Oil emulsions as medium of natural gas hydrate formation

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Abstract. Results of research into kinetics and a mechanism in water-in-oil emulsions with various contents of the water phase have been given. The study was undertaken with application of the differential scanning calorimetry technique and statistical analysis of drop distribution according to their size prior and post hydrate formation. Rate constants of hydrate formation in emulsions have been identified to be in accordance with system overcooling, not with the ratio of water and oil phases. The anticipated mechanism of formation of natural gas hydrates in emulsions has been shown to depend on their water content and to occur according either to the micro reactor type with formation of weakly stable thinly dispersed hydrates, or the relay type with formation of coalescence of water drops and stable hydrate agglomerates. Effects of the water phase content of emulsions on processes of water drop enlargement have been determined.

1. Introduction

Today, about 80% of Russian oil is extracted with large volumes of water. This problem becomes even more pronounced at the stage of oil extraction from oil reservoirs heavily underlain by water and further – at the stage of separation of the extracted water-in-oil emulsion.

Water influx in crude oil in combination with dissolved natural gas would result in gas hydrate formation, notably in oil and gas fields located in the Extreme North and the Arctic with their severe climatic conditions and low reservoir temperatures. In this case, there is a threat of formation of gas hydrate deposits on oilfield equipment, promptly leading to a drop in production of hydrocarbon raw materials. Thus, one of the key factors of successful development of Arctic deposits is a solution of problems referring to the issue of hydrate formation in wet crude oil.

There have been a large number of studies on physical and chemical features of gas hydrate formation and decomposition in oil emulsions [1-8]. These works mainly focus on study of hydrates of simple gases in reverse oil emulsions containing synthetic surfactants (SAS). In addition, the hydrate synthesis process is carried out by mixing organic and gas phases, that distorts the true nature of the hydrate formation process in water-oil emulsions. However, in practice, the formation of oil emulsions occur in the presence of natural emulsifiers, that are part of their composition: asphaltenes, naphthenes, resins, and paraffins.

The research by [1] has showed that the rate of hydrate formation in oil emulsions depends on the water quantity in emulsions. It has been identified that with an increase of water content in 0-50 wt.\%
emulsions, the rate of methane hydrate formation increases, while in emulsions with the water content of 80 wt%, hydrate formation proceeds according to a two-step mechanism with the presence of an inversion phenomenon. Therefore, study of hydrate formation in oil with large volumes of water has practically never been conducted.

The objective of this paper is research of effects of water cuts in the range 20-80 wt. % in “the water-in-oil” emulsion on kinetic features of formation of natural gas hydrates.

2. Research methods
The subjects of the research were emulsions of paraffineous oil of the Irelyakskoe gas and oil field (Sakha Republic (Yakutia) and water produced by mechanical mixing of oil and water with ratio 20/80, 40/60, 60/40 and 80/20 without adding synthetic SAS. Natural gas from the Srednevilyuiisky gas condensate deposit (Sakha Republic (Yakutia) containing 92.88 vol.% of methane, 5.25 vol.% of ethane, 1.21 vol.% of propane, and 0.24 vol.% of other homologs has been used as hydrate forming gas.

Synthesis of natural gas hydrates in oil emulsions and research into its kinetics have been performed on the differential high-pressure scanning calorimeter DSC 204 HP Phoenix by Netzsch (Germany). The obtained DSC-grams have been applied to construct kinetic curves of transformation $\alpha_{\text{micro}}$ of the water phase into the hydrate one in oil. Then, the kinetic curves have been analyzed applying the Avrami equation [9]. The Avrami index characterizing the mechanism of the crystallization process and rate constants of hydrate formation in oil have been obtained.

In order to define peculiarities of the crystallization mechanism of the water phase into hydrate in emulsions according to digital micro-images obtained with application of the optical microscope Olympus BX 41, we have performed the statistical analysis of distribution of water droplets by size prior to and post hydrate formation.

3. Results and discussion
Real kinetic parameters of formation of natural gas hydrates in oil-in-water emulsions have been studied by cooling and heating of DSC thermograms.

![Figure 1. DSC – thermograms of cooling (segment Exo.) and heating (segment Endo) of water-oil emulsions in the presence of natural gas.](image)

The segment of cooling of DSC thermograms of all emulsions reveals only one registered asymmetric exothermal signal, while in the segment of heating, there are two consecutive and independent endothermal effects, those of ice melting and decomposition of natural gas hydrate (Figure 1). Thus, formation of a hydrate-containing mixture has been identified in oil-in water emulsions, and it has been defined to consist of phases of ice and natural gas hydrate.
The shape of the crystallization peak of the emulsion with composition 80/20 resembles the classical Gaussian curve, thus evidencing freezing of thinly dispersed emulsions. The crystallization peak of the emulsion with the 20/80 composition is asymmetrical and has the abrupt commence and extended termination, which is characteristic of the thermal effect of freezing of the continuous phase. These peculiarities of peak shapes are likely to predetermine the mechanism of crystallization of emulsions in the presence of natural gas. Crystallization of the emulsion containing 20 wt.% of water is likely to proceed according to the micro-reactor mechanism, while, in case of the 40-60 wt.% water content, the mechanism of crystal formation is mixed, and, with the 80 wt.% water content, droplets of the water phase are crystallized according to the relay mechanism. Transfer from the micro-reactor mechanism of water phase crystallization to the relay mechanism with an increase of its quantity in the emulsion is related with an increase of the degrees of freedom of the crystallization process which is characterized by the increase of the parameter $n_{cr}$ (Table 1).

