Study of hydrates formation in mineralized solutions and kinetic regularity of their decomposition

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Abstract. Processes of hydrate formation in water solutions of electrolytes that imitating the composition of reservoir water of eastern Siberian platform were studied. The investigation of hydrates properties, obtained from mineralized solutions showed notable influence of electrolytes on the processes of their growth and decomposition, as well as texture and component composition of gases in hydrates. Equilibrium conditions of hydrate formations in solutions of electrolytes shifted to the field of higher pressures and lower temperatures. The texture of the hydrates depends on the type of cation in the electrolyte solutions. If filiform crystals of hydrates are formed in the water, sodium cations promote to the formation of granular forms and calcium does to the formation of laminate hydrates. The research of the component composition of the gas obtained by the decomposition of hydrates showed that the mineralization of solutions leads to the concentration of hydrocarbons C₂-C₄ in clathrate phase and to increasing of the fatty coefficient. The shape of the kinetic curves of hydrate decomposition depends on the type and mineralization degree of the model reservoir waters.

1. Introduction

In the terms of stratification of oil and gas fields, which referred to the permafrost area, the low stratum temperature promotes a transition of hydrocarbon gases to the hydrate form [1–3]. For the fields of Eastern Siberia, high mineralization of formation water is typical, which obstructs processes of hydrate formation both in free volume and in porous media. However despite of the high antihydrate activity of the reservoir waters, the possibility of hydrate formation in the bottom hole of the reservoir zone due to abnormally low formation temperatures and in the borehole in the result of thermal cooperation with surrounding frozen rocks is not excepted [4]. From the other side, for the commercial production of natural gas hydrates with the purpose of storage and transportation it is possible to use water from natural sources that contain different quantity of dissolved substances so research of the influence of the composition of electrolyte solution on the kinetics of formation and decomposition of natural gas hydrates is an actual problem [5,6].

The oil and gas fields of the east of the Siberian platform are placed within the Leno-Tunguska and the Lena-Vilyui oil and gas provinces. The fields of the Leno-Tunguska oil and gas provinces are characterized by abnormally low reservoir temperature and reservoir pressure [7], and its reservoir waters are referred to the chloride-calcium type, and on type of the dominated cation either to the calcium or sodium subgroup of waters. The mineralization of reservoir water is able to reach 400 g/l and higher [8]. For the fields of the Lena-Vilyui oil and gas provinces an abnormal high reservoir
pressure is 36.3 MPa, the temperatures reach +66°C [7]. The mineralization of reservoir waters is from 40 up to 180 g/l, there can be waters of chloride-calcium and bicarbonate-sodium types [8].

2. Experimental part
For hydrate formation aqua solutions of calcium and sodium chlorides, sodium hydrogen carbonate, imitating the composition of a stratum waters of the East Siberian platform were used. The concentration of solutions of chlorides varied from 50 up to 180 g/l, and of bicarbonates from 2.5 up to 20 g/l. The composition of natural gas is: methane – 92.7; ethane – 5.24; propane – 1.21; isobutane – 0.10; n-butane – 0.12; carbon dioxide – 0.05; nitrogen – 0.58% mol. The molar mass of the gas is 17.25 g/mol, the relative density on air is 0.596.

The conditions of natural gas hydrate formation in the absence of salts that dissolved in reservoir water were calculated by Sloan’s method [9], where the equation of state of Redlich-Kwong is used. Then these conditions for mineralized reservoir water of the chloride-calcium type for the sodium and calcium subgroups were recalculated on the methods proposed in the work [10]. The results of calculations of the equilibrium conditions of natural gas hydrates formation are presented on figure 1, where the dot-dash graph matches to an absence of dissolved salts in the reservoir water. With increasing of mineralization of electrolyte solutions the equilibrium pressures increase at given temperature and a hydrate formation temperatures decrease at a given pressure.

![Figure 1](image)

**Figure 1.** The equilibrium conditions of the natural gas hydrate formation depending on the concentration of calcium chloride (solid graph) and sodium chloride (dashed graph) solutions.

