Research of Formation and Decomposition Processes of Natural Gas Hydrates of Different Composition in Model Stratum Waters of a Bicarbonate-Sodium Type

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Abstract. The paper presents the results of an experimental study of the behaviour of formation and decomposition of natural gas hydrates of the Srednevilyuiskoe and Otradninsko gas condensate fields depending on the concentration of sodium bicarbonate solution. Natural gases used in the hydrate formation process differ in their component composition and physicochemical properties. It was found that with increasing concentration of solutions, the gas pressure at which the hydrate formation process ends is increased. During hydrate formation, the initial dry natural gas of the Srednevilyuiskoe field turns into semi-wet gas, and that of the Otradninsko field turns into wet gas. The decomposition of natural gas hydrates is described by sigmoid curves without an induction period. For the decomposition reaction of hydrates formed by natural gas of the Srednevilyuiskoe field, the reaction acceleration period is shorter than the deceleration period, while the opposite is observed for the Otradninsko field. Therefore, in the first case, hydrates decompose faster than in the second. Thus, it was found that the hydrate formation process in model solutions of the sodium bicarbonate type and the decomposition reaction of the resulting hydrates depend on the composition of natural gas.

1. Introduction
The formation of gas hydrates in natural conditions is possible with a combination of low temperatures and high pressures. They can form clusters or reside in a dispersed state on the oceanic shelf and in the permafrost zone [1–9]. The occurrence conditions of oil and gas fields located in the permafrost area facilitate the transition of hydrocarbon gases to a hydrated state [10-14]. In this case, hydrate formation is possible inside the wellbore as a result of thermal interaction with frozen rocks and at the wellhead due to a decrease in gas temperature due to throttling effect [15-19]. The liquid phase in this case is ground water, which at a greater or lesser degree contains dissolved substances. The stratum waters of the gas fields of Eastern Siberia can belong to different genetic types [20-21]. The most common waters are calcium chloride (calcium and sodium subgroups) and sodium bicarbonate (sodium subgroup) types. Their mineralization can vary over a wide range, reaching values up to 400 g/l for calcium chloride type waters. The waters of the sodium bicarbonate type are characterized by a low salt content [22]. For example, in the Srednevilyuiskoe gas condensate field (GCF), the mineralization of these waters in the Jurassic deposits varies from 2.24 to 20.47 g/l [22]. Stratum water can be used in industrial methods for producing hydrates for the storage and transportation of natural gas.
gas, in particular, in the development of methods for underground storage of gases in under permafrost aquifers [23-26].

The aim of the work was to study the effect of the composition of natural gas on the formation and decomposition of hydrates obtained in solutions of sodium bicarbonate.

2. Experiment

Hydrates were prepared in sodium bicarbonate solutions with concentrations of 0.25; 0.5; 1 and 2% of the mass, which corresponds to the salinity of the stratum water of the specified field. The solutions were prepared from distilled water and analytical grade NaHCO₃. Natural gas from the Srednevilyuiskoe and Otradinskoe gas condensate fields was used as hydrate-forming gases. The gas composition (Table 1) was determined by gas adsorption chromatography according to GOST [27].

| Component     | Composition of natural gas, % mol. |
|---------------|-----------------------------------|
|               | Srednevilyuiskoe GCF | Otradinskoe GCF |
| methane       | 93.9                  | 85.4            |
| ethane        | 4.44                  | 4.24            |
| propane       | 1.10                  | 1.24            |
| isobutane     | 0.087                 | 0.128           |
| n-butane      | 0.108                 | 0.371           |
| isopentane    | 0                     | 0.0891          |
| pentane       | 0                     | 0.1129          |
| hexane        | 0                     | 0.0728          |
| carbon dioxide| 0.0559                | 0.0452          |
| nitrogen      | 0.33                  | 8.08            |
| hydrogen      | 0                     | 0.052           |
| helium        | 0                     | 0.127           |
| Molar mass, g/mol | 17.11                | 18.32           |
| Relative density | 0.592              | 0.634           |
| Fat content coefficient | 6.1                  | 7.3             |

Table 1. Component composition and physicochemical properties of natural gases.

Natural gases of these fields differ in their composition and, therefore, physicochemical properties. Natural gas of the Srednevilyuiskoe field, in contrast to the gas of the Otradinskoe field, is characterized by a high methane content and the absence of C₅+, hydrogen and helium components in it. And in the natural gas of the Otradinskoe there is a high nitrogen content. For natural gases, their fat content coefficient were calculated as the ratio of the sum of methane homologs to the methane content. According to the fat content coefficient, hydrocarbon gases are classified as dry (<8%), semi-wet (8–20%), wet (20–30%) and high-wet (>30%) [28]. By this indicator, the gases of both fields are classified as dry.

