Research on Efficiency of Solvents of Paraffin Deposits

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Abstract. Differential scanning calorimetry has been used to study the phase transition of commercial paraffins in asphaltene-resin-paraffin deposits (ARPD). Paraffin deposits have been collected from the surface of oil field equipment in the Irelakhskoye oil and gas field (Sakha Republic (Yakutia). Gas condensate (GC) that is currently used in this field to remove deposits, as well as its mixture with cyclohexane and p-xylene, have been studied as ARPD solvents. The degree of crystallinity (DC) of paraffins has been identified to depend on the degree of aliphaticity of the mixed solvents used, with an increase in the degree of aliphaticity of the solvent, the DC of paraffins increases. Paraffins in the triple solvents are found to possess low DC and high melting points. The results of the research led to the conclusion that it is necessary to use GC with addition of aromatic concentrate to remove paraffin deposits in the oil field.

1. Introduction
One of the key problems in development of oil fields in Eastern Siberia is removal of asphaltene-resin-paraffin deposits (ARPD). Intensification of deposition of high-molecular weight compounds of oil in the form of deposits on the surface of oil field equipment and in wellbores for oil production in this area is caused by impacts of permafrost and low temperature climatic condition. There are various methods to fight against ARPD: physical methods - thermal effects, exposure to ultrasound or magnetic fields, and chemical ones - use of additives, surfactants, inhibitors, and solvents. The conventional method involves using of hydrocarbon (HC) solvents in the form of gas condensate or gasoline [1] produced in a particular field, as well as mixtures based on them. Thus, in the Irelakhskoe oil and gas field, gas condensate produced there is used to remove ARPD from oilfield equipment. Alkane HC dominates in the composition of this gas condensate, while aromatic and naphthenic HC occur in subordinate amounts [2]. The experience of its application has shown [2] that complete removal of ARPD from the equipment with use of this solvent is hard to perform. This could be explained by the fact that ARPD is a complex dispersion system, mainly represented by paraffins, resins and asphaltenes, which dissolve to some extent in HC solvents in accordance with their nature and solvent properties. Paraffins are better dissolved in paraffin HC, while resins dissolve in paraffin, naphthenic and aromatic HC, and asphaltenes are dissolved only in aromatic HC. Therefore, the most promising solvents should match the composition of ARPD and should be a mixture of aliphatic, naphthenic and aromatic hydrocarbons.
Hence, it is necessary to research effects of aliphatic, aromatic, and naphthenic hydrocarbons on properties and phase transitions of paraffins in ARPD in order to develop formulation guidelines for the most effective composition of reagents for removal of paraffin deposits at abnormally low layer temperatures.

In this paper, we continue the research conducted in [3].

2. Experimental part

ARPD selected from the surface of oilfield equipment from the Irelyakhskoye oil and gas condensate field have been used as objects of research. ARPD are of the paraffineous type and consist (%, mass.) of 59.6 of HC mixture, 20.0 of paraffin, 4.1 of asphaltene, 12.6 of resins, and 3.7 of mechanical impurities. The GC currently being used in the Irelyakhskoye oil and gas field for removal of ARPD has been studied as solvent of ARPD. Binary and ternary systems based on GC were prepared using naphthenic components - cyclohexane and aromatic p-xylene. The objects of the study were 10 mass% solutions: ARPD in GC and in the following model systems based on it: GC+ p-xylene (components ratio 1:1); GC+ p-xylene+ cyclohexane (components ratio 1:1:1).

As the review of modern scientific literature has shown [4-19], the differential scanning calorimetry (DSC) is widely used for study of processes of paraffin phase transitions in oil systems due to its accuracy and the reproducibility of the obtained results. The listed advantages and approved methods allow us to use DSC in the current study. Temperature and enthalpies of phase transition of petroleum and commercial paraffins in the above-mentioned systems were measured applying the differential scanning calorimeter DSC 204 HP Phoenix (Netzsch, Germany). The shooting mode of thermograms consisted of two segments: cooling to -10°C with the temperature decrease at a rate of 2.5°C/min., thus obtaining the crystallization peak; and heating to + 50°C with the temperature increase at a rate of 2.5°C/min., observing the peak of paraffin melting. The experiments were conducted in a helium atmosphere. For each of the samples under study, no less than 2 thermograms were obtained at coordinates "signal [mW/ mg] - time (temperature) [min, (° C)]" [3]. The degree of crystallinity (DC, %) of the test samples was calculated by division of the amount of heat absorbed by the moment of melting by that of paraffins with 100% crystallinity, $\Delta H_{\text{cryst}}$. For petroleum paraffins, it is assumed that $\Delta H_{\text{cryst}}$ is equal to 200 J/g [7].

