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Investigation of cationic surfactants as clean flow improvers for crude oil and a mechanism study

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ABSTRACT

Cetyl trimethyl ammonium chloride (CTAC), cetyl trimethyl ammonium bromide (CTAB), and octadecyl trimethylammonium chloride (OTAC) were evaluated as clean flow improvers for crude oil. The results showed that all of them have some effect on the viscosity of crude oil in a certain temperature range, and can depress the pour point, among which CTAC is the most potent one. The viscosity was reduced to below 540 mPa s under different concentration at 35 °C by CTAC, and it can depress the pour points by 7.5 °C with the concentration of 0.03%. DSC analysis and microscopic morphology analysis discovered the interaction of CTAC and saturated hydrocarbon component of the crude oil, which can reduce the wax peak temperature and wax precipitation point of crude oil. CTAC may precipitate and pack with the long-chain alkane to form the crystal nucleus, while the cationic part and the corresponding Cl^- anion can act as a wax crystal modifier and block the wax crystal to grow up, thereby reduce the risk to form three-dimensional networks.

1. Introduction

With the decreasing of light crude oil resources, the development, gathering and transportation of heavy oil gradually increase in oil production in the world (Liu et al., 2007; Ramirez-Garnica et al., 2008; Smith et al., 2013). In recent years, a large number of high pour point and high viscosity crude oil reservoirs have been found in China. The production, storage and transportation of these heavy crude oil products have become a complex and highly technical operation (Borthakur et al., 1996; Truttle et al., 1982). The oilfields face such problems as wax deposition, high pour point, high viscosity and poor flowability. Therefore, various crude oil flow improvers have been used to improve heavy oil flowability (Al-Sabagh et al., 2013; Chen et al., 2011; Taraneh et al., 2008). Dilution with lighter crudes or alcohols, and heating are some of those common methods, but it depends on the feedstock of the lighter crudes, and the cost is very high using amount of alcohols. In general, as long as the flowability of crude oil is improved, these additives can be described as crude oil flow improver. The two common types of crude flow improver are pour point depressant and viscosity reducer (Chen et al., 2016a; Gu et al., 2012). Polyethylene derivatives are the most popular flow improvers (Al-Sabagh et al., 2013; Borthakur et al., 1996; Chen et al., 2011; Gu et al., 2012; Taraneh et al., 2008) with wax-like paraffinic groups. During the application, the wax-like paraffinic groups can cocrystallize with wax of crude oil to form a complex of oil and flow improver, and the polar groups out of he complex can modify the crystal surface and limit the grow of the cocrystals, so as to improve the flowability of crude oil. Polymers with these properties are homo and copolymers of alpha olefins, ethylene-vinyl acetate copolymers, polyalkyl acrylates, methacrylates, alkyl esters of styrene-maleic anhydride copolymers, and alkyl fumarate-vinyl acetate copolymers (Al-Sabagh et al., 2009; Gu et al., 2012; Ren et al., 2011). Although these polymers display perfect performance for some crude oil samples from global, the long molecular chain, large molecular weight, and high thermostability are problems in the oil refining process. Besides, the selectivity of these polymers for the crude oil can not be ignored. So, it is still a challenge work to seek for cleaner and universal additives for crude oil with low/small molecules, and we have devoted to such work for years. In this work, a series of cationic surfactants including cetyl trimethyl ammonium chloride (CTAC), cetyl trimethyl ammonium bromide (CTAB), and octadecyl trimethylammonium chloride (OTAC) were evaluated as clean

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flow improvers for crude oil, and the mechanism was discussed in detail.

2. Experimental

2.1. Materials

Chemicals (cetyl trimethyl ammonium chloride (CTAC), cetyl trimethyl ammonium bromide (CTAB), and octadecyl trimethylammonium chloride (OTAC)) were purchased from Fluka, and Aldrich Chemical Companies. Consistent with our reported studies (Chen et al., 2015), the crude oil sample of JH32P1 used in this study were obtained from Jinghe Oilfield China, and the physical parameters were shown in Table 1.

2.2. Evaluation tests

The viscosity of the treated heavy oil was determined using a BROOKFIELD DV-II + programmable Viscometer at certain temperatures according to Industrial Standard of China Petroleum, SY/T0520-2008. Viscosity reduction for the oil, $\Delta\eta\%$, was calculated from $((\eta_0-\eta)/\eta_0) \times 100$, where η_0 and η (mPa•s) are respectively the viscosities of the oil before and after the reaction [16]. Firstly, the crude oil was heated to 70 °C in the condition of constant temperature and airtight and kept for about 1 h. Then, 30 g samples were placed in a container at a certain temperature. About 20 min later, CTAB, CTAC and OTAC with different concentration was added into the samples and stirred constantly at certain temperature respectively. After 1.5 h, the viscosity of crude oil was measured by the rotary viscometer, and a control experiment was carried out under the condition. Each test run was repeated three times to check repeatability and the maximum errors of the product distribution fell within a reasonable range of ±2.0%. Only the average data were reported hereinafter. Similarly, the performance of CTAB, CTAC and OTAC in crude oil (JH32P1) as pour point depressants was evaluated according to Industrial Standard of China Petroleum, SY/T0541-2009.

