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Preparation of a kind of reactive pour point depressant and its action mechanism

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HIGHLIGHTS

- A series of pour point depressants (PPDs) have been prepared.
- The action mechanism of the PPD was investigated by IR and DSC.
- The chemical reaction between PPD and resin/asphaltene was firstly certified.
- The results were important for guiding the development and design of PPD.

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ABSTRACT

A series of reactive pour point depressants (PPD) with anhydride group were prepared, and their action mechanism had been investigated by Fourier transform infrared spectroscopy (FTIR), differential scanning calorimeter (DSC) and cross-polarized light microscope. The results showed that the prepared pour point depressants had obvious pour point depressing effect on crude oil. Its action mechanism was concluded that PPD could react with the resin and asphaltene in the crude oil to generate a new macromolecule when crude oil was treated with PPD-3 at 90 °C. The new macromolecule further formed a new agglomerate structure by association with the asphaltene and resin in crude oil, which worked as a new nucleator to provide nucleation sites for wax crystal instead of the original asphaltene–resin agglomerate structure, and then improved the flowability of crude oil.

1. Introduction

Paraffin wax deposition from crude oils at low temperature which may block the pipelines is one of the serious problems in petroleum transportation industry [1–4]. Several methods have been available to improve the low-temperature flowability of crude oil [5–7]. Pour point depressant (PPD), alternatively known as flow improver or wax crystal modifier, can retard the growth of the wax crystal and change the process of wax crystal [8]. In recent decades, the action mechanism of PPD has become a new research hotspot about the crude oil flowability. Now adsorption, co-crystallization, nucleation, and improving wax solubility have been accepted as the most widely used theories in explaining the mechanism [9–12]. Till now, all the action mechanisms of PPD were based on the physical interaction between PPD and the components of crude oil.

Crude oils contain plenty of asphaltene and resin, which affect on the solubility of n-paraffins [13–19]. Asphaltene and resin are composed of numerous non-hydrocarbon compounds with different structures, and there are many amino and hydroxyl groups in their molecule [20–27]. Castillo and Ranaudo [28] indicated that the asphaltenes tend to form agglomerates even in good solvent. The mechanism of asphaltene aggregation involve π/π overlap between aromatic sheets, hydrogen bonding between functional groups and other charge transfer interactions [29]. The resin was derived from the asphaltene in the process of crude oil formation, and contained several fused five- and six-carbon rings in its molecule which structure was similar to asphaltene [30,31]. Therefore, the resin tended to interact with asphaltene to form resin-asphaltene agglomerates by absorbing on the polar and aromatic portions of the asphaltene, which consequently changed the structure of asphaltene agglomerate and the precipitation property of asphaltene [29,32–36].

The mechanism of asphaltene-PPD-resin agglomerates formed through intermolecular force had been studied in our previous studies, which acted as the efficient nucleator of crude oil beneficiated

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with PPD [37]. Actually, the asphaltene and resin in crude oil contain a large numbers of amino groups which have strong reactivity [38,39]. So asphaltene and resin can be chemically combined with PPD containing reactive groups in crude oil, and the reaction products may work as a more efficient nucleator of crude oil beneficiated with PPD. In the present work, a series of pour point depressants containing anhydride group in its molecular were prepared, and an attempt had been made to investigate the effect of chemical reaction between PPD and the components of crude oil on the action mechanism of PPD.

2. Experimental section

2.1. Materials

The reagents, maleic anhydride(MA), vinyl acetate(VA), toluene, octadecyl acrylate(SA), dibenzoyl peroxide, n-heptane and methyl alcohol were of laboratory-grade chemicals from Sinopharm Chemical Regent Co., Ltd. Cude oil was from Jianghan oil field of China.

2.2. Crude oil component analysis

Wax was isolated from crude oil and quantified according to SY/T 7550-2004. Asphaltene was isolated by the IP procedure NO. 143 using n-heptane. Resin was isolated according to the method adopted by the literature [19]. Meanwhile, the deasphalted and deresinated crude oil was also prepared. The deresinated crude oil was confected in proportion by adding asphaltene into the deasphalted and deresinated crude oil at 90 °C, and stirred well to blend. All of the organic solvents were analytical-reagent grade. The physical characteristics of Jianghan crude oil was listed in Table 1.