In accordance with the obtained thermograms at the coordinates ($\alpha$ – $t$, min) the kinetic curves of paraffin dissolution in the systems under study have been constructed. The degree of dissolution ($\alpha$) was calculated as the ratio (1):

$$\alpha(t) = \frac{\int_0^t \left( \frac{dQ_{\text{dissol}}}{dt} \right) dt}{\int_0^{t_\infty} \left( \frac{dQ_{\text{dissol}}}{dt} \right) dt} \cdot 100\%$$

where $\alpha(t)$ – degree of paraffin dissolution; $Q_{\text{dissol}}$ – amount of heat absorbed by the moment $t$ during dissolution; $t_\infty$ – total time of dissolution.

The obtained curves were analyzed using the Avrami equation [20] for topochemical reactions (2):

$$-\ln \left( 1 - \frac{\alpha}{100} \right) = kt^n$$

where $\alpha$ – degree of dissolution of paraffins, n -constant that determines the nature of dissolution: with $n\leq1$ - diffusion process; $n=1$ – kinetic process; $n=1$ – first order reaction, where the rate of chemical interaction is comparable with the diffusion rate; k – the constant of dissolution rate; t - time, min.

Constants of the dissolution rate (min$^{-1}$) were calculated using the Sakovich formula [21]:

$$K = nk^{1/n}$$

3. Results and discussion

The results of the study showed that DC of commercial paraffins in ARPD depends on the degree of aliphaticity of solvents (figure 1, A). Thus, DC of paraffin in ARPD has its maximum value in the predominantly aliphatic solvent of GC and is equal to 1.8%. The high value of paraffin DC in this solvent can be attributed to the natural affinity of GC composition to that of paraffins, which favors an
emergence of embryos and growth of paraffin crystals. The paraffin DC decreases with addition of the aromatic and naphthenic components to GC, and this agrees with the results published in [6]. In this study, the decrease of paraffin DC upon addition of an aromatic additive to the aliphatic solvent is explained by introduction of molecules of the aromatic component between paraffin molecules. The presence of the naphthenic component is likely to contribute to disordering effects on the process of paraffin crystallization.

Research into dependency of paraffin melting points on its DC allowed us to reveal that, despite the minimum values of the DC of commercial paraffins in ternary solvents, its melting point is at its maximum value, making 10.4°C (figure 1, B). It is worthwhile to note here that paraffin has the similar values of DC in binary and ternary systems, but their melting points differ significantly and make 7.3 and 10.4°C respectively, which can be explained by the specific properties of paraffin structures in these solvents [3].

It is known [22] that up to 80% of the effectiveness of the solvent to remove deposits is due to the process of dissolution, therefore, the kinetic parameters of this process in the systems under study were calculated using the Avrami equation. Figure 2, A shows the obtained kinetic curves for the

![Graph A](image1.png)

**Figure 1.** A- Dependence of degree of crystallinity of commercial paraffin on degree of aliphaticity of solvent; B - Dependence of melting point on degree of crystallinity of commercial paraffin in 10% ARPD solvents in gas condensate (GC) and gas condensate mixtures.
dissolution of paraffins in ARPD in GC and mixtures based on GC at the coordinates “degree of dissolution (α) - time (t)”. The kinetic curves are evident to be S-shaped, which is typical for topochemical reactions. The curves differ by the duration of the induction period. The acceleration period for all the curves covers the range of transformation degree values from 5 to 95%. The acceleration periods are known to be more informative on the ongoing process; therefore, this very section of the curves is more interesting for kinetics analysis.

The logarithmic anamorphoses of the kinetic curves of paraffin dissolution at ln[-ln(1-α/100)] – lnt coordinates (figure 2, B) within the range α are obtained by taking the logarithm of the equation (2). The validity of the application of the Avrami equation is proved by straightening logarithmic anamorphoses within these limits. The parameter is defined as tangent of the inclination angle of the trend lines of the obtained anamorphoses.