Under laboratory conditions, natural gas hydrates in sodium bicarbonate solutions were obtained at a temperature of 278 K and a pressure of 8 MPa. The experiments were conducted on a closed installation in static conditions simultaneously in 4 high-pressure chambers. Each chamber (Figure 1) is a steel cylinder (1) with a volume of 1000 cm³, closed with a steel cover (2), equipped with a pressure gauge (3) of the type MO-160 (accuracy 0.4) and an inlet gas valve (4). 100 ml of the electrolyte solution of the indicated concentration (5) is introduced into the chamber, then natural gas is supplied from the cylinder (6) and an experiment is conducted. The change in pressure in the chambers was recorded at certain intervals. The process of hydrate formation in aqueous solutions was considered completed when gas pressure in the chambers became constant.

Based on the obtained data, gas absorption curves were normalized to the initial gas pressure, depending on time (Figure 2). Figure 2 shows that with an increase in the concentration of solutions, the gas pressure at which the hydrate formation process ends increases. This is characteristic of both
the process of hydrate formation of natural gas of the Srednevilyuiskoe GCF (Figure 2a) and the natural gas of the Otradinskoe field (Figure 2b). However, the course of hydrate formation curves depends on the composition of the gas. The hydrate formation of natural gas in the Srednevilyuiskoe field ends at higher pressures compared with the formation of gas hydrates from the Otradinskoe gas condensate field. In the second case, the concentration of the solutions practically does not affect the change in the pressure of hydrate formation.

**Figure 1.** Scheme of experimental facility for gas hydrates generation: 1 - steel glass; 2 - cover; 3 - standard pressure gage; 4 - refueling faucet; 5 - solution; 6 - balloon with natural gas.

**Figure 2.** Gas absorption curves normalized to the initial pressure during the formation of natural gas hydrates in sodium bicarbonate solutions: a - gas of the Srednevilyuysky gas condensate field, b - gas of the Otradinsky gas condensate field.

Next, the decomposition of the obtained hydrates was studied, the technique of which was described in detail in [29]. The volumes of gases released during the decomposition of hydrates formed by natural gases of different compositions are comparable despite different final hydrate formation pressures (Table 2).

**Table 2.** Volumes of gases released during decomposition of hydrates.

| Concentration of NaHCO₃ solutions, % | Gas volume V_c, l | Srednevilyuiskoe GCF | Otradinskoe GCF |
|-------------------------------------|-------------------|----------------------|-----------------|
| 0.25                                | 17.77             | 17.79                |
| 0.5                                 | 18.86             | 15.10                |
| 1                                   | 18.43             | 18.08                |
| 2                                   | 16.20             | 16.12                |

Table 3 shows the ratio of the content of gas components in the hydrate to the content of components in natural gas. The enrichment of the solid clathrate phase with C2-C4 components during hydrate formation of both gases was established (Table 3). Concentration of hydrocarbons occurs correspondingly to a decrease in the dissociation pressure of simple hydrates formed by the individual components of natural gas [30]. Due to the concentration of methane homologs, the molar masses,
relative densities, and fat content coefficients of gases in hydrates increase (Table 4). The fat content coefficients of gases bound into hydrates are 2.5–3 times higher than the fat content coefficients of the initial gases. During hydrate formation, the initial dry natural gas of the Srednevilyuiskoe GCF turns into semi-wet, and that of the Otradinskoe GCF - into wet gas.

**Table 3. Distribution of natural gas components during hydrate formation.**

| Component | Srednevilyuiskoe GCF | Otradinskoe GCF |
|-----------|----------------------|-----------------|
|           | 0.25 | 0.5 | 1.0 | 2.0 | 0.25 | 0.5 | 1.0 | 2.0 |
| CH₄       | 0.89 | 0.91 | 0.90 | 0.90 | 0.93 | 0.92 | 0.93 | 0.93 |
| C₂H₆      | 2.36 | 2.17 | 2.44 | 2.43 | 2.61 | 2.46 | 2.53 | 2.39 |
| C₃H₈      | 4.32 | 3.69 | 3.8 | 3.79 | 4.11 | 4.58 | 4.54 | 4.34 |
| i-C₄H₁₀    | 5.40 | 4.83 | 4.28 | 4.28 | 3.53 | 5.11 | 4.89 | 4.09 |
| n-C₄H₁₀    | 2.00 | 1.99 | 1.97 | 1.97 | 2.69 | 2.41 | 2.62 | 2.34 |
| CO₂       | 1.07 | 1.93 | 1.72 | 1.72 | 3.43 | 2.15 | 3.12 | 2.26 |
| N₂        | 0.37 | 0.24 | 0.61 | 0.40 | 0.46 | 0.35 | 0.44 |       |