2.3. Differential scanning calorimetry analysis

The differential scanning calorimetry (DSC) analysis of crude crud oil 1 and PAA1 treated crud oil 1 are performed using a Mettler-Toledo DSC822e DSC apparatus. The chemicals, suppliers and purities used for the DSC calibration were: *n*-C7 (Scharlau, 99%), *n*-C8 (Panreac, 99%), *n*-C12 (Alfa-Aesar, >99%), *n*-C16 (Alfa-Aesar, >99%), *n*-C18 (Fluka, P99.8%) and Indium (Mettler Toledo). Repeatability and reproducibility tests shows that this calorimeter is capable of producing data of enthalpies of fusion with an uncertainty of 1.5%, temperatures of fusion between 0.1 and 0.2 K, and heat capacities with an uncertainty of 1.5%, all at a 95% confidence level. The temperature profile follows two steps: (1) Previous step: Sample is heated at 3 °C/min from room temperature to 40 °C to completely dissolve possible solid phase and to remove any thermal history by holding for over 40min.; (2) Cooling step: Sample is cooled down from 40 °C to −20 °C at 3 °C/min.

2.4. Optical microscopy

The saturated hydrocarbon component was separated from the crude oil using the standard method for the optical study. Wax crystal morphologies were observed using a BX41-P OLYMPUS polarizing microscope. Samples were initially heated to 50 °C and then cooled to 15 °C for 5 min. A small amount of wax crystal was loaded onto the glass slide inside a copper stage with a central window. During the measurement, the temperature of the copper stage was controlled at 15 °C in a circulating bath.

Table 1
The physical parameters of the crude oil of JH32P1.

Pour point (°C)	$\rho^{30°C}$ (g·cm^{-3})	Saturated HC (%)	Aromatic HC (%)	Resin (%)	Asphaltene (%)
15.0	0.884	57.43	13.67	28.12	0.78

3. Results and discussion

3.1. Viscosity reduction performance

The performance of CTAB in crude oil (JH32P1) as viscosity-reducer was evaluated firstly. As shown in Fig. 1, CTAB has obvious effect on the viscosity of crude oil from 15 °C to 50 °C, and the viscosity reduction depends on both the additive concentration and the temperature. The general trend was obtained that the viscosity of crude oil reduces to a low level with rising temperature at various dosages of additive. It is evident that the viscosity reduction ratio can be reduced to approximately 65.5% with a concentration of 0.15% at a normal temperature, 25 °C. As the temperature rises to 35 °C, the viscosity was reduced to approximately 2000 mPa s, and the viscosity almost remains stable, under such condition the crude oil can be transported safely. Compared with the control test, without CTAB the viscosity reduces to about 2000 mPa s at about 50 °C, which means 0.15% CTAB can decrease the transport temperature by about 15 °C. In addition, it can be seen that, above 35 °C, the viscosity of crude oil is mainly affected by temperature rather than additive concentration, so the viscosity reduction efficiency of CTAB reaches to similar at any concentration above 40 °C.

Furthermore, CTAC and OTAC were also evaluated as a viscosity reducer for crude oil JH32P1, and the results were shown in Fig. 2 and Fig. 3. Like CTAB, CTAC also has obvious effect on the viscosity of crude oil in a certain temperature range, and the viscosity reduction depends on both the additive concentration and the temperature. The maximal viscosity reduction ratio can reach to approximately 82.0% with 0.15% at a normal temperature, 25 °C. On the other hand, there are some differences between CTAB and CTAC. Compared to CTAB, the efficiency of CTAC reaches to similar under different concentration above 30 °C instead of 40 °C. The viscosity was reduced to below 540 mPa s under different concentration at 35 °C. The similar results were obtained using OTAC as additive, as shown in Fig. 3. The maximal viscosity reduction ratio reaches to approximately 87.1% with 0.15% at a normal temperature, 25 °C, and the viscosity was reduced to as low as 670 mPa s at 35 °C.

3.2. Pour point depressing

The influence of the three surfactants mentioned above on the pour points of crude oil sample was evaluated, and the results were

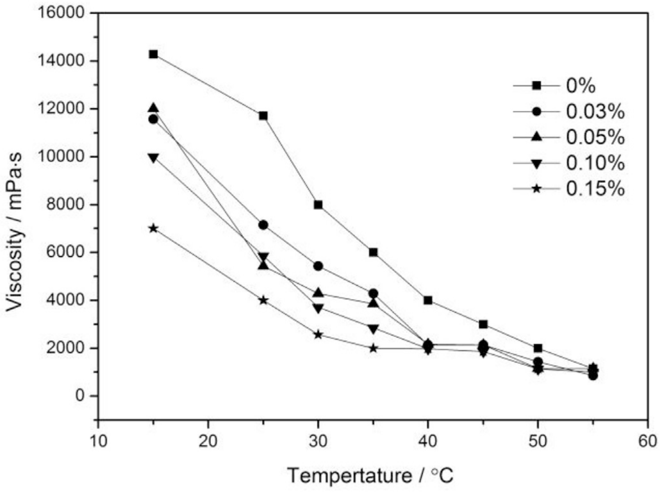

Fig. 1. Effect of CTAB on the viscosity of crude oil JH32P1.