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# Study of viscosity-temperature properties of oil and gas-condensate mixtures in critical temperature ranges of phase transitions

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## Abstract

Transport of oil and gas-condensate mixtures of various compositions is found to be accompanied by a slight increase in viscosity in the coldest period when ground temperatures at depth of a condensate pipeline reach 0 – minus 4°C. Fall in temperature of oil fluids under study to minus 10 – minus 30 °C is accompanied by a sharp increase in all structural and rheological parameters of the mixture. Even a slight amount of oil added to a gas-condensate mixture causes a significant decrease in viscosity in the negative temperature range. As a result, cloud and pour point of a mixture falls, its amount decreases, the structure of paraffin deposits changes.

*Keywords:* oil, gas-condensate, oil and gas condensate mixture, viscosity-temperature properties, activation energy of viscous

## 1. Introduction

The problems associated with transport of oil and gas-condensate mixtures (**OGCM**) have become especially important due to a significant increase in a share of high-viscosity and high pour-point gas condensates (**GK**) and paraffin oils in such mixtures. The major problems that occur during pumping of such raw materials are associated with low mobility, high pour point and paraffin sediments on pipeline walls.[1,2]

In order to solve such problems, the crystal structure of solid paraffins which make up the major part of a

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dispersed phase[3–9] is destructed by different methods. The most common of them include heating of a condensate pipeline, or addition of depressant and dispersant additives to heavy GKs to change their low-temperature properties. Pressurization of a pipeline allows destructing crystal structures which form at temperatures lower than the paraffin chilling and melting temperature. In addition, a thinner – light GK or tarry oil – may be added to the mixture with heavy GK in optimal proportions.[10]

Mixing of oils and GKs may disturb stability of the colloid system and lead to precipitation of solids demonstrating that these components are incompatible with each other. A wide range of methods based on knowledge of a composition have been developed for analyzing incompatibility of oils to be mixed.[11] Nowadays, there are not any incompatibility criteria which take into account the effect of the temperature factor on molecular processes that occur during phase transitions of colloidal particles in a dispersed phase at critical temperatures.

According to the colloidal chemical concepts, mixing of condensates and oil induces internal restructuring and rearrangement of components between a dispersed phase and a dispersion medium. Due to diffusion processes resulting in rearrangement of oil components among a nucleus, a solvation layer of structural units and a dispersion medium, as well as adsorption of the most surface-active components, dispersity of the colloidal system changes. Such a change affects rheological properties and energy parameters of viscous flows of oil and gas-condensate mixtures.

This paper is aimed to study the viscosity-temperature behavior of model heavy GK mixtures with oils when temperature drops below the critical temperatures of phase transitions.

## 2. Subjects and methods

The OGCM model mixtures were produced using samples of stable paraffin gas condensates GK1 and GK2, and paraffin oil M573 from fields of the Western Siberia. The physical and chemical parameters of the initial samples are presented in Table 1.

Table 1. Physical and chemical properties of gas condensates and oil

| Parameter | GK1 | GK2 | M573 |
|---|---|---|---|
| Standard density, kg/m$^3$ | 728.0 | 711.0 | 871.0 |
| Viscosity at 20 °C, mPa·s | 3.3 | 1.8 | 21.3 |
| Pour point, °C | 4.4 | -13.3 | 7.8 |
| Cloud point, °C | 18.5 | 20.9 | 11.0 |
| Paraffin content, % (w/w) | 3.2 | 2.8 | 9.4 |
| Resin content, % (w/w) | – | – | 2.5 |
| Asphaltene content, % (w/w) | – | – | 1.3 |

Unlike paraffin GKs that do not contain resins and asphaltenes, the high-paraffin oil M 573 is characterized by high pour points (Tp) and contains about 4% (w/w) of resin and asphaltene components. The content of asphaltenes and resins in oil was determined by adsorption chromatography based on aluminum oxide as per ASTM D2007. The content of paraffin hydrocarbons was determined as per ASTM E1519. Cloud and pour points of the samples were measured as per ASTM D5773-10 and D97.

OGCM mixtures were prepared at a room temperature by continuous mixing and adding 0.2 – 5 % (w/w) oil to gas condensates GK1 and GK2.

