The influence of technological parameters on the efficiency of the hydrate formation reaction in the system methane — SDS aqueous solutions

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Abstract. The article deals with methane hydrate synthesis in the presence of sodium dodecyl sulfate. The search for optimal conditions for this synthesis in a cylindrical continuous stirred tank reactor was provided. The limit after which the increasing of pressure in the reactor does not make a significant contribution to an increase in the gas content of the product was experimentally detected. The analysis of the impact of cooling rate on intensity of the hydrate formation had been carried out. The mode of gas supply to the reactor, cooling rate and working pressure, ensuring the highest efficiency of the methane hydrate synthesis under the specified conditions, are found.

1. Introduction
Gas hydrates are inclusion compounds in which gas molecules are enclosed in crystalline cells consisting of water molecules held by a hydrogen bond.

The hydrate structure is stabilized by trapped gas molecules trapped inside the crystal lattice [1]. There are three widely known hydrate structures: sI, sII and sH. Each of these structures has characteristic lattice parameters and the number of water molecules that form a hydrate structure [2]. Among gas hydrates, methane hydrate is the most common and widely studied. Natural gas is an important source of energy, while hydrates have great potential for its storage and transportation. One volume of methane hydrate can store about 170 volumes (at standard temperature and pressure) of methane, thus, the storage of natural gas in this form attracts great interest [3, 4]. In addition, the storage and transportation of natural gas based on hydrates has several advantages compared with other technologies, such as compressed natural gas and liquefied natural gas, which usually require extreme pressure and temperature, respectively [5]. As a result, natural gas hydrate has attracted consideration over the past few decades, and more and more attention has been paid to means to quickly form natural gas hydrates along with high storage capacity, which is crucial for industrial use in the transportation and storage of natural gas.

Many researchers have used surfactants to intensify the formation of gas hydrates, and over the past two decades various types of surfactants have been used, among which the greatest attention has been paid to sodium dodecyl sulfate (SDS) [6—14]. For example, in [13] it was shown that SDS can promote the formation of gas hydrates through the formation of micelles, which can improve the rate of formation of natural gas hydrates by more than 700 times compared to deionized water. The content of natural gas in such a hydrate reached 90—150 V(CH₄)/V(H₂O) in 3 hours. In [14] used SDS and linear alkylbenzene sulfonate (LABS), cetyltrimethylammonium bromide (CTAB) and ethoxylated
nonylphenol (ENP) to promote the formation of methane hydrate at 276.2 K and 8.3 MPa and found that adding SDS provides better results at concentration of 300—1000 ppm. In this case the formation of methane hydrate occurs within 1—3 hours, and its capacity for gas reaches 140—150 $V(\text{CH}_4)/V(\text{H}_2\text{O})$. In [12] used anionic surfactants with the same carbon chain and various parent groups: sodium dodecyl sulfate (SDS), sodium dodecyl sulfonate (SDSN) and sodium dodecyl benzene sulfonate (SDBS) to intensify the formation of methane hydrate at 275.15 K and initial 6 MPa. The addition of SDS and SDSN due to the capillary effect led to the fact that the growth of methane hydrate was completed within 40 min, while the capacity of the hydrate reached about 120 $V(\text{CH}_4)/V(\text{H}_2\text{O})$. However, the addition of SDS leads to massive foam formation during the dissociation of the hydrate, which significantly affects the application of this method for the technology of storage and transportation of natural gas. To prevent foaming in [15] they used the addition of silver nanoparticles. These options significantly complicate and increase the outlay of technology. Furthermore, in [16], it was shown that foam notably increases the rate of nucleation upon formation of methane hydrate. In addition, there are technological solutions to the problems associated with the formation of foam during the dissociation of gas hydrates, allowing the reaction with the use of surfactants. Thus, the use of SDS leads to a significant increase in the rate of hydrate formation and has several advantages, such as availability and low cost. Despite the abundance of works on the formation of methane hydrate using surfactants, almost all of them are carried out under similar conditions. In this work, we studied the influence of technological parameters, such as the gas supply mode, the pressure in the reactor and the cooling rate to the methane content in the obtained methane hydrates.

2. Materials and methods

2.1. Materials

Reactions were carried out in a cylindrical continuous stirred tank reactor with a 500 ml cooling jacket equipped with a magnetic stirrer. The pressure in the reactor was measured using an AIR-10N pressure sensor with an accuracy of 0.001 MPa. The reactor was cooled by a LOIP FT cryostat that maintains the temperature with an accuracy of 0.1°C. In part of experiments, the climate test chamber was used to control the temperature with an accuracy of 0.5°C, into which the reactor with a magnetic stirrer and sensors were placed. The volume of gas obtained by the decomposition of methane hydrate was registered using a gas flow meter Ritter TG/05. Data received from the sensors were transmitted to the computer. Scheme of laboratory plant is shown in figure 1.

