Peculiarities of hydrate formation in “natural gas/asphaltene-resin-paraffin deposits/water” systems

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Abstract. The results of research into kinetic parameters of formation and decomposition of hydrates synthesized in “natural gas/asphaltene-resin-paraffin deposits (ARPD)/water” model systems and in a “natural gas/water” system have been considered. The synthesis and decomposition of hydrates have been conducted in a calorimetric cell of the high-pressure differential scanning calorimetry (DSC). Calculations of kinetic parameters of the processes under study: the rate constants and order of reaction of formation/decomposition of a hydrate – containing phase in paraffin deposits and water, have been performed applying the Avrami equation. The rate of decomposition of hydrate - paraffins has been identified to be half that of hydrates formed in distilled water, thus indicating the stability of hydrate - paraffins. The degree of water conversion into the hydrate has been determined to decrease with an increase of the water content in ARPD emulsions.

1. Introduction

Hydrate plug formation is a major problem of exploitation of oil and gas condensate fields in the Arctic shelf, Far North, Western and Eastern Siberia. Hydrates are formed during the reaction of associated petroleum gas dissolved in oil with water emulsified in oil [1-6], and during condensation of water vapors on paraffin deposits in the form of a drop or film [7]. Low climatic temperatures and specific thermobaric conditions of occurrence of oil deposits under the effects of permafrost thickness favor this process. The above-mentioned factors initiate either hydrate formation, or deposition from petroleum of high molecular weight paraffins on the surface of oilfield equipment including formation of paraffin plugs in wellbores. In their turn, paraffin deposits on the walls of drill tubing form neckings that lead to an even greater intensification of hydrate formation. Hence, formation of gas hydrates in oil, as well as paraffin and hydrate plugs in wellbore complicate oil production technology, transportation, and storage on the shelf and in areas with low average annual temperatures.

As the review of scientific literature has shown, there is a considerable quantity of works on research and a thermodynamic description of phase equilibrium of gas hydrates in water-in-oil emulsions applying the method of high-pressure differential scanning calorimetry (HP DSC) [8-17]. A special attention is paid to kinetics of hydrate formation in these systems, since detailed knowledge of formation, accumulation, and decomposition of hydrates is a key factor in development of new technologies to prevent problems in hydrate formation. In [8], the classical crystal growth theory helps describe kinetics of methane hydrate growth in water droplets. Four parameters have been used in this model: the rate constant, supersaturation of methane in the oil phase, and the mean and standard deviation of the induction period. The induction period of hydrate formation has been shown in [10] to
be strongly dependent on the degree of overcooling of the system, affecting the symmetry of signals of the thermal curves. It has also been concluded that each water droplet in water-oil emulsions behaves like a micro reactor where, irrespective of other droplets, the process of hydrate nucleation occurs. The Avrami model has been shown in [17] to be applicable to description of kinetics of hydrate formation in water-in-oil emulsions. The rate of hydrate formation has been defined to depend on the water quantity in the emulsion [16]: as the water content increases, the rate of hydrate formation decreases, while kinetic parameters of hydrate formation in emulsions defined by this model can help to assess the risks of hydrate formation in oil pipelines.

The analysis of the above-mentioned literature has shown that research into gas hydrates in oil dispersed systems is focused on theoretical and experimental study of thermodynamics and kinetics of growth/disassociation of methane hydrates in water-in-oil emulsions with various compositions, but the process of hydrate formation in natural gas mixtures in emulsions of paraffin deposits has not been thoroughly studied yet.

In this paper, we present the data of the research of kinetics of formation/decomposition of natural gas hydrates applying the method of high-pressure differential scanning calorimetry in emulsions of asphaltene-resin-paraffin deposits of oil at the Irelyakhskoye oil and gas field (Sakha Republic (Yakutia)).