The dynamic viscosity of the samples was measured by rheometer LVDVIII Ultra (Brookfield, USA) using the thermostatically controlled cylindrical measurement system of cone-cone type at fixed shear rate of 85 rad/s and reduction of temperature from +10 °C to -30 °C at cooling rate of 0.5 °C/min. Control of parameters (temperature, shear rate, measuring frequency) was performed using the special-purpose software RheoCalc.

The microstructure of the deposits was measured by microscope Axio Lab.A1 (Carl Zeiss) in transmitted light at 800x magnification.

## 3. Results and discussion

Fig. 1 presents the temperature dependencies of change in dynamic viscosity of OGCM based on GK1 and GK2 with 0.2 – 5 % (w/w) oil when oily mixture is cooled from (10) °C to (–35) °C. Addition of 0.2 % (w/w) oil leads to

decreasing viscosity of initial GK1 and GK2 by 15 – 20 %. With increasing the oil concentration to 5 % (w/w), viscosity of GK1 increases throughout the temperature range. 1 % (w/w) oil added to GK2 leads to increasing viscosity by 20 – 25% as well. However, with the further growth of oil concentration in the mixtures up to 2 – 5% (w/w), viscosity decreases by 20 – 25 % (*b*).
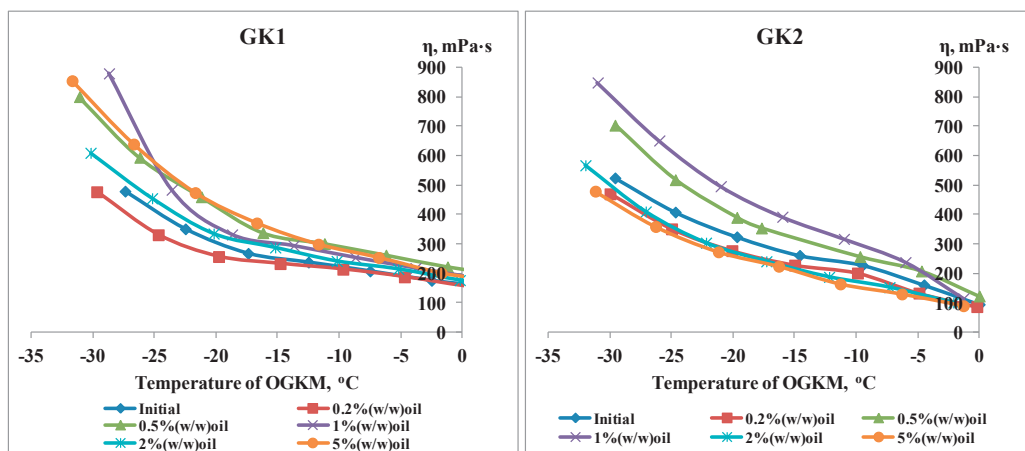


Fig. 1. Change in dynamic viscosity η of the gas condensate mixture with addition of oil as reaction to temperature drop

The study of the effect of oil addition on cloud point Tc of the GK1-based mixture shows that, with increasing oil concentration, Tc decreases only by 1.6 – 2.4 °C (Fig. 2).
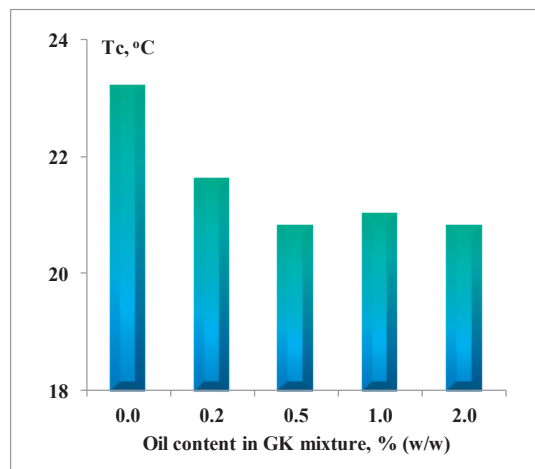


Fig. 2. The effect of the oil component on cloud point $T_c$ of the GK1-based mixture