![Figure 1. Schematic of the tank reactor setup for hydrate formation. 1 — gas cylinder, 2 — magnetic stirrer, 3 — cooling jacket, 4 — reactor internal volume, 5 — gas flow meter, 6 — cryostat, 7 — computer.](image-url)
Methane was used with a purity of 99.6% (Moscow Gas Processing Plant). To intensify the hydrate formation process, solutions of sodium dodecyl sulfate (NaC12H25SO4) manufactured by PanReacApplyChem with a purity of 95% was used. Deionized water with a conductivity of 1.17±0.1 μs/cm at 298.15 K were used to prepare the solution.

2.2 Methods
An aqueous solution of SDS with a mass concentration \( = 0.1 \text{ wt.}\% \) was prepared and loaded in a reactor with a magnetic stirrer anchor. Reactor was sealed and then flushed with pure methane. The reaction usually proceeded with constant methane pressure, and the volume of the initial solution was 100 ml, unless otherwise noticed. Mixing the solution was carried out from the beginning of the reaction until the solution was completely frozen in order to intensify the mass transfer. The solution was cooled to –3.0°C and kept at this temperature for four hours. Then additional cooling and maintaining the product for another hour at –10°C was carried out in order to increase the stability of the hydrates obtained. Cooling was performed using a cryostat or climate test chamber. Then the reactor was disconnected from the gas supply line, volume of extra methane dumped and decomposition of the hydrate was observed to determine the gas content.

3. Results and discussion

3.1. Comparison of the effectiveness of the formation of methane hydrate in a constant volume and constant pressure
One of the main parameters affecting hydrate formation is the methane pressure. Therefore, in our work we considered pressure and various production modes as the main technological parameter in the preparation of methane hydrate. In the first series of experiments, the methane content in the resulting hydrate was compared for a solution volume of 200±1 ml and an initial pressure of 5.0±0.1 MPa. However, in the first experiment, a one-time injection was applied to a predetermined pressure, and in the second, pressure was maintained at a predetermined level throughout the entire experiment. The decomposition of methane hydrate was observed at a temperature of 20.0°C. The data obtained are presented in table 1.

From the data obtained it follows that while maintaining a constant pressure in the reactor by supplying methane, it is possible to achieve higher gas content in the product than in the mode of conducting the reaction with a constant volume of gas and gradually decreasing pressure. This suggests that on the scale of an industrial plant for the production of natural gas hydrate it is more expedient to conduct reactions at constant pressure.

| Concentration of surfactant (wt.%) | Volume of solution (ml) | Initial pressure (MPa) | Reaction mode | Mass content of methane in hydrate (wt.%) |
|-----------------------------------|-------------------------|------------------------|---------------|------------------------------------------|
| 0.1                               | 200.0                   | 5.0±0.1                | P=const       | 9.8                                      |
| 0.1                               | 200.0                   | 5.0±0.1                | V=const       | 4.9                                      |

3.2. Comparison of the efficiency of reaction of hydrate formation in pressure range from 2.5 to 5.0 MPa
In our work, the reaction proceeded in the mode of maintaining constant given pressure. The ratio of the mass content of methane in samples obtained at different pressures is shown in the figure 2. The results at a pressure of 2.5 MPa the gas content of the obtained product is not substantial, then already at 3.2 MPa the efficiency of gas saturation increases significantly. However, the graph shows that the optimum pressure is about 3.2 MPa, at which it is possible to obtain a hydrate with 10 wt.% methane. With increasing pressure, the efficiency of hydrate formation increases not so much and does not justify an increase in gas consumption.
3.3. Influence of cooling rate on hydrate formation efficiency and product stability

Another parameter studied during this study was the cooling rate of the reaction medium. The solution was exposed to controlled cooling from 20 to −3.0±0.5°C with speeds of 1, 2, 3, and 10 °C • h⁻¹. The temperature regime was provided and monitored by means of the climate test chamber in which the reactor with the pressure sensor and the stirrer was placed. As it can be seen in figure 3 the gas content of the product practically does not change when the initial solution is frozen at speeds from 10.0 to 3.0 °C • h⁻¹. At 2.0 °C • h⁻¹, the gas content increases slightly, but is still quite far from optimal. Methane hydrate obtained at a freezing rate of 1.0 °C/h decomposes almost instantaneously, but the degree of saturation with methane in this sample increases noticeably.

4. Conclusion

Based on the results of this work, a list of recommendations on the technological parameters of the hydrate formation reaction for the production of methane hydrate can be formulated. Continuous gas supply to the reactor is preferable to conducting the reaction in a closed volume, since it increases the gas content of the product twice.
The recommended pressure of 3.2 MPa allows to achieve sufficient gas saturation, but to avoid excessive gas consumption. In this case, there is an increase in the mass content of methane in the resulting hydrate by a factor of 4.4 compared with the reaction at a pressure of 2.5 MPa. At a pressure of 5.0 MPa the best results are observed, but an increase in the efficiency of the reaction only 1.1 times is insignificant compared to the cost of gas to maintain pressure. The highest content of methane in the hydrate (12.8 wt.%) can be achieved at a cooling rate of 1°C • h⁻¹, but the product instantly decomposes when the pressure is released. The most stable product was obtained with a relatively fast freezing of 10.0 °C • h⁻¹, but the mass concentration in it is relatively small and amounts to only 10 wt.%. 

5. References

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