In the laboratory conditions hydrates of natural gas in salt solutions obtained at a temperature of 278 K. The experiments were carried out in a closed type facility in static conditions at the same time in 4 high pressure chambers. The gas pressure, which exceeded the equilibrium pressure of hydrate formation in advance, was pressurized to avoid refueling the chambers. Each chamber (figure 2) is a steel glass (1) with a volume of 1000 cm³, closed with a steel cap (2) with a standard gage (3) of the type MO-160 (precision is 0.4) and a gas valve (4). In the hydrate chamber, 100 ml of distilled water (or electrolyte solution of the specified concentration) is introduced (5), then natural gas is introduced from the balloon (6) up to a pressure of 8 MPa and an experiment is conducted. The end of hydrate formation process in aqueous solutions is fixed by the constant of pressure in the chambers.
The texture of synthesized hydrates depends on the type of solutions. In the absence of mineralization, white filiform crystals are formed, which occupy the entire volume of the chamber (figure 3a). Hydrates obtained in solutions of chloride and sodium bicarbonate have a granular structure (figure 3b and 3c), and in solutions of calcium chloride a stratified structure (figure 3d). With increasing of mineralization of solutions the volumes of synthesized hydrates decreased. This regularity is observed both for hydrates obtained in solutions of chloride and sodium bicarbonate, and in solutions of calcium chloride.

![Figure 3. The texture of synthesized hydrates, depending on the type of solution used for hydrate formation: a – water; b – sodium chloride solution; c – sodium bicarbonate solution; d – calcium chloride solution.](image)

To determine the volume of gas contained in hydrates, an experimental facility was assembled (figure 4). The experiment was carried out as follows. At the end of the hydrate formation process the pressure in the chamber (1) decreased to atmospheric one. Then the chamber was placed in a thermostat (2), connected to a gasometer of the tympanic type (3). If gas sampling was required for research of the component composition a gas burette (4) with an expansion capacitance (5) was connected to the facility. The volume of gas made during the decomposition of hydrates was measured every minute.
Figure 4. The scheme of the facility for natural gas hydrates decomposition: 1 – high pressure chamber; 2 – thermostat; 3 – gasometer of the tympanic type; 4 – gas burette; 5 – an expansion capacitance of the gas burette.

It is established that the maximum volume of gas contains hydrates obtained in solutions of sodium bicarbonate (table 1). The volume of gas in the hydrates obtained in solutions of chlorides always decreases with increasing of a concentration.

Table 1. The volume of gas in hydrates obtained in solutions of salts.

| ω, % | The volume of gas, l | NaCl | CaCl$_2$ | ω, % | The volume of gas, l | NaHCO$_3$ |
|------|----------------------|------|----------|------|----------------------|-----------|
| 0    | 14.3                 | 14.3 |          | 0.25 | 17.77                |           |
| 5    | 11.7                 | 6.8  |          | 0.5  | 18.86                |           |
| 10   | 5.4                  | 2.1  |          | 1.0  | 18.43                |           |
| 15   | 1.7                  | 3.9  |          | 2.0  | 16.20                |           |

Analysis of the gas composition in hydrates obtained in solutions of chlorides indicated that under its formation in mineralized solutions reallocating of the components of the sourced gas mixture occurs (table 2). The reallocating coefficient $B$ is calculated as the ratio of the content of hydrocarbons in the hydrated gas to its content in natural gas.

Thus, the composition of the gas in hydrates depends on the composition and concentration of model reservoir water. The maximum concentration by the formation of natural gas hydrates in salt solutions is observed for isobutane and propane. With the increase in the concentration of solutions their content in hydrates increases. In the presence of calcium cations the reallocating coefficients of specified components of natural gas are higher than in solutions containing sodium cations.

Table 2. Coefficients of the natural gas components reallocating $B$ at the formation of its hydrates depending on the type and concentration of solutions.

| Component      | $B$ | H$_2$O | NaCl | CaCl$_2$ |
|----------------|-----|--------|------|----------|
| iso-C$_4$H$_{10}$ | 3.75 | 5.3 | 10.7 | 15.4 | 10.0 | 12.45 | 17.85 |
| C$_3$H$_8$    | 5.12 | 5.79 | 9.60 | 12.58 | 9.43 | 11.74 | 13.29 |
| C$_2$H$_6$   | 2.63 | 2.91 | 3.11 | 2.57 | 2.90 | 3.81 | 2.77 |
| $n$-C$_4$H$_{10}$ | 2.04 | 1.75 | 2.08 | 1.75 | 1.71 | 5.17 | 1.88 |
| CH$_4$        | 0.85 | 0.83 | 0.76 | 0.75 | 0.77 | 0.69 | 0.72 |
A composition of gases in hydrates lets to estimate fatty coefficients. A fatty coefficient (the ratio of the sum of homologues of methane to methane content) can be dry (0.3 – 8%), bold (8 – 20%), fat (20 – 30%) and high-fat gases (>30%). Fat and high-fat gases are a valuable raw material for the oil and gas chemical industry. The sourced natural gas according to Vysotsky's classification [11] refers to dry (table 3). However in the process of hydrate formation in electrolyte solutions when the sodium-type changes to calcium one the fatty coefficient of the gas in the hydrate increases due to an increase of the C2-C4 alkane content.