Only addition of 0.2 % (w/w) oil to GK1 is accompanied by a certain decrease in pour point of OGCM by 1.3 °C, while the further growth of the oil concentration in the mixture leads to increase in Tp (Fig. 3). It is known from the Arrhenius equation that the condition of any thermodynamic system depends on a relationship between energy of intermolecular interaction and heat motion. Therefore, activation energy of viscous flow and the associativity (structuredness) of a fluid[12] are interrelated for the oil system. The temperature dependence equation arising from the diffusion theory of viscosity can be used for studying the structure of flowing liquid phases: $\eta = A \cdot e^{-E/RT}$,
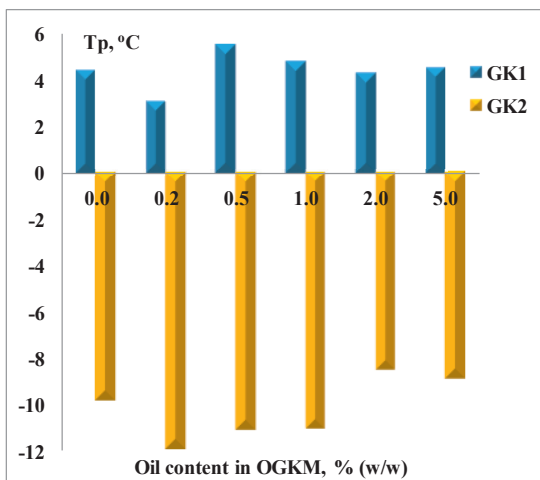
where *η* is the dynamic viscosity;

Fig. 3. The effect of oil addition on pour point Tp of the GK2-based mixture

*A* is the preexponential factor;

$e^{-E/RT}$ is the share of active molecules in the reaction mixture which are very sensitive to temperature change;

*E* is the activation energy of viscous flow $E^a_{vf}$ or mean excess energy of reacting molecules in comparison with other "inactive" molecules;

*R* is the universal gas constant;

*T* is the absolute temperature.

In order to calculate the activation energy of viscous flow $E^a_{vf}$, the semilogarithmic temperature dependence of the OGCM dynamic viscosity $\ln(\eta)$ - $1/T$ in the range from 10 to -32 °C was graphically presented (Fig. 4).
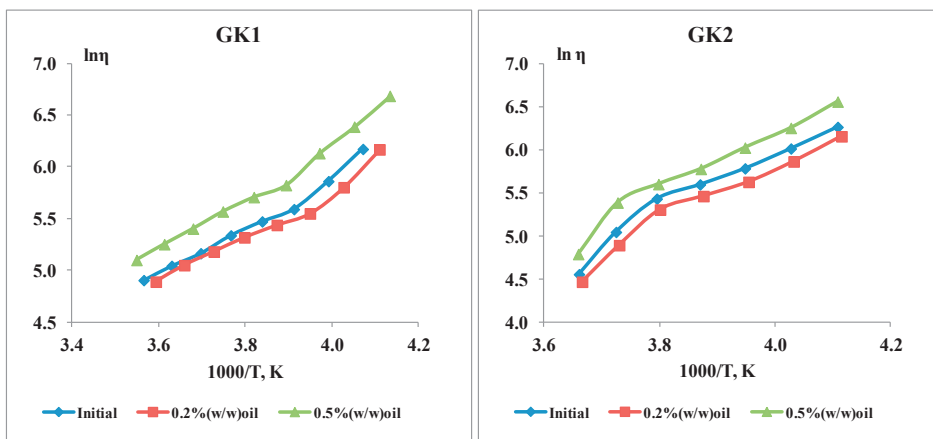


Fig. 4. Temperature dependence of OGCM effective viscosity in Arrhenius coordinates

The value *E* is determined by the slope of the curve of the curvilinear relation and characterizes bond strength of aggregates in each structural condition. The graph for oil-containing systems with high content of paraffines is usually represented by two sections which correspond to certain types of structuring and are separated by a point of inflection. This point corresponds to phase-transition temperature at which the crystal structure of paraffines ($T_{pt}$) that is typical for oil-containing systems under given conditions is destructed or generated. This

point is sometimes taken as paraffin saturation point.[13]

$T_{pt}$ for GK1 is -17.4 °C. $T_{pt}$ for GCs with addition of 0.2 % (w/w) oil migrates towards the negative-temperature region by 2.4 °C, while $T_{pt}$ for GCs with addition of 0.5 % (w/w) oil, on the contrary, migrates towards the positive-temperature region by 1.2 °C (Fig. 4). Migration of phase-transition points is not observed for GK2 with a minimal oil component. With increasing oil concentration, the phase equilibrium migrates towards the high-temperature region.