2.3. Preparation of the PPDs

In a reaction flask equipped with a mechanical stirrer, a reflux condenser and a temperature controller, all PPDs were prepared through solution polymerization with monomer mixture of maleic anhydride, vinyl acetate and octadecyl acrylate in toluene. Polymerization was initiated by dibenzoyl peroxide in nitrogen atmosphere, and carried out at 90 °C for 3 h under continuous stirring. Purification of the polymeric products was undertaken by cooling the reaction mixture to room temperature, precipitating from toluene by using excess methanol while stirring, then filtering and vacuum drying.

2.4. Characterization of the products

The chemical structure of the prepared pour point depressants were characterized by means of infrared (IR) spectroscopy using Thermo Nicolet IR spectrophotometer model IR 460. The weight-average molecule weight (Mw) of the prepared pour point depressants was determined by gel permeation chromatography (Waters Model 1515).

2.5. Evaluating test of pour point

The pour point of the treated and untreated crude oil was determined by ASTM Standard D-97.

2.6. Rheological measurement

Apparent viscosity of the treated and the untreated crude oil were measured by a Brookfield Synchrolectric Viscometer (USA).

Table 1
Physical characteristics of Jianghan crude oil and the prepared oils.

Crude oil	Pour point (°C)	Viscosity (mPa s, 50 °C)	Component of the crude oil (wt%)			
			Asphaltene	Resin	Wax	Liquid oil
Jianghan	34	147	1.65	46.06	7.87	44.42
Deasphaltened	32					
Deresinated	31					
Deasphaltened and deresinated	29					

Spindle No. 1 was used for measuring apparent viscosity at a speed of 60 rpm.

2.7. Differential scanning calorimetery (DSC)

DSC measurements were performed using DSC 822 (Swiss METTLER TOLEDO Ltd) in the temperature range from 90 to 0 °C at a cooling rate of 5 °C/min.

2.8. Microscopy

A cross-polarized light microscope (OLYMPUS BX51, Japan) was used to evaluate the wax crystal morphology of the treated and untreated crude oil at room temperature.

3. Result and discussion

3.1. Pour point depressing effect

Before pour point and rheological measurements, crude samples were conditioned at 90 °C for 4 h to remove previous shear and thermal history of the crude oil [40]. Table 2 showed the pour point depressing effect of the prepared PPD. The results showed that monomer molar ratio of octadecyl acrylate and maleic anhydride had an important influence on the pour point depression of crude oil. PPD-3 had the best Pour Point depressing effect, which could make the pour point of the treated crude oil drop 9 °C when it was used in a dosage of 500 ppm. And the pour point depressing effect would be increased further as its application dosage increased.

Fig. 1 exhibited the effect of treating temperature on the pour point depressing. It could be seen that when crude oil was treated with PPD-3 in a dosage of 1000 ppm, pour point of the treated crude oil was decreased obviously with the increase of treated temperature, and the pour point depression kept the same when the treated temperature was higher than 90 °C.

Table 2
Pour point depression of the crude oil treated with PPDs.

Kind of PPD	Molar ratio of mixed monomers used to synthesize PPD	Dosage of PPD (ppm)	Pour point depression (°C)
PPD-1 (SA:MA:VA)	8:1:1	500	7
PPD-2 (SA:MA:VA)	7:2:1	500	8
PPD-3 (SA:MA:VA)	6:3:1	500	9
PPD-4 (SA:MA:VA)	5:4:1	500	7
PPD-5 (SA:MA:VA)	4:5:1	500	6
PPD-6 (SA:VA)	9:1	500	4
PPD-3 (SA:MA:VA)	6:3:1	100	2
PPD-3 (SA:MA:VA)	6:3:1	300	6
PPD-3 (SA:MA:VA)	6:3:1	700	10
PPD-3 (SA:MA:VA)	6:3:1	1000	12