Abstract

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Hydrophobically modified polymeric additives for paraffin inhibition and pour point temperature reduction of oils

**General description**. This work is aimed to the development of hydrophobically-modified multifunctional polymers that could be used as additives (depressants) to crude oil in order to prevent paraffin deposition processes in pipes and tanks, reduce pour point temperature of high-viscosity and high-paraffin oils of Kazakhstan. The relevance of research consists in the development of reagents that are not inferior in terms of characteristics to imported additives from foreign companies. The novelty of the project lies in the fact that for the first time in world practice, hydrophobically-modified monomers and polymers containing long-chain hydrocarbon “tails” (C12-C18) and hydrophilic zwitterionic “heads” were synthesized according to the Michael reaction. The addition of a polymer additive in amount of 200 to 1000 ppm leads to decrease oil viscosity, paraffin deposition (80-99%) and pour point temperature (up to -30 °C) compared to heat-treated or crude oil. In addition, hydrophobically-modified polymers can be used as enhanced oil recovery reagents. A potential consumer of polymer additives is KazTransOil JSC, where tests were carried out on the basis of the scientific and technical center of KazTransOil JSC by using methods developed there.

**The work was carried out** as part of the project “Development of a technology for producing hydrophobically-modified polymer additives for inhibiting paraffin deposition and pour point temperature reduction” from the Ministry of Education of the Republic of Kazakhstan, subprogram 102 “Grant funding for scientific research 2015-2017”, priority: “Rational use natural resources, processing of raw materials and products”, state number Registration: 0115РК01023.

**The relevance of the work.** For the production, oil refining and transportation of oil, Kazakhstan imports chemicals (polymers, surfactants, corrosion inhibitors, additives and etc.) and also catalysts from foreign countries. The price of that are high and, thereby, Kazakhstan becoming technologically dependent from this. In this regard, the development of reagents for the oil industry of Kazakhstan, competing with foreign counterparts, is put forward as a primary task and is of particular relevance. During oil pipeline transport, temperature decrease results in the precipitation of high molecular weight oil compounds, mainly consisting of paraffin hydrocarbons, deposits on a various surfaces of oilfield equipment, pipelines or tanks. Today, transportation of high paraffinic oils from the different oilfield to the production pipeline is most acute. In the main oil pipeline, oil from various fields is averaged. It should be noted that composition of crude oils of various oilfields differ significantly and contain paraffins of various structures and concentrations. The problems caused by paraffin deposition during transportation of oil are decreasing diameter of the pipe due to paraffin deposits on the walls; increasing the pressure required to oil transport and reducing fluidity due to the formation of crystallite (increase viscosity).

Various transport methods are known for high paraffinic oils. The most common and reliable method is the "hot transfer", however, heating furnaces are source of emissions. Also, the possibility of emergency situations is not excluded, which can lead to environmental and technical problems. Recently, depressant have become widely used for the transport of high paraffinic oils, depressants participate in the process of paraffin crystallization and prevent formation of a single crystalline structure of paraffin during oil cooling. This leads to an improvement in the rheological properties of the oil by lowering the pour point temperature, decreasing effective viscosity and decreasing friction pressure loss.

One of the promising areas is synthesis of paraffin inhibitors based on hydrophobically-modified polybetaine structures. Such polymers, developed by Kazakhstani scientists, found practical application in relation to Malaysian oil with high pour point temperature. There was possible to achieve pour point temperature decrease by 12 ° C (origin pour point of crude oil was 57 ° C) and double viscosity reduction. These results indicate the prospects of Kazakhstani developments in terms of regulating the rheological characteristics of high viscous and high paraffinic oils.

This work is a branch of above described studies and mainly aimed to developing method for the synthesis of hydrophobically-modified polybetaines with different lengths of the hydrophobic part (C12-C18), studying the additives effect on the thermal characteristics of oil and ability to inhibit the formation of paraffin deposits in the pipeline.

In light of the foregoing, chemical technologies and application of reagents in pipeline transport, in particular depressant additives, their development, production, and use are an important and urgent task.

**The purpose of research.** Synthesis and study of hydrophobically-modified monomers and polymers aimed to prevent paraffin deposition processes and decreasinf pour point temperature of high-viscosity and high-paraffin oils of Kazakhstan, that could be stored in tanks and transported through oilfield and main pipelines.

**The main scientific tasks were as follows:**

1) Synthesis of hydrophobically-modified monomers and polymers,

2) Study of the physicochemical properties of hydrophobically-modified polymers,

3) Establishing the structure of polymeric materials,

4) Creating a model tank and oil pipeline to assess the effectiveness of polymer additives,

5) Study of the effectiveness of polymer additives as a pour point depressants and paraffin inhibitor in a model reservoir and oil pipeline.

**The objects of study** were hydrophobically-modified monomers and polymers based on alkylaminocrotonates and unsaturated carboxylic acids, which could prevent paraffin deposition processes and reduce the pour point temperature of high-viscous and high-paraffinic oils in model tank and pipeline, tested on Buzachi-Mangyshlak oil-mixture and Mangyshlak oil.

**The subjects of the study:**

1) The formation reaction of alkylaminocrotonates based on acetoacetic ester and long chain alkylamines according to the Michael addition mechanism.

2) Radical polymerization of alkylaminocrotonates in the presence of (meth) acrylic acid.

3) Physico-chemical properties and characteristics of the synthesized polymers.

4) The effect of additives on the pour point temperature, viscosity and rheological properties of the studied oils.

5) The paraffins crystallization processes in the presence of depressant during temperature changing.

6) Depression abilities of polymer, formation of asphaltene-resin-paraffin deposits in a model reservoir and pipeline.

