtained via solvent evaporation. Its appearance was observed through scanning electron microscope (from American FEI Company, Inspect F50) at amplification of 10,000 times. For comparative purposes, the untreated asphaltenes as reference sample also were observed. By this way, it can be comprehended how flow improvers effect asphaltenes aggregates in the macro aspect.

2.8. Rheological measurement

The apparent viscosity of asphaltenic crude oil of 100 g after beneficiating with 800 ppm of flow improvers at different temperature was respectively obtained using a NDJB-8S digital viscometer (Shanghai Changji Geological Instrument Co., Ltd.). The treated crude oil samples