2. Experimental part

ARPD samples have been taken from the tubing surface at the Irelyakhskoye oil and gas field (Sakha Republic (Yakutia)) with the following composition: 59.6 wt.% of hydrocarbons; 20.0 wt.% of paraffins, 4.1 wt.% of asphaltenes, 12.6 wt.% of resins; 3.7 wt.% of mechanical impurities with 0.882 g/cm³ density. Emulsion samples were prepared by mechanical mixing of ARPD and distilled water in the H₂O/ARPD weight ratio of: 20/80, 40/60, 60/40 and 80/20 without addition of any synthetic surfactants using a household mixer with blades at a free rotation speed of 11000 rpm during 30 minutes. Mixture of water and ARPD with a weight ratio of 80/20 revealed the maximum saturation of ARPD with water and the actual component ratio in this sample to be 60/40, therefore sample 80/20 was excluded from the study. Natural gas of the Srednevilyuisk gas condensate field (GCF) (Sakha Republic (Yakutia) with a high content of methane has been used as model of a gas - hydrate-forming agent. The choice of this gas as a model has been predetermined by the similarity of its composition to that of reservoir gases of the Irelyakhskoye oil and gas field [18].

Hydrates of this gas synthesized in ARPD emulsions were selected as subjects of the investigation. Their phase transitions were studied in a calorimetric cell of the high-pressure differential scanning calorimetry DSC 204 HP Phoenix HP DSC (Netzsch, Germany). The relative error in the enthalpy measurements makes ±3%, while the error in the temperature measurements makes ±0.1°C. Steel crucibles closed with perforated aluminum caps were used in the experiments. The weight of the ARPD emulsion loaded into the crucible was equal to 35 mg. The discharge pressure in the cell was 50 bar, and it was dynamically maintained up to +6 °C, then was switched to a stationary mode. The shooting mode of thermograms consisted of two segments: cooling to -12 ÷ -22 °C with a rate of a temperature decrease of 0.1 °C/min with the crystallization peak of the hydrate-containing phase consisting of ice and hydrates; and heating to +20 °C with a rate of the temperature increase of 0.2 °C/min with the peaks of ice and hydrate melting. For each of the samples under study, no less than 2 thermograms were obtained within the coordinates "signal [mW/mg] - time (temperature) [min, (°C)]".

Experimental curves of the conversion degree of water into the hydrate-containing phase (α) and hydrate decomposition (β) are obtained in the coordinates (α or β - t, min) in the automatic mode according to the procedure given in the original software of the DSC. The obtained curves of the degree of conversion of the water contained in emulsions into hydrate, and the curves of the degree of hydrate decomposition were analyzed using the Avrami equation [19] for topochemical reactions:

\[-\ln\left(1 - \frac{q}{100}\right) = kt^n,\]
where $q$ is a degree of crystallization (ice+hydrate) ($\alpha$) upon cooling or a degree of hydrate decomposition ($\beta$) upon heating; $n$ is a constant that determines the character of crystallization/decomposition (with $n < 1$ – the diffusion process, $n = 1$ – reaction of the first order where the rate of chemical interaction is comparable with the diffusion rate); $k$ is a constant determining the rate constant of crystallization/decomposition; $t$ is time, min.

The rate constants of crystallization/ decomposition (min$^{-1}$) were calculated using the Sakovich equation [20]:

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

On the basis of the enthalpy of ice melting, the quantitative composition of hydrates in paraffin deposit emulsions was calculated according to the following relations:

$$\alpha(\text{hydrate}) = \frac{\Delta H_{\text{mel}}}{\Delta H_{\text{CH}_4}} \times 100\%$$

where $\alpha$ (hydrate) is the hydrate content, wt.%, $\Delta H_{\text{mel}}$ is the specific heat of ice melting, J/g, 334 is the enthalpy of ice melting, J/g, $\Delta H_{\text{CH}_4}$ is the enthalpy of hydrate methane melting 438.54 J/g [9].

