Choice of the Effective Solvent to Remove Paraffin Deposits in Conditions of Abnormally Low Reservoir Temperatures

I K Ivanova¹,², M E Semenov²
¹M.K. Ammosov North-Eastern Federal University, Yakutsk, Russia
²Institute of Oil and Gas Problems, Siberian Branch, Russian Academy of Sciences, Yakutsk, Russia

E-mail: iva-izabella@yandex.ru

Abstract. The results of research on dissolution kinetics of petroleum paraffins and asphaltene-resin-paraffin deposits (ARPD) of the paraffin type in aliphatic, aliphatic-aromatic, and aliphatic-naphthenic-aromatic systems within the temperature range from 10 to 60° C have been discussed. The half-life periods, order of reactions, dissolution rate constants and activation energy of destruction of paraffins and ARPD have been calculated. Differential scanning calorimetry has been used to study the phase transitions of petroleum and commercial paraffins in aliphatic and mixed hydrocarbon solvents. Based on the conducted research, recommendations for selection of an effective solvent to remove paraffin deposits at low temperatures of reservoirs have been proposed.

1. Introduction
One of key problems in development of oil fields is formation and removal of asphaltene-resin-paraffin deposits (ARPD). This problem is particularly acute during oil extraction in the Arctic zone where intensification of formation of high-molecular weight compounds of oil in the form of deposits on the surface of oil field equipment and in wellbores are determined by impacts of permafrost and low temperature climatic condition.

The major reason for formation of deposits in oil production systems is formation of fine-crystalline particles of paraffin in the fluid flow, their transportation to suitable places, accumulation and deposition with formation of solid deposits [1]. It occurs because the concentration of fine-crystalline paraffin in the liquid exceeds a certain critical value, which mainly depends on the process temperature and the composition of the liquid. It is worthwhile to note here, that the onset temperature of formation of crystal embryos, and the temperature of mass crystallization of paraffins cannot be accurately calculated and are determined only experimentally for an individual field and a specific composition [2,3].

There are various methods to fight against paraffin deposits in oil fields: 1) physical methods - thermal effects, exposure to ultrasound or magnetic fields, and 2) chemical ones - use of additives, surfactants, inhibitors, and solvents [4]. The conventional method involves using of hydrocarbon (HC) solvents in the form of gas condensate or gasoline produced in a particular field, as well as mixtures based on them. In the Irelyakske oil and gas condensate field (OGCF) (Sakha Republic, Yakutia), produced gas condensate is used to remove ARPD from equipment there. The experience of its application has shown [5] 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 solubility of paraffins, resins, and asphaltenes in the composition of ARPD depends on the chemical properties of the solvent. Paraffins are better dissolved in aliphatic HC, while resins are dissolved in aliphatic, naphthenic, and aromatic HC and asphaltenes are dissolved only in aromatic HC. Therefore, the results of our research on effects of aliphatic, aromatic, and naphthenic HC on dissolution kinetics of ARPD and phase transitions of paraffins in the composition of ARPD are given in this paper. These results allowed us to develop guidelines for selection of an effective solvent for paraffin deposits under impacts of permafrost.

2. Experimental part

The subject of the research has been ARPD selected from the surface of the tubing in the Irelyakhskoye (OGCF), and high-purity petroleum paraffins (grade B) for comparison. Table 1 presents the group composition of ARPD.

**Table 1.** Group composition of ARPD in the Irelyakhskoye field, % mass.

| Object | hydrocarbon fraction | paraffins (P) | asphaltenes (A) | resins (R) | mechanical impurities | P/(R+A) |
|--------|----------------------|---------------|-----------------|-----------|----------------------|---------|
| ARPD   | 59.6                 | 20.0          | 4.1             | 12.6      | 3.7                  | 1.2     |

The ARPD under study refers to the paraffin type, as the ratio of resins (R) and asphaltenes (A) to paraffins (P) in the composition of ARPD is more than 1.

The gas chromatography - mass spectrometry was used to study the individual composition of the hydrocarbon fraction isolated from ARPD (figure 1). Research was conducted applying the gas chromatograph Agilent 6890 with the high-performance interface and the mass-selective detector Agilent 5973N.

![Figure 1. Molecular mass distribution of n-alkanes in ARPD in the Irelyakhskoye field.](image-url)
In the composition of the fraction, n-alkanes of the homologous series C₁₅ – C₃₄ were identified. The molecular mass distribution (MMD) of n-alkanes in ARPD are evident to be mono-modal with its maximum at n – C₂₇, i.e. the composition of ARPD is formed from high-molecular weight n-alkanes.

Study of dissolution kinetics of petroleum paraffin and commercial ARPD in HC systems, which are mixtures based on hexane (hexane-benzene (HBM) and hexane-cyclohexane-benzene (HCHBM) mixtures), was carried out applying the gravimetric method using the torsion scales WT-500 at temperatures of 10, 25, 40, and 60°C under static conditions. The Avrami equation was applied to calculate kinetic parameters [6]. Paraffin phase transitions in 10% mass solutions of petroleum paraffins and ARPD in mixed solvents based on n-undecane (n-C₁₁) were studied by differential scanning calorimetry (DSC) using the DSC 204 HP Phoenix (Netzsch, Germany) according to the mode described in [7]. The degree of crystallinity (DC, %) of the test samples was calculated by division of the sample melting enthalpy by that of paraffins with 100% crystallinity, ΔHcryst. For petroleum paraffins, it is assumed that ΔHcryst is equal to 200 J / g [8].