Table 1. Values of Avrami parameter of crystallization $n_{cr}$ of water phase in water-in-oil emulsions with various contents of water phase in presence of natural gas ($R^2$ - approximation accuracy).

| Water quantity in emulsion, wt % | $n_{cr}$ | $R^2$ |
|---------------------------------|----------|-------|
| 20                              | 2.5      | 0.998 |
| 40                              | 2.5      | 0.999 |
| 60                              | 2.7      | 0.997 |
| 80                              | 3.9      | 0.984 |

Water droplets of emulsions containing 60 and 80 wt.% of water where the relay mechanism of crystal formation prevails, have been defined to increase in size by 2-6 µm (Table 2) following hydrate formation. Thus, the process of hydrate formation in emulsions with the water phase content more than 60 wt. % leads to coalescence of water droplets with their final enlargement in size.

Table 2. Average diameters of water droplets ($D_n$) prior and post hydrate formation in oil emulsions with various water contents.

| Water content in emulsion wt.% | $D_n$ prior to hydrate formation µm | $D_n$ post hydrate formation µm |
|-------------------------------|-----------------------------------|-------------------------------|
| 20                            | 15.30±7.65                        | 14.65±8.48                    |
| 40                            | 15.42±9.17                        | 14.98±7.84                    |
| 60                            | 16.17±8.74                        | 18.55±8.97                    |
| 80                            | 17.74±11.39                       | 23.02±10.70                   |

The processes of formation of methane hydrates in oil emulsions accelerate with cooling of the system, which is defined as a difference between an equilibrium temperature of hydrate formation and the DSC temperature of crystallization experimentally observed.
Values of rate constants of crystallization $K_{cr}$ of oil emulsions are not dependent on its water content, and they increase with a temperature decrease (Figure 2). Thus, the higher overcooling of the “water and oil emulsion-natural gas” system, the higher the rate of hydrate formation.

As a rule, values of the melting constant evidence stability of gas hydrates. The hydrates of natural gas produced in emulsions are shown to be 2-2.5 times more stable than those synthesized from distilled water (Figure 3). Hydrates synthesized in emulsions with 80 wt. % of the water content have been identified most stable. Thus, the lower the melting constant of natural gas hydrates produced in oil emulsion, the higher their stability.

The increase of stability of natural gas hydrates is likely to be predetermined by changes in dispersity of hydrates formed from emulsions with various water contents. So, thinly dispersed easily melting hydrates form in emulsions with 20 wt. % of water, while slowly decomposing hydrate agglomerates grow in emulsions with 80 wt. % of water.

Thus, the general scheme of the mechanism of hydrate formation in oil emulsions in accordance with their water content is presented as follows (Table 3):
Table 3. Mechanism of natural gas hydrate formation in oil emulsions with various contents of water phase.

| Water content in oil emulsions (less than 40 wt.%) | “Micro-reactor” mechanism: |
|--------------------------------------------------|-----------------------------|
| Water content | low degree of crystallization freedom ($n_{cr}=2.5$); |
|                | without enlargement of water droplets; |
|                | formation of thinly dispersed weakly stable gas hydrates ($K_{eq}=0.28 \text{ min}^{-1}$) |

| Water quantity in oil emulsions (40-60 wt.%) | Mixed mechanism: |
|---------------------------------------------|------------------|
| n_{cr}=2.7;                                 | enlargement of droplets by 0-2 mcm; |
| $K_{eq}=0.16 \text{ min}^{-1}$              | |

| Water quantity in oil emulsion (more than 60 wt.%) | “Relay” mechanism: |
|---------------------------------------------------|------------------|
| n_{cr}=3.9;                                       | high degree of crystallization freedom ($n_{cr}=3.9$); |
| $K_{eq}=0.12 \text{ min}^{-1}$                    | enlargement of water droplets up to 6 mcm; |
|                                                   | formation of stable agglomerates of natural gas hydrates |

4. Conclusion

Thus, the research has shown that the mechanism of formation of natural gas hydrates in emulsions is defined by the water quantity and proceeds according to the micro reactor type with formation of weakly stable thinly dispersed hydrates or according to the relay type with coalescence of water droplets and formation of stable hydrate agglomerates. Here, the rate of crystallization of water droplets is not affected by the water content in emulsions and it depends on the super-cooling of the system.

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