

Effect of SDS concentration on the process of hydrate formation by explosive boiling of liquefied freon 134a in water with SDS volume

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Abstract. This work is part of a comprehensive study of a method for obtaining gas hydrates, based on the explosive boiling of a liquefied hydrate-forming gas in a volume of water during pressure release. The method shows high efficiency and productivity. Freon 134a is used as a hydrate-forming gas. The paper presents the results of an experimental study on the effect of the concentration of the kinetic promoter sodium dodecyl sulfate (SDS) on the conversion of water into a gas hydrate state. The change in pressure and temperature in the process of hydroformation is shown.

Introduction

Gas hydrates are crystalline supramolecular compounds, otherwise called clathrates. Gas hydrates consist of water molecules (host), which form a frame with cavities, in which the molecules of the hydrate-forming gas (guest) are contained and are held in them by van der Waals forces. Gas hydrate can be obtained using almost any gas, as well as stored for a long time, subject to the thermobaric conditions inherent in the selected gas. There are several types of gas hydrate structures. Cubic structure I (sI), cubic structure II (sII) and hexagonal structure sH, which does not occur in nature. Cubic structures sI can be represented by both pentagonal dodecahedrons (5^{12} , S-cage) and tetradehedrons ($5^{12}6^2$, M-cage), and their unit cell consists of two S-cages and six M-cages. In turn, the sII structure is characterized by a hexahedral structure ($5^{12}6^4$, L-cage) and consists of sixteen S-cells and eight L-cells [1].

Gas hydrates have many useful properties, the most important of which is the ability to concentrate large volumes of gas one volume of methane gas hydrate can contain up to 170 volumes of pure methane. It is important to note that it is in the form of gas hydrate that more than 80 % of the world's natural gas reserves are contained, which can be found on the shelf at a depth of more than 300 meters, as well as in the permafrost zone. These natural formations represent a potential source of natural gas, which attracts the attention of scientists from all over the world to study this issue.

In this case, gas hydrates are not a chemical compound, but are formed from a hydrate-forming gas and water through a phase transition. They also have the property of "self-preservation", which makes it possible to stably store gas hydrate outside its stability zone and create technologies for transporting and storing natural gas in a hydrated state at a temperature of $-20\text{ }^{\circ}\text{C}$ [2-3].

Currently, in order to deliver natural gas without using a pipeline, it is liquefied and transported in special tankers at a temperature of $-162\text{ }^{\circ}\text{C}$, which is energy-intensive and places high demands on the equipment of transport ships. The properties of gas hydrates can be used not only in the oil and gas industry for transportation needs, but also for desalination and water purification, gas separation, utilization of harmful and greenhouse gases, as well as for cooling and air conditioning systems. The optimal choice of a hydrate-forming gas that is stable at low pressure in the temperature range from 5 to $11\text{ }^{\circ}\text{C}$ can increase the efficiency of using hydrates compared to using ice [4-5].

Despite many useful properties, there are currently no technologies for the industrial production of hydrates due to the complexity of the process of their formation. Studies of the physicochemical properties and thermodynamic conditions for the formation of hydrates are carried out to develop production technologies [6-17]. Specialists also study the synthesis of gas hydrates under different conditions and their dissociation during combustion, analyze thermal and convective processes [18-23]. However, the existing methods for producing gas hydrates have disadvantages, which include low efficiency and productivity, therefore, a team of authors developed a new method based on the explosive boiling of liquefied hydrate-forming gas in a volume of water during decompression, which combines several factors, such as the introduction of a large volume of gas in a liquefied state, mixing, cooling and removal of the generated heat [24-26]. In this study, the effect of stirring the reaction medium on the hydrate formation process was studied, and a kinetic promoter (SDS) was added to evaluate its effect on the hydrate formation process.

1. Experimental setup

The experimental studies were performed on an “autoclave” type setup, a cylindrical vessel for work with high pressure (Fig. 1, 2). The test section of the vessel is made of stainless steel and has an internal diameter of 100 mm and a height of 300 mm. The cooling of the test section is ensured by pumping of coolant from the LOIP FT-316-40 cryostat through the cooled jacket located on the inner surface of the vessel wall. The setup enables conduction of experimental studies at a working pressure of up to 25 MPa. The mixing was executed by the agitator built into the test section (maximum speed of 1400 rpm). The pressure monitoring was performed with the use of built-in pressure (PD 100) sensor in the vessel lid. The use of two RTD temperature sensors determines the temperature in the gas area and in the water area. The pressure relief was controlled by the AALBORG gas flow regulator. In the experimental studies, deionized distilled water was used, sodium dodecyl sulfate (SDS) played the role of kinetic promoter, and Freon 134a was used as the hydrate-forming gas.