3. Results and discussion

Table 2 presents the results of study of dissolution kinetics of paraffins and ARPD in various HC systems: limiting stages of dissolution processes (n), dissolution rate constants (K), the time during which half the amount of paraffins or ARPD goes into solution (τ₁/₂), as well as effective activation energies (Ea) of destruction of ARPD in the hydrocarbon systems under study have been calculated.

| Model                      | ℃  | n        | K, min⁻¹ | τ₁/₂, min | Ea, kJ/mol |
|----------------------------|----|----------|----------|-----------|------------|
| Paraffins + Hexane         | 10 | 0.83±0.04| 1.53*10⁻²| -         | 125.2      |
|                            | 25 | 1.17±0.07| 2.23*10⁻¹| 3.11      |            |
|                            | 40 | 1.12±0.09| 6.27*10⁻¹| 1.11      |            |
|                            | 60 | 1.58±0.06| 1.72     | 0.40      |            |
|                            | 10 | 0.90±0.12| 2.62*10⁻²| 26.46     |            |
| Paraffins + Hexane + Benzene (1:1) (HBM) | 25 | 1.11±0.09| 1.81*10⁻¹| 3.83      | 90.3       |
|                            | 40 | 1.45±0.07| 6.32*10⁻¹| 1.10      |            |
|                            | 60 | 2.11±0.03| 3.52     | -         |            |
| Paraffins + Hexane + Cyclohexane + Benzene (1:1:1) (HCHBM) | 10 | 1.92±0.15| 1.47*10⁻¹| 4.72      | 34.6       |
|                            | 25 | 1.25±0.05| 3.08*10⁻¹| 2.25      |            |
|                            | 40 | 1.86±0.08| 1.32     | 0.53      |            |
|                            | 10 | 0.84±0.04| 1.43*10⁻²| -         |            |
| ARPD + Hexane              | 25 | 0.97±0.03| 4.89*10⁻²| 14.17     | 57.5       |
|                            | 40 | 1.40±0.03| 1.81*10⁻¹| 3.83      |            |
|                            | 60 | 1.74±0.11| 2.97*10⁻¹| 2.33      |            |
| ARPD + Hexane + Benzene (1:1) (HBM) | 10 | 1.00±0.07| 3.10*10⁻²| 22.36     | 31.6       |
|                            | 25 | 1.05±0.13| 6.10*10⁻²| 11.36     |            |
| ARPD + Hexane + Cyclohexane + Benzene (1:1:1) (HCHBM) | 10 | 1.05±0.03| 7.28*10⁻²| 9.52      | 24.5       |
|                            | 25 | 0.94±0.06| 1.23*10⁻¹| 5.64      |            |
|                            | 40 | 1.29±0.11| 3.58*10⁻¹| 1.94      |            |
|                            | 60 | 1.08±0.12| 1.18     | 0.59      |            |

Dissolution of paraffin and ARPD in hexane at 10°C is evident to be less than one, i.e. the process is controlled by diffusion, but when heated to 25°C the dissolution proceeds as a first-order reaction.
Hence, as the temperature rises, diffusion processes intensify, and the rate of physicochemical interaction of paraffin and ARPD components with a solvent becomes comparable with the speed of their diffusion. In all other solvents, the dissolution process at these temperatures proceeds as a first-order reaction. In all systems, the values of $\tau_{1/2}$ decrease, as the temperature increases. The dissolution rate constant, except for HCHBM, increases by an order of magnitude as the temperature rises from 10 to 25°C. Besides, the constant of the dissolution rate of paraffins and ARPD increases when they are added to hexane both separately and instead of cyclohexane and benzene, while the activation energy decreases, which indicates the ease of destruction of petroleum paraffins and ARPD in binary and ternary mixed systems. Thus, a positive synergistic effect of the ternary solvent on paraffins and ARPD has been observed: $\tau_{1/2}$ has low values, the rate constants are an order of magnitude larger compared to binary systems and the process is characterized by a lower activation energy value.

Therefore, aliphatic-naphthenic-aromatic solvents can be recommended for the removal of ARPD of paraffin type in the Irelyakhskoye field. However, the final selection of an effective mixed 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 onset temperature of paraffin crystallization/melting in these solvents. It requires research into the effects of chemical nature of components of the mixture on temperatures of phase transitions of paraffin in these systems.

Therefore, the next stage of the research has been study of phase transitions of petroleum and commercial paraffins in the composition of ARPD, applying differential scanning calorimetry (DSC). The differential scanning calorimetry (DSC) is widely used for study of phase transitions in paraffin systems [8-21]. Figure 2 shows the DSC curves obtained by cooling and heating solutions of petroleum paraffins and ARPD in $n$-$C_{11}$ and $n$-$C_{11}$-based mixtures.

