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Effect of ammonium-containing polyalkyl acrylate on the rheological properties of crude oils with different ratio of resins and waxes

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ABSTRACT

A composite additive for oil pipeline pumping has been tested as a viscosity modifier and crystallization modifier (depressant) in two crude oils and gas condensate of West Siberian deposits with the different content of resins and waxes. The additive represents a toluene solution of a cationic surfactant and an amphiphilic copolymer of alkyl acrylate C16-C20 with a salt of acrylic acid and higher amine. Pour points, rheological characteristics, phase transition temperatures, energies of the destruction of supramolecular structures were determined for investigated oils with different concentrations of the additive. The comparison of the efficiency was made for the composite additive, a commercial depressant and surfactant-free additive.

1. Introduction

Crude oils contain a wide range of hydrocarbon components and have a complex nature. Depending on the place of production, crude oil may contain considerable amounts of waxes, resins and asphaltenes. These heavy oils are viscous fluids with high pour points exhibiting non-Newtonian flow behavior below pour point temperature (Barry, 1971). A variety of difficulties arises during the production, separation, transportation and refining of such oils (Speight, 1998; Uhde and Kopp, 1971). The most important among them is the relatively low solubility of paraffins causing their precipitation when crude oil is cooled below the certain temperature. Furthermore, the viscosity of heavy oils at 25 °C varies from 1000 to 100,000 cP or more (Messick, 1982; Schumacher, 1980). This leads to complications when pumping oil through the pipeline up to its complete blockage. At the same time heavy crude oils account for a large fraction of the world's recoverable oil reserves (Meyer et al., 2007) and production of such oils is constantly increasing.

Several methods are used to overcome the above problems, for example, stream heating, the use of electrically heated pipelines, dilution with lighter crudes or alcohols, mechanical scraping, the use of chemical additives (Kelland, 2014; Martínez-Palou et al., 2011), and formation of emulsions (Ashrafizadeh and Kamran, 2010; Langevin et al., 2004). In the latter method heavy oil is suspended in water using surfactants to form an O/W emulsion, and thus a decrease in the apparent viscosity is achieved.

The most simple, convenient and cost effective method is to use the chemical additives which can be classified as pour point depressants (PPDs), flow improvers (FIs), and paraffin inhibitors. But the additives efficiency is strongly dependent on the composition of oil and the ratio of resins, asphaltenes and paraffins in it, and this dependence is very complicated. Therefore, typically for each crude oil sample the most effective additive is selected empirically, so for different oils different polymers are more effective. In particular, the active components of many well-known asphaltene-resin-paraffin inhibitors are surfactants of various types including salts of higher amines (Ravindranath, 2004), although more often the nonionic and anionic surfactants are used (Kelland, 2014; Martínez-Palou et al., 2011; Rocha Junior et al., 2006).

Various synthetic polymers are widely used as crystal structure

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modifiers (Martínez-Palou et al., 2011). Authors (Pedersen and Rønningsen, 2003) investigated the effect of 12 different commercial wax crystal modifiers on the waxy North Sea crude oil with about 15 wt% wax content. The highest pour point depression was exhibited by the additives based on polyalkyl methacrylates, copolymers of ethylene and vinyl acetate (EVA) and the composition of EVA with copolymers of maleic acid anhydride and α-olefin. It should be noted, however, that additives with the same polymer base substantially differently reduced the viscosity of oil.

In a number of studies the effect of the structure of side alkyl groups in comb-like macromolecules on the effectiveness of additives was examined. Waxy Egyptian crude oil (wax and asphaltene content, %, respectively, 8.4, 3) was treated with the copolymers of octadecene and maleic anhydride chemically modified by three n-alcohols (C12, C16, and C22) to estimate the influence of copolymers composition on their efficiency as FIs and PPDs (El-Ghazawy et al., 2014). In this case, the best action (depressor and rheological) was shown by the additives based on C16 alcohols. Rows of efficiency were as follows:

PPDs: C16 > C22 > C12; FIs: C16 > C22.

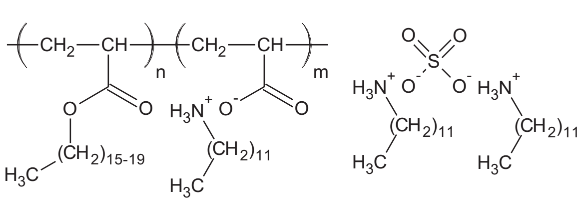
Effective depressants for many crude oils are the copolymers of higher alkyl acrylates with the preferred number of carbon atoms in the alkyl substituent of 16 or more (Kelland, 2014). Contradictory data presented for Nada crude oil (India) in (Deshmukh and Bharambe, 2008). For copolymers of n-alkyl acrylates with N-hexadecylmaleimide, apparent and plastic viscosities depend on the alkyl chain length randomly, and as PPDs the copolymers are arranged in row:

C14 ≈ C18 > > C16 > C10 ≈ C12.