**The scientific novelty of the work.** Alkylaminocrotonates based on acetoacetic ester and long-chain alkylamines (C12 - C18) were obtained. Using such methods as FTIR, 13C and 1H NMR, GC-mass spectroscopy, the structure of hydrophobically-modified monomers and polymers based on alkylaminocrotonates and acrylic acid was established.

The thermal, hydrodynamic and conformational characteristics of polymers in the solid state, aqueous and organic solvents are determined. The isoelectric point, average hydrodynamic size, and zeta potentials of macromolecules in water and organic solvents are determined. It is shown that in an aqueous solution, hydrophobically-modified polybetaines form a micellar structure, which is stabilized by the hydrophobic interactions of long aliphatic “tails”. It was shown that in an organic solvent, DMSO, the formation of reverse micelles stabilized by intra- or interionic interactions of betaine groups occurs.

A model tank and oil pipeline were developed and created in order to test the effectiveness of polymer additives. The physicochemical and rheological properties of the Buzachi-Mangyshlak oil-mixture and Mangyshlak oil are investigated. The pour point temperature, component composition, paraffin distribution, and acid number were determined.

The effect of polymer additives on the viscosity and rheological properties of oils was studied. By using optical microscopy, the paraffin crystallization process was observed and critical temperature parameters, that may affect on pour point temperature, were established. An optimal concentration of hydrophobically-modified polymers (200 - 1000 ppm) was found, maximum pour point depression for Mangyshlak oil – 24 °С and Buzachi-Mangyshlak oil mixtures – 39 °С. Polymer depressants improve the rheological parameters of oil by modifying the surface of paraffin crystals and decreasing effective viscosity.

The results of polymer depressant tests in a model tank and oil pipeline showed the most optimal concentration of additives was equal 500 ppm (treatment temperature 60 °C), moreover, addition of 500 ppm of depressant can significantly reduce the amount of asphaltene-resin-paraffin deposits. Pilot tests of polymer additives CRO series were performed and potential recommendation for JSC KazTransOil were developed.

**Protection provisions:**

- Synthesis of hydrophobically-modified monomers and polymers based on alkylaminocrotonates,

- Physico-chemical properties of hydrophobically-modified monomers and polymers,

- The effect of polymer additives on the physicochemical properties of the tested oils (pour point temperature, viscosity, rheology),

- Tests of polymer additives in model tank and oil pipeline in the presence of polymer additives,

- Inhibition efficiency determination of asphaltene-resin-paraffin formation.

**Scientific significance.** A method has been developed for the preparation of hydrophobically-modified monomers, radical polymerization of monomers with unsaturated acids. The effect of reducing pour point temperature of Mangyshlak and Buzachi-Mangyshlak treated oil mixtures, changes of viscosity and rheological properties of tested oils, inhibition ability of asphaltene-resin-paraffin formation in a model pipeline.

**Practical significance** concludes in the development of products and technologies that could compete with world analogues. The results of the research will serve as a prerequisite for the development of a new scientific direction “Polymers for the extraction and transportation of high-paraffin and high-viscosity oils and oil mixtures”.

**Research Methods.** The general research methodology includes a synthetic, research and practical part. The methods of polymerization, gravimetry, potentiometric titration, NMR, gas chromatography, infrared spectroscopy, gas-liquid chromatography, transmission electron microscopy, optical microscopy, differential scanning calorimetry, X-ray fluorescence analysis, viscometry, rheology were used.

**Approbation of work.** The results of the work were presented and discussed at international conferences:

- Seventh All-Russian Scientific and Practical Conference “Oil, Gas, Oil Production, Preparation, Transport”, Tomsk, Russia, September 19-23, 2016,

- 8th International IUPAC Symposium “Macro- and Supramolecular Architectures and Materials” (MAM-17), Sochi, Russia June 6-10, 2017,

- VII All-Russian Kargin Conference Polymers-2017, Moscow, Russia, June 13-17, 2017,

- VII International Workshop "Specialty polymers for environment protection, oil industry, bio-, nanotechnology and medicine", Almaty, Kazakhstan, September 7-9, 2017,

- 12th International Symposium on Polyelectrolytes, ISP, Wageningen, Netherlands, August 27-31, 2018

**Publications.** During the PhD programm studies, 11 works were published, including: 4 - in journals included in the Scopus and Web of Science databases, 1 - in journals recommended by the Committee for Monitoring in Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan , 5 - in the materials of international conferences, 1 – chapter monograph, 1 – patent.

**Summary of the dissertation.**

**The introduction** contains main aspects and provisions of the topic.

**The first chapter** of the PhD thesis focused on the analysis of current state of technological and scientific achievements in the field of oil and oil products pour point temperature decreasing. Certain causes and patterns of paraffin crystals precipitation and asphalt-resin-paraffin deposits were summarized. A connection has been established between oil composition and paraffin crystallization process. The main types of polymer depressant are given.

**The second chapter** provides information about the chemical materials, that have been used, and the main methodological data. Synthetic protocol for production of hydrophobically-modified monomers and polymers were described.

**The third chapter** is devoted to the physicochemical properties of the obtained hydrophobically-modified monomers and polymers. The results of laboratory tests of polymer depressant are presented. The results of pour point temperature of treated Mangyshlak oil and oil mixtures Buzachi-Mangyshlak (67-33%) with depressants are shown. The influence of the additives on the rheological properties of the studied oils were established. The effectiveness of paraffin deposition inhibition tested by using “cold finger” method. The results of paraffin deposits inhibition ability in model oil pipeline are presented. Tests data of CRO additives performed at Scientific and Technical Center of KazTransOil JSC are presented.

**In conclusion**, the main results and outputs are summarized.