**Table 4. Physicochemical properties of gases in hydrates.**

| Physicochemical properties | Srednevilyuiskoe GCF | Otradinskoe GCF |
|---------------------------|----------------------|-----------------|
|                           | 0.25 | 0.5 | 1.0 | 2.0 | 0.25 | 0.5 | 1.0 | 2.0 |
| Molar mass, g/mol         | 19.15 | 18.84 | 19.01 | 19.03 | 20.062 | 20.22 | 20.18 | 20.01 |
| Relative density          | 0.664 | 0.653 | 0.659 | 0.660 | 0.696 | 0.702 | 0.701 | 0.695 |
| Fat content coefficient   | 19.2 | 17.4 | 18.5 | 18.2 | 22.0 | 23.1 | 23.3 | 21.5 |

The kinetic parameters of hydrate dissociation were found on the basis of their degree of conversion α. The degree of conversion is considered to be the ratio of the gas volume $V_t$ measured at time t to the volume of gas $V_∞$ released during the complete decomposition of the hydrate: $\alpha = \frac{V_t}{V_∞}$.

Based on these data, curves of the degree of conversion on time were constructed (Figure 3), which are sigmoid curves without an induction period. For the decomposition reaction of hydrates formed by natural gas of the Srednevilyuiskoe GCF, the reaction acceleration period is shorter than the deceleration period (Figure 3a), and the opposite is observed for the Otradinskoe GCF (Figure 3b). Therefore, in the first case, hydrates decompose faster than in the second. However, there is no clear dependence of the hydrate decomposition process on the concentration of solutions.

The experimental data obtained during the decomposition of hydrates were processed according to the Erofeev equation. This equation is used to describe the formal kinetics of topochemical reactions. The methodology for determining the constants n and k according to the Erofeev equation is described in detail in [29].

The decomposition of natural gas hydrates of different fields is characterized by values of n greater than unity in the entire studied range of concentrations of sodium bicarbonate solutions. The process of dissociation of hydrates occurs in the kinetic region. The values of the constants K for the decomposition of hydrates of natural gas of the Srednevilyuiskoe GCF are comparable, except for the rate constant of the decomposition of hydrates obtained in a 0.25% solution. Hydrates of natural gas from the Otradinskoe field, except for the hydrate obtained in a 0.5% solution, decompose at almost the same rate. A comparison of the decomposition constants of hydrates of different gases shows a decrease in the decomposition rate with an increase in the molar mass of the gas.
Figure 3. Kinetic decomposition curves of gas hydrates formed from solutions of sodium bicarbonate and natural gas: a - gas of the Srednevilyuysky gas condensate field, b - gas of the Otradninsky gas condensate field.

Table 5. Kinetic parameters of the hydrate decomposition reaction.

| Concentration of NaHCO₃ solutions, % | Srednevilyuiskoe GCF | Otradninskoe GCF |
|-------------------------------------|----------------------|------------------|
|                                     | n       | k      | Kₘᵢₙ⁻¹  | n    | k   | Kₘᵢₙ⁻¹ |
| 0.25                                | 1.6181  | 0.0493 | 0.2519  | 2.5031 | 0.0094 | 0.3879 |
| 0.5                                 | 1.6921  | 0.1499 | 0.5512  | 1.5427 | 0.1741 | 0.4968 |
| 1                                   | 2.1759  | 0.0412 | 0.5024  | 1.5039 | 0.0728 | 0.3818 |
| 2                                   | 1.5359  | 0.1889 | 0.5189  | 1.9427 | 0.0424 | 0.3595 |

The influence of salt concentration in model waters of the sodium bicarbonate type and the composition of natural gas on the formation and decomposition of hydrates obtained has been established. Thus, it was found that with increasing salt concentration, the completeness of the hydrate formation process decreases regardless of the composition of the gas, and this effect is leveled out with an increase in the molar mass of natural gas. It was also shown that the decomposition rate of hydrates is more influenced by the composition of the gas than the concentration of salt. And the lower the relative density of the gas in the hydrate, the faster the hydrate formed from it decomposes.

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