The calculated values of activation energy of viscous flow $E^a_{vf}$ for gas condensates with addition of 1 – 5 % (w/w) oil are given in Table 2. The formation of GKM aggregates with a minimal share of oil component (0.02 w/w) is accompanied by a slight decrease in $E^a_{vf}$ due to reduction of their size and aggregative stability.

Table 2. The effect of oil concentration in GK on energy activation of viscous flow $E^a_{vf}$(kJ/mol)

| Oil concentration in GKM % (w/w) | GK1 | GK2 |
|---|---|---|
| 0 | 12.5 | 15.9 |
| 0.2 | 10.3 | 15.7 |
| 0.5 | 12.1 | 16.2 |
| 1.0 | 25.0 | 18.4 |
| 2.0 | 13.2 | 15.7 |
| 5.0 | 14.5 | 15.4 |

The maximum growth of $E^a_{vf}$ is observed for oil-containing mixtures with addition of 1 % (w/w) oil (by 50% and 13.6%). This suggests that the rigid and stable crystal structure forms in GKM of this composition, and much more energy is needed to destruct this structure as compared with mixtures containing less and more oil (Fig. 5).
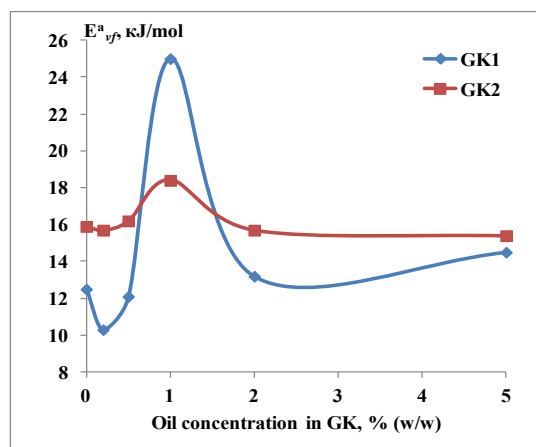


Fig. 5. The dependence of $E^a_{vf}$ on oil concentration in OGCM based on GK1 and GK2

Resin-asphaltene components are known[14,15] to be natural surface-active substances, and their presence in oil dispersed systems leads to significant weakening of the coagulation bonding strength. The small concentration of resin-asphaltene components in oil dispersed systems inhibits generation of the volume crystal lattice, and paraffin crystals remain in flowing conditions in intermicellar form which leads to decrease in viscosity and pour points of OGKM.

The structure of GK1 and OGKM was studied with the microscopic method. The microanalysis of the gas-condensate dispersed phase with and without addition of oil performed by dried-droplet method is presented in Fig. 6.

Fig. 6. (a) GK1; (b) 0.5 % oil; (c) 2 % oil micrographs of OGKM deposits based on GK1 with addition of oil

Larger (around 100 – 150 μm) lamellar crystal formations are present in the structure of GK1 deposit along with small branching (Fig.6 a). Large paraffin aggregates are not observed after addition of 0.2 and 0.5% oil in the sediment structure; only smaller lamellar structures of 20 – 25 μm are present (Fig. 6 b). Addition of 1 %, 2 % and 5 % (w/w) oil in the deposit structure results in formation of large paraffin aggregates of mixed type (Fig. 6 c).

## 4. Conclusion

Thus, the study of temperature effects on structural and rheological parameters of paraffin gas condensates with addition of paraffin oil demonstrates that the addition of 0.2 % (w/w) leads to decreasing cloud point and viscosity of gas condensates in the negative-temperature range. The addition of paraffin tarry oil can lead to decrease (GK1 mixture) or increase in pour point (GK2). Aggregates of a rigid crystal structure with maximum thermodynamic stability form in gas condensate mixtures with addition of 1% (w/w) oil.

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