Equilibrium Conditions of the Natural Gas Hydrates Formation in the Pore Space of Dispersed Rocks

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Abstract. In this work, the kinetic parameters and equilibrium conditions of the formation of natural gas hydrates in moist fresh and saline sand samples were studied by the method of differential thermal analysis. It was found that, in comparison with the systems "water-natural gas" and "sodium chloride solution-natural gas" in dispersed rocks, the equilibrium curves of hydrate formation are shifted to the region of high pressures and low temperatures. It is shown that the salinity of the pore solution leads to a decrease in the amount of absorbed gas and a decrease in the rate of hydrate formation.

1. Introduction

In recent years the interest in the study of the hydrate formation in dispersed rocks is due to the need to study the behavior of gas hydrate systems during underground storage of natural gas and conservation of toxic and greenhouse gases. This issue is of particular relevance for the northern regions with a sharply continental climate. Underground storages serve as a kind of gas accumulators to ensure its uniform supply with seasonally variable consumption. Such storage facilities are created in porous formations of depleted gas and gas condensate fields or aquifers located near the route of gas pipelines or large centers of the gas consumption. An alternative to such storage facilities can be underground gas storage facilities in a hydrated state. The advantages of this storage method are that the storage is more compact and stable, i.e. the gas in the hydrate state occupies a much smaller volume than in the free state at the same temperature and pressure, and in addition, during the transition to the hydrate state, all free stratum water is bound. In the permafrost zone, these reservoirs can be subpermafrost aquifers, which can be located directly under the permafrost base at depths of 500 - 600 m.

The P, T-conditions of the hydrate formation in natural porous media are studied by Dallimore et al., Wright et al., Klapproth A., Zhang et al., Tao et al., E.M. Chuvilina, A.G. Groisman, V.A. Istomin, V.S. Yakusheva et al [1-17]. The kinetics of the hydrate formation was investigated by R. Livio, E.M. Chuvilin, V.P. Melnikov, A.N. Nesterov, V.M. Buleiko and others [18-21]. In these works, the thermodynamic and kinetic regularities of the formation and decomposition processes of methane hydrates and its model mixtures are considered, depending on the dispersion, salinity and mineral composition of the soil. To create underground gas storage facilities in a hydrate state, it is necessary to study the quantitative parameters of the formation / decomposition processes of natural gas hydrates in the pore space of rocks, taking into account the mineralization and genetic type of aquifers stratum water.
Thus, this paper presents the experimental results of studying the equilibrium conditions and kinetic parameters of the natural gas hydrate formation in wet and saline porous media.

2. Experimental

The objects of the study were natural gas hydrates obtained in samples of the sand mined in the river Lena. Determination of the granulometric composition of the sand showed that 55.58% of the total mass of the sample falls on the fraction of 0.4 - 0.315 mm. Hydrates were obtained in this sand moistened with distilled water and sodium chloride solution with a mineralization of 51.48 g / l, which corresponds to the chloride type mineralization of underground waters in Yakutia. The initial weight moisture content of soils with water and sodium chloride solution was 17.66 and 16.78%, respectively.

To obtain gas hydrates, the natural gas (NG) of the Srednevilyui gas condensate field of the following composition, % mol., was used: methane - 93.9; ethane 4.44; propane - 1.10; isobutane - 0.087; n-butane 0.108; carbon dioxide - 0.056; nitrogen - 0.33.

The study of phase transformations occurring during the formation and dissociation of natural gas hydrates in a porous medium was carried out on a DTA analysis unit. The experimental procedure is as follows: 21.7 g of sifted river sand was placed in one of the cuvettes located in the measuring cell, to which a given amount of water or a salt solution was added. In this case, the second comparison cuvette remained empty. Next, the measuring cell was placed in the beaker of the high-pressure chamber and closed with a lid with integrated thermocouples so that the thermocouples were placed in the center of the cell section and immersed to a half of the level of the substance placed in the cell. Then the chamber was sealed and a gas was supplied to it to a predetermined pressure value. After that, the chamber was placed in an air thermostat programmed to cool the system from 20.0 to -6.0 °C at a rate of 3 °/hour. During the experiment, the temperature and pressure values were recorded every 40 seconds.

Based on the obtained DTA - thermograms, the equilibrium temperatures and pressures of the hydrate formation in the samples under study were determined (figure 1). For comparison, by the method of D. Sloan [22], the values of thermobaric parameters of the hydrate formation in free volumes of water and sodium chloride solution were calculated. The rates of gas transition to the hydration phase were calculated from the change in pressure during hydrate formation according to the method [21].