3. Results and discussions

One or two peaks of crystallization of the water phase are observed within the temperature range of -1.87÷21.8°C in the process of cooling of all samples in the systems under study; while one or two peaks are observed upon heating: the peak of ice melting falls within the temperature range of -1.10÷2.06°C, and the second peak of hydrate melting is within the temperature range of 7.87÷10.70°C. It is worth noting here that melting endotherms are characterized by the absence or presence of a peak of ice melting, and the peak of hydrate melting has been recorded in all the samples under study.

Figure 1 shows curves of the degree of phase transformations: crystallization of water droplets in the composition of emulsions into the hydrate-containing phase upon cooling and a curve of hydrate melting upon heating.

![Figure 1](image)

**Figure 1.** Kinetic curves of crystallization of hydrate-containing phases (A) and hydrate melting (B), synthesized in distilled water and «H$_2$O/ARPD» systems.

![Figure 2](image)

**Figure 2.** Logarithmic anamorphoses of kinetic curves of crystallization of hydrate-containing phases (A) and hydrate melting (B), synthesized in distilled water and «H$_2$O / ARPD» systems.
Data on crystallization and melting of hydrates synthesized in distilled water are also compared in this figure. The kinetic curves of crystallization of hydrate – containing phases of ARPD emulsion samples are evident to be S-shaped (Fig. 1 A), while the curves differ among themselves in duration of the induction period. The curve of crystallization of a hydrate-containing phase in distilled water is characterized by the maximal initial speed, since the acceleration period immediately follows the initial period on this curve, i.e. the crystallization process starts immediately over the entire reaction surface or throughout the whole liquid phase volume. The acceleration period for all crystallization curves covers the range of transformation degree values from 10 to 70%.

The decomposition curves of hydrate emulsions of ARPD and water (Fig.1 B) are also S-shaped, while their induction periods are clearly pronounced, as compared with the crystallization curves, which is apparent to relate with a slow release of gas as a result of hydrate melting. During acceleration period, mass hydrate melting and enhanced gas evolution occur within the range of the curve from 10 to 70%. Periods of acceleration are known to be more informative on the ongoing process; therefore, this very section of the curves is more interesting for kinetics analysis. The values of the Avrami equation parameter \( n \), the half-lives \( \tau_{0.5} \), and the rate constants \( K \) of crystallization/decomposition have been calculated for the sections of crystallization and melting curves in accordance with the periods of acceleration (Fig.2 A and B), and also the values of approximation accuracy \( r^2 \) have been given (Table 1). Based on the obtained results, the quantitative content of hydrate \( \alpha(\text{hyd}) \) in the emulsions and distilled water under study has been calculated (Fig.3).

Table 1. Kinetic parameters of crystallization of hydrate-containing phases and hydrate decomposition in distilled water and systems «H₂O/ARPD»

| Sample H₂O/ARPD | \( n \) | \( K \), min⁻¹ | \( r^2 \) | \( \tau_{0.5}\), (graph), min |
|-----------------|---------|---------------|---------|--------------------------|
| **Crystallization** |         |               |         |                          |
| 20/80           | 2.1     | 0.04          | 0.999   | 43.4                     |
| 40/60           | 2.5     | 0.32          | 0.996   | 6.6                      |
| 60/40           | 2.8     | 0.24          | 0.992   | 10.5                     |
| Distilled Water | 1.5     | 3.40          | 0.991   | 0.4                      |
| **Melting**     |         |               |         |                          |
| 20/80           | 4.6     | 0.16          | 0.998   | 22.5                     |
| 40/60           | 4.3     | 0.18          | 0.999   | 21.1                     |
| 60/40           | 4.3     | 0.18          | 0.999   | 22.0                     |
| Distilled Water | 2.0     | 0.46          | 0.992   | 3.4                      |