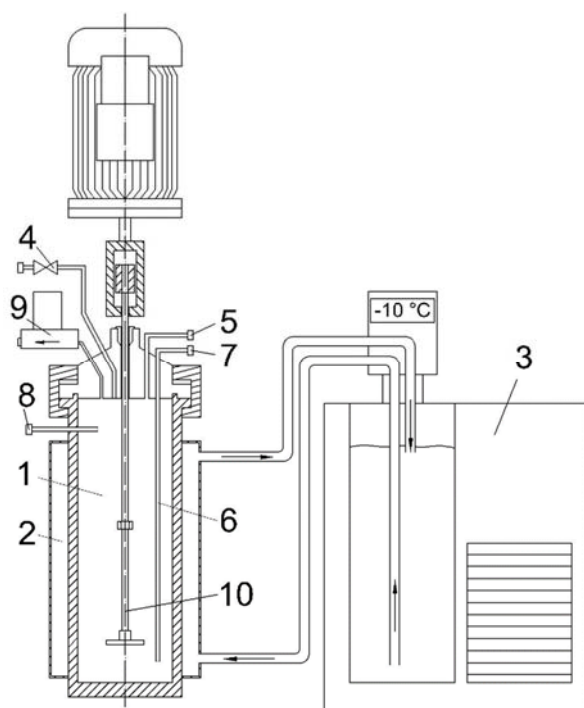


Fig. 1. Scheme of the experimental setup. 1 – working volume of the installation; 2 – cooling jacket; 3 - cryostat; 4 - inlet valve; 5 – pressure sensor; 6 – sleeve for temperature sensor; 7, 8 – temperature sensors, 9 – flow controller; 10 - stirrer.



Fig. 2. Photo of the experimental setup.

2. Experimental Method

The methodology of the experimental study was as follows. The solution was prepared by adding sodium dodecyl sulfate (SDS) powder of various masses to it in order to obtain a concentration from 0 ppm to 1500 ppm in increments of 250 ppm. After that, the solution was placed on the working section of the cooled experimental setup, which was then hermetically sealed. After cooling the solution to a temperature of 8 °C, the vent was opened and the hydrate-forming gas freon 134a in gaseous form, weighing 200 g, entered the installation. It is important to note that the stirrer was not involved in the entire process. After the saturation pressure was reached, freon began to condense on the cooled walls, flow down to the water surface, where it formed into drops and, already in this form, fell to the bottom of the experimental section. After reaching a water temperature of 6 °C, pressure relief began, which was accompanied by intense boiling of liquefied gas in the volume of water. The released gas bubbles rose on the surface of the water. Boiling of liquefied hydrate-forming gas led to intensification of the process of hydrate formation due to a combination of several processes simultaneously: the inclusion of a large volume of gas into the hydrate formation process at once, since it is in the volume of water in a condensed state; cooling of the medium and removal of heat released in the process of hydrate formation as a result of freon phase transition; intensive mixing by emerging gas bubbles and a developed interfacial surface area on which gas hydrate grows. After the pressure in the system dropped to 0.1 MPa, the discharge was stopped. During the pressure release, not all of the gas passed into the gas hydrate state, which required additional pressure releases. to stabilize the pressure at a value of 0.1 MPa. These manipulations are necessary for the complete boiling off of liquefied gas, but for the freon hydrate to be in a stable state.

The use of liquefied freon significantly accelerates the process of hydrate formation, however, it does not allow describing the process using pressure drop. Therefore, after the pressure in the system was set to 0.1 MPa, the cooling of the system was stopped and the heating of the working section began. As a result, the hydrate began to melt with the release of gas, creating additional overpressure in the system. Using which, using the equation of state of an ideal gas, the mass of gas that passed the hydrate was determined.

$$\Delta m = \frac{V_0 M_g (\Delta P T_0 - P_0 \Delta T)}{R (T_0 + \Delta T) T_0}, \quad (1)$$

where Δm is mass of gas converted to gas hydrate, M_g is molar mass of carbon dioxide, ΔP is pressure change during gas hydrate decomposition, P_0 is pressure in the system before decomposition, R is universal gas constant, ΔT is temperature change during heating, T_0 is temperature of the system before heating (determined by a sensor that measures the temperature of the gas).

The mass of the synthesized hydrate is determined as follows:

$$m_h = \frac{\Delta m}{\gamma}, \quad (2)$$

$$\gamma = \frac{M_g}{M_g + 17 M_w}, \quad (3)$$

where M_g is molar mass of carbon dioxide, M_w is molar mass of water.

Using the data obtained, the coefficient of water conversion to the hydrated state was determined relative to the initial mass of water.

$$K_w = \frac{m_h - \Delta m}{m_{w_{init}}}, \quad (4)$$

where $m_{w_{init}}$ is initial mass of water.

3. Results

In this paper, an experimental study of the effect of SDS concentration in water on the process of hydrate formation was carried out by the method of explosive boiling up of a liquefied hydrate-forming gas in a volume of water during decompression. On Fig. 3 shows the change in pressure in the system during the production of hydrate according to the method described above with the concentration of SDS in water 0 and 1500 ppm. For pure water, during decompression, the pressure first drops, and then begins to increase with continued pressure release. This is characterized by the explosive nature of the process, where the liquefied freon overheats, which leads to its volumetric boiling. It should be noted that for water with the addition of SDS, this effect is not observed starting from a concentration

of 750 ppm. After reaching the pressure value in the system up to 0.1 MPa, the pressure relief stops, however, liquefied gas is still present in the system, which leads to an increase in pressure, therefore, an additional pressure relief was carried out until the liquefied gas was found in the system.