Figure 1, A and B shows that the curve of the natural gas hydrate formation in a porous medium is shifted to the region of high pressures and low temperatures. At high temperatures, the hydrate formation in a porous medium moistened with both fresh water and a salt solution proceeds at higher pressures as compared to a liquid media (figure 1, B). Comparison of the experimental data of the hydrate formation in dispersed media showed that the process in a sodium chloride solution proceeds at higher pressures and lower temperatures than in fresh water (figure 1, C). Analysis of the thermobaric conditions of the natural gas hydrates formation in the pore space showed that there is a tendency to increasing of the deviation from the equilibrium curve in the free volume. Thus, according to the baric (∆P) scale of the hydrate formation, in comparison with free water in the pore space, the deviation reached 2.21 MPa at a temperature of -0.13 °C, and at a temperature of 10.22 °C - 4.60 MPa. ∆P for the systems “sodium chloride solution + NG” and “sand + sodium chloride solution + NG” was 4.36 and 7.11 MPa at temperatures of 1.00 ° C and 2.30 °C, respectively.

To determine the kinetic parameters of the hydrates formation / decomposition, the curves of the dependence of the hydrate formation rate dn / dt (figure 2, A), the amount of gas released n during the hydrate decomposition (figure 2, B) on time were plotted for all samples at given pressures of the hydrate formation. As can be seen from Figure 2, A, at the beginning of the process, the hydrate formation proceeds at a low rate, after a certain period of time, the hydrate formation rate reaches its maximum value, and then it decreases. The maximum rate of the hydrate formation is observed with a sharp decrease of pressure in the system, which corresponds to an inflection in the pressure change curve. Experiments have shown that the higher the set pressure, the less time it takes to reach maximum speed. On the hydrate decomposition curve (figure 2, B), one can distinguish a section of the intense gas evolution (I) and slowing down of the process (II), which corresponds to the end of the hydrate decomposition.
Figure 1. Equilibrium curves of the natural gas hydrates formation in the river sand: A - distilled water (■ - calculated for free water; ● - experimental points); B - sodium chloride solution with a salinity of 51.48 g/l (▲ - calculated for the free volume of sodium chloride solution; ♦ - experimental points; C - distilled water and sodium chloride solution.
Figure 2. The hydrates formation rate and the pressure in the system (A); time dependence of the amount of released gas (B) in the sample "sand + NG + water" at 7 MPa.

It was found that with an increase in the specified pressure, the maximum hydrate formation rate increases both in fresh water and in a sodium chloride solution (Table 1). However, the hydrate formation rate at the same pressures in the brine is lower. Mineralization of the pore solution leads to a decrease in the amount of both adsorbed during hydrate formation and released during the natural gas hydrates decomposition in comparison with a sample moistened with water.

| Sample                  | Set pressure, MPa | Maximum hydrate formation rate $*10^{-2}$, mol/h | The amount of adsorbed gas $*10^{-2}$, mol | The amount of released gas $*10^{-2}$, mol |
|-------------------------|-------------------|--------------------------------------------------|------------------------------------------|-----------------------------------------|
| «Natural gas+sand+water»| 6,5               | 4,302                                            | 3,192                                    | 2,729                                   |
|                         | 7,0               | 6,144                                            | 3,193                                    | 2,789                                   |
|                         | 9,0               | 6,436                                            | 3,634                                    | 2,577                                   |
| «Natural gas+sand+ NaCl»| 6,5               | 3,773                                            | 2,642                                    | 1,955                                   |
|                         | 7,0               | 4,261                                            | 2,772                                    | 2,030                                   |
|                         | 9,0               | 5,351                                            | 3,184                                    | 2,100                                   |

As one can see from the table 2, the amount of the gas adsorbed during the hydrate formation stage is greater than the amount of the gas released during the decomposition. This may be due to the adsorption of the part of the gas in the pore space of the sand.

Thus, in dispersed rocks there is a shift in the thermobaric conditions of the hydrate formation in comparison with the systems "water-natural gas" and "sodium chloride solution-natural gas" in the region of higher pressures and low temperatures. Experimental data have shown an increase in pressure and a decrease in the temperature of the hydrate formation in saline pore water compared to the hydrate formation in pure water. Also, the salinity of the pore space leads to a decrease in the hydrate formation rate and the amount of adsorbed and released gases. The obtained thermobaric and kinetic parameters of the hydrate formation can be used in the development of scientific foundations of technology for underground storage of the natural and associated petroleum, as well as greenhouse and toxic gases in a hydrated state.

3. References

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Acknowledgments
The work was performed within the framework of the State Order AAAA-A17-117040710035-7.