Table 3. Fatty coefficient of natural gas and gases in hydrates.

| Solution | NG | A gas in hydrates obtained in different liquid phases |
|----------|----|-----------------------------------------------------|
|          |    | H2O | Mineralization NaCl, g/l | Mineralization CaCl2, g/l |
| C2 / CH4 |    | 7.07 | 26.26 | 29.95 | 41.45 | 43.83 | 40.51 | 56.37 | 49.02 |

To study the particularities of hydrate decomposition reactions obtained in mineralized solutions kinetic parameters were found by the Erofeev equation, which is more often used for the analysis of isothermal solid-phase reactions [12]:

\[
\alpha = 1 - \exp(-kt^n)
\]

(1)

where \(\alpha\) is the degree of conversion, \(k\) is the generalized speed constant, \(t\) is the decomposition time, and \(n\) is the kinetic parameter. The rate of conversion is defined as the ratio of the gas volume emitted during the reaction to the volume of gas emitted upon complete decomposition of the hydrate: \(\alpha = V_t / V_c\).

The equation (1) in twice logarithmic type is a straight equation, that lets to calculate the values of the parameters \(n\) and \(k\). The first of them characterizes the main driving force of the reaction: when \(n > 1\) the process is determined by the kinetics, when \(n < 1\) is determined by the diffusion. The parameters \(k\) and \(n\) let us to find the speed constant of reaction \(K\) according to Sakovich's formula:

\[
K = nk^{1/n}
\]

(12)

The parameters of the hydrate decomposition process are summarized in table 4, where you can see that the values of \(n\) for the decomposition reactions of all hydrate samples are more than one. It means that these reactions occur in kinetic region, in other words, the speed of decomposition of hydrates is determined by the speed of physical desorption of the gas from the clathrate lattice.

Table 4. Kinetic characteristics of decomposition reactions of hydrates synthesized in different liquid phases.

| Solution     | H2O 5% | H2O 10% | H2O 15% | NaCl 5% | NaCl 10% | NaCl 15% | CaCl2 5% | CaCl2 10% | CaCl2 15% | CaCl2 0.25% | CaCl2 0.5% | CaCl2 1% | CaCl2 2% | NaHCO3 0.25% | NaHCO3 0.5% | NaHCO3 1% | NaHCO3 2% |
|--------------|--------|---------|---------|---------|---------|---------|---------|---------|---------|----------|---------|---------|---------|---------------|---------------|---------|---------|
| A type of graph | Sigmoidal with induction period | Sigmoidal without induction period |
| n            | 1.499  | 2.264   | 1.791   | 1.330   | 1.698   | 1.664   | 1.551   | 1.213   | 1.026   | 1.015    | 1.159   |
| k, min^{-1}  | 0.029  | 0.004   | 0.047   | 0.127   | 0.037   | 0.045   | 0.092   | 0.074   | 0.066   | 0.076    | 0.063   |
| K, min^{-1}  | 0.141  | 0.191   | 0.324   | 0.282   | 0.245   | 0.257   | 0.333   | 0.142   | 0.072   | 0.080    | 0.107   |

Note that the hydrates decomposition speed obtained in solutions of sodium bicarbonate at the maximum gas content has minimal decomposition speed. It should be considered in the industrial production of hydrates with the purpose of the natural gas storage and transportation.
3. Conclusions

The processes of growth and decomposition of natural gas hydrates in model solutions of various mineralizations, imitating the reservoir waters of the East Siberian platform are researched. It is established that equilibrium hydrate formation curves in electrolyte solutions are shifted to the field of high pressures and low temperatures. The texture of the hydrates depends on the type of cation in the electrolyte solutions. If filiform crystals of hydrates are formed in the water sodium cations promote the formation of granular hydrates and calcium-layered hydrates. The mineralization of solutions leads to the concentration of C₂-C₄ hydrocarbons in the clathrate phase, and to an increase of the fatty coefficient and caloric power of the gas. The shape of the kinetic curves of hydrate decomposition depends on the type and degree of mineralization of model reservoir waters. A conversion of natural gas to hydrates for storage and transportation is expediently carried out in diluted solutions of electrolytes, because it increases their thermodynamic stability.

Acknowledgments

The work is carried out within the framework of State Order №0377-2016-003. The reported research was partly funded by Russian Foundation for Basic Research and the Government of the Republic of Sakha (Yakutia) of the Russian Federation, grant №18-45-140035.

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