In the work (Erceg Kuzmić et al., 2008) the efficiency of 22 copolymer additives (based on polyalkyl acrylates) as PPDs and FIs were investigated on the three samples of crude oils with different contents of paraffins (the resin and asphaltene contents was not given). The dependence of the pour point depression on the paraffin content in most cases could not be traced. Terpolymer containing units of acrylic acid, together with alkyl acrylates and 1-vinyl-2-pyrrolidone was more effective as FIs for highly paraffinic oil, while styrene-containing terpolymer worked better in oil with lowest paraffins content.

The action of conventional FIs can be improved by adding wax dispersants. Usually the structure of wax dispersants is similar to that of FIs but they often have more polar functional groups and possess properties of surfactants. Polar nitrogen containing polymers (for example, having amine or amide groups) can be wax dispersants and flow improvers simultaneously.

Recently, compositions of polymers and surfactants as additives for crude oils have attracted attention of researchers (Kelland, 2014). According to (Matras et al., 2008) the synergistic effect on drag reduction was achieved for the mixture of a polymer and surfactant. Molecular aggregates are formed where a polymer film is formed around surfactant's micelle. Under flow, such aggregates take preferred orientation according to the minimum resistance principle and reduce drag more efficiently than the additives alone. Recently, we have shown (Prozorova et al., 2015) the high efficiency of the composition of a cationic surfactant and copolymer of alkyl acrylate with an ammonium salt of acrylic acid (Scheme 1) as an asphaltene-resin-paraffin inhibitor for two crude oils and gas condensate (GC) of West Siberian deposits of Russia with the different content of resins and waxes.



Scheme 1. Structure of ammonium-containing composite additive.

The purpose of this work was to compare the efficiency of the composition shown in Scheme 1 as a flow improver and depressant in the same objects and to determine the dependence of the additive efficiency on the ratio of resins and waxes in crude oils.

Gas condensate was used as a basis for comparison, showing the effect of the additive in the absence of resins and waxes. Also the efficiency of the synthesized composite additive was compared with those of a commercial depressant (Flexoil WM 1470) and surfactant-free additive (the analog of the composite additive but containing no dodecylammonium sulfate and units of dodecylammonium acrylate).

2. Experimental

2.1. Materials

Acrylic acid (AA), azobisisobutyronitrile (AIBN), hydroquinone, dodecylamine (DDA) and toluene were obtained from Aldrich and used without further purification. The blend of linear fatty alcohols C16-20 (NAFOL 1620 from Sasol, Germany) had a composition, wt%: C16-65.7, C18-24.6, C20-9.7.

The composition and physicochemical characteristics of crude oils and gas condensate used are listed in Tables 1 and 2. Crude oil from the Verkhne-Salatskoye deposit (W, waxy) contains a large amount of paraffins and relatively small amount of resins which leads to a high pour point. Crude oil from the Urmanskoye deposit (R, resinous), in contrast, contains a small amount of paraffins and is rich in resins. Asphaltenes in both oils are either absent or in small quantities. Gas condensate from the Urengoyskoye deposit contains no waxes, resins and asphaltenes, so it has a low viscosity and pour point.

2.2. Synthesis of monomers and the preparation of the monomer mixture

A mixture consisting of fatty alcohols C16-20, AA (the ratio of AA to alcohols of 1.05:1), sulfuric acid, hydroquinone, toluene were heated at 100–120 °C for 4 h. Water formed during the reaction was removed as an azeotrope with toluene. The total conversion of alkyl acrylates determined by gas chromatography was approximately 96%. Then neutralization of the reaction mixture was carried out by gradual addition (while stirring and cooling) of n-dodecylamine (the ratio $[H^+]$: RNH_2 was 1:1.1) at the reaction temperature of 40–60 °C. Thus, unconverted AA and sulfuric acid was neutralized to form corresponding ammonium salts. The procedure is described in more detail in Kazantsev et al. (2014).

2.3. Synthesis of the polymer additive

The monomer mixture obtained in the previous step, consisting of alkyl acrylates C16-20, dodecylammonium acrylate and dodecylammonium sulfate in the toluene solution was purged with

Table 1
The composition and pour points for crude oils and GC.

Object	Composition, wt%			Pour point, °C
	Waxes	Resins	Asphaltenes	
GC	–	–	–	−19.7
W	10.3	5.5	–	+18.8
R	6.6	13.1	1.6	−7.3