![DSC curves](image)

**Figure 2.** Thermograms of phase transitions of 10% solutions of petroleum paraffin (A) and ARPD (B) in $n$-undecane and in $n$-undecane-based mixtures: 1- $n$-$C_{11}$, 2- $n$-$C_{11}$ + $p$-xylene, 3- $n$-$C_{11}$ + $p$-xylene + cyclohexane. The cooling segments are designated Exo., the heating segments are Endo.
The transition from the crystalline state to melting is evident to occur in two stages. This corresponds to the results of earlier published works, according to which a minor peak when heated is associated with the phase transition in the solid state, followed by melting of the sample. Table 3 summarizes the results of processing the obtained thermograms.

**Table 3** Degree of crystallinity, temperature and enthalpy of phase transitions of petroleum and commercial paraffins in ARPD in their 10% solutions in n-undecane and n-undecane-based mixtures.

| System | Crystallization | Melting | DC, % |
|--------|-----------------|---------|-------|
|        | T_{onset,cr}, °C | T_{cr}, °C | ΔH_{cr}, J/g | T_{melt}, °C | ΔH_{melt}, J/g |       |
| Paraffins + n-C_{11} | 24.3 | 23.9 | 21.0 | 8.1 | 14.5 | 7.3 |
| Paraffins + n-C_{11} + p-xylene | 22.5 | 22.0 | 24.9 | 7.1 | 13.6 | 6.8 |
| Paraffins + n-C_{11} + p-xylene + cyclohexane | 27.1 | 26.6 | 23.6 | 9.8 | 12.3 | 6.15 |
| ARPD + n-C_{11} | 8.6 | 8.0 | 3.7 | 7.1 | 2.9 | 1.5 |
| ARPD + n-C_{11} + p-xylene | 7.8 | 7.1 | 4.3 | 5.1 | 1.9 | 0.95 |
| ARPD + n-C_{11} + p-xylene + cyclohexane | 12.3 | 11.7 | 5.4 | 7.5 | 1.8 | 0.9 |

As crystallization of multicomponent systems produces crystals containing a significant amount of amorphous zones, the indicator “degree of crystallinity” (DC) widely used to characterize polymers was applied to quantify crystalline regions in the paraffin deposits. In the individual n-C_{11}, the onset temperature of petroleum paraffin crystallization is 24.3°C, while addition of p-xylene reduces the temperature to 22.5°C. And, the results of calculations show that the largest proportion of the crystalline phase is 7.3% in the paraffin deposits from n-C_{11}, and in its mixture with p-xylene, DC of paraffin deposits decreases to 6.8%. This fact is in good agreement with the published data [16], where the result has been explained by introduction of aromatic molecules between long chain molecules of paraffin, which leads to decrease in the interactions between paraffin molecules and distortion of their long-range order, which in its turn reduces the DC of the paraffin. The presence of cycloalkane in the composition of solvents increases the onset temperature of paraffin crystallization to 27.1°C in the ternary system, but as compared with aliphatic and aliphatic-aromatic solvents, it lowers DC of its deposits to 6.15% in the ternary composite. It may occur due to the additional contribution of cyclohexane molecules into the disordering effect on paraffin crystallization and greater amorphization of its deposits. Research into the melting points of petroleum paraffins from the n-C_{11}-based systems has showed that paraffins in aliphatic-aromatic solvents have lower melting points, as compared with aliphatic ones, that is consistent with their DC decreasing due to introduction of aromatic components between paraffin molecules and distortion of the order of their crystal lattice. However, paraffin has the highest melting point (9.8°C) in the triple aliphatic-naphthenic-aromatic system, although its DC has the minimum value of 6.15%.

Table 3 shows that the crystallization process of paraffins, as part of ARPD, commences from n-C_{11} at 8.6°C. Addition of p-xylene reduces both the onset crystallization temperature from 8.6 to 7.8°C and the DC of deposits from 1.5 to 0.95%, respectively. In the ternary system, the onset crystallization temperature increases to 12.3°C, and DC is 0.9%. Low values of DC of the deposits compared to petroleum paraffins of Grade B2 can be explained by the fact that the ability of paraffins to form crystalline structures in the presence of natural surfactants (resins, asphaltene) is largely suppressed, therefore these crystalline formations have a significant amount of amorphous zones, which is
reflected on their DC. The deposits from the ternary system has the highest melting point, while the deposit from the aliphatic-aromatic solvent possesses the smallest one.

4. Conclusions
Thus, as a result of this study, aliphatic-aromatic solvents can be recommended for cleaning oil field equipment from paraffin deposits at low temperatures. Since the destruction of deposits in this solvent proceeds at a high rate, it is characterized by a low value of the effective activation energy, as well as a by low onset temperature of paraffin crystallization. Besides, the melting point of paraffin in this solvent has the minimum value, which makes it possible to combine thermal methods of deposit removal with aliphatic-aromatic solvents in order to achieve the best cleaning effect.

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