The values of the Avrami equation parameter n, the values of approximation accuracy (r²), the half-life periods τ_{1/2} - the time during which 50% of the total mass of paraffins in ARPD go to the solution, and the rate constants of dissolution K are given in table 1.

![Figure 2](image-url)

**Figure 2.** A – Kinetic curves of dissolution of commercial paraffins in gas condensate (GC) and mixtures based on GC; B – logarithmic anamorphoses of these curves.

The values of the Avrami equation parameter n, the values of approximation accuracy (r²), the half-life periods τ_{1/2} - the time during which 50% of the total mass of paraffins in ARPD go to the solution, and the rate constants of dissolution K are given in table 1.
Table 1. Kinetic parameters of dissolution of commercial paraffins in gas condensate and its mixtures.

| Solvent                                      | n   | r²  | K, min⁻¹ | τ₁/₂, min |
|----------------------------------------------|-----|-----|----------|-----------|
| Gas condensate                               | 2.9 | 0.985 | 0.45     | 5.8       |
| Gas condensate+p-xylene (1:1)                | 2.5 | 0.979 | 0.58     | 3.5       |
| Gas condensate+p-xylene +cyclohexane (1:1)   | 2.8 | 0.955 | 0.60     | 3.3       |

High values of reliability approximation of the obtained anamorphoses indicate the validity of the equation choice for description of kinetics of paraffin dissolution. It is evident that for all processes, the value of the parameter \( n \) is greater than 1, indicating a complex dissolution mechanism. The rate constant of paraffin dissolution increases with the transition from gas condensate to its ternary composite and makes 0.45 and 0.60 min⁻¹, respectively, showing better solubility of paraffins in the ternary system. This is likely to be explained by a decrease in the DC of paraffin in the ARPD by adding aromatic and naphthenic additives to GC (figure 1, A). The values \( τ_{1/2} \) of paraffins decrease proportionally as the dissolution rate constant increases.

However, the final selection of an effective solvent to remove paraffin deposits in oil wells located in the permafrost should be preceded by preliminary laboratory tests of potential reagents for determining the temperature of the commence of paraffin crystallization in these solvents.

Construction of the curve of the temperature dependency of the mass fraction of the crystalline precipitate from ARPD solutions in GC and its mixtures during cooling (figure 3) suggested that formation of crystallites from GC commences at higher temperatures, while that from a mixture of GC and p-xylene occurs at the lowest temperatures, and GC’s ternary mixture occupies an intermediate position.

![Figure 3. Temperature dependence of mass fraction of commercial precipitated paraffin in various systems based on gas condensate.](image)

As compared, effectiveness of solvents used to remove deposits vary; for example, the seasonal operation temperatures of a well in the Irelyakhskoye oil and gas field are 10 and 25°C; at these temperatures 98 to 15% of paraffin from GC is deposited in the sediment, thus making its application in the field technologically inefficient. It is clear that addition of p-xylene to GC leads to precipitation of about 85% paraffin at 10°C, and the paraffin is in a dissolved state already at 20°C. In the ternary system, more than 90% of paraffin is in a crystalline state at 10°C and is completely dissolved at 22°C.
It is important to note here that the temperature of the commence of crystallization, the melting point and DC of paraffin in the aliphatic and aromatic solvents, as compared with other systems, are characterized by minimal values. The listed facts, both economically and technologically, argue in favor of use of GC with addition of aromatic concentrates, i.e. by - products of oil refining and petrochemical industries, such as xylene, butylbenzene, ethylbenzene fractions, etc. for paraffin removal in the Irelyakhskoye field.

4. Conclusions
Thus, phase transition of commercial paraffins in reagents of various chemical nature has been studied applying the method of differential scanning calorimetry, and effects of aliphatic, naphthenic and aromatic HC on the degree of crystallinity and melting points of the samples have been shown. Paraffin DC in the solvents under study has been shown to increase in the range: aliphatic-naphthenic-aromatic → aliphatic-aromatic → aliphatic solvents. The crystallization temperature and melting points of paraffin in aliphatic and aliphatic- naphthenic- aromatic solvents are found to be characterized by maximal values, as compared with those in aliphatic- aromatic solvents. According to the data obtained by the DSC analysis, the temperature dependency of the quantity of the crystalline phase of paraffin deposited from various reagents allows us to assess their effectiveness in removal of paraffin at various temperatures.

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