High values of reliability approximation demonstrate the validity of the Avrami equation for description of kinetics of hydrate formation and decomposition in ARPD emulsions. It is evident that, as compared with ARPD emulsions, crystallization of the hydrate-containing phase in bulk-distilled water proceeds an order of magnitude faster, values of the half-life are minimal, and the content of the hydrate phase makes only 3% (Fig. 3). The hydrate-containing phase in ARPD emulsions is crystallized by an order of magnitude slower, while the half-life varies from 6.6 to 43.4 min. The slow rate of crystallization could be determined by the high viscosity of emulsions [13], as well as by inhibitory effects of the asphaltene in the ARPD content on the hydrate formation process [21]. Resulting from slow crystallization, the process proceeds with a high degree of water conversion into hydrate, and the hydrate content is within the range of 49 - 82%, while with an increase of the water mass fraction in the emulsion, the content of the hydrated phase in the samples decreases (Fig.3).

The mechanism of crystallization of hydrate-containing phases in emulsions, regardless of the water cut, proceeds in the kinetic area (\( n>1 \)), i.e. the growth of the hydrate is directed towards the dispersed water droplets. The process of crystallization in distilled water occurs in the diffusion-kinetic area (\( n=1.5 \)), i.e. the hydrate is formed at gas – water interface. The obtained values \( n \) correlate well with sample images (Fig.4), it is evident that in distilled water, hydrates are formed on its surface (Fig. 4 (A)) in the form of white inclusions, while in ARPD process of hydrate formation occurs in droplets, dispersed all over the ARPD volume (Fig. 4 B).
Figure 3. Dependence of hydrate quantity $\alpha(\text{hyd})$ on water content (w(H$_2$O)) in ARPD emulsion.

Figure 4. Images: (A) – hydrates, synthesized in distilled water and (B) – H$_2$O/ARPD sample with component ratio of 40/60 in the cross-sectional view: the arrows indicate inclusions of ice/hydrate.

The values of n>1 of hydrate decomposition indicate the complexity of this mechanism, and in cases of melting of hydrate - paraffins, this index has the maximum values and lays within the range from 4.3 to 4.6. The rate of decomposition of the hydrate synthesized in distilled water is two times higher, while its period of semi-decomposition is six times less, compared with hydrate - paraffins, which indicates the stability of the latter. The stability of hydrate - paraffins is believed to be due to their high sorption ability, resulting to coating of hydrates in these systems with a film of liquid and solid hydrocarbons such as: resins, asphaltenes, and paraffins that strengthen hydrates and make them more resistant to destruction.

4. Conclusions
The Avrami equation has been shown to be applicable to description of kinetic processes of formation of hydrate containing phases and hydrate decomposition, synthesized in ARPD emulsions. The crystallization rate of the hydrate – containing phase in bulk distilled water has been identified to be an order of magnitude faster than that of hydrate crystallization in ARPD emulsions. It has been demonstrated that the degree of conversion of water into hydrate in ARPD emulsions is in agreement with the water content and crystallization rate: the lower the rate constant and the quantity of water phase in emulsion are, the higher degree of water conversion into hydrate is. Hydrate growth in dispersed water droplets of ARPD emulsion is directed inwards the droplets, while hydrate formation in bulk water occurs at the “water-gas” interface. The analysis of the melting curves has shown that hydrated paraffins are more resistant to decomposition as compared with hydrates synthesized in distilled water. With the ARPD water cut of 20 to 80 wt.%, stable hydrate paraffins have been defined to be formed, causing blockage of the wellbore and creating an emergency situation in gas-oil wells of the Nepa-Botuoba anteclise.

Acknowledgments
The research has been performed with the financial support provided by the Russian Federation Ministry of Education and Science, within the framework of the basic part of the State task, Project
“Organization of Performance of Scientific Research” and State Task of the Federal Agency for Scientific Organizations №0377-2016-0003 and by Russian Foundation for Basic Research (RFBR) and the Government of the Sakha Republic the Scientific Project № 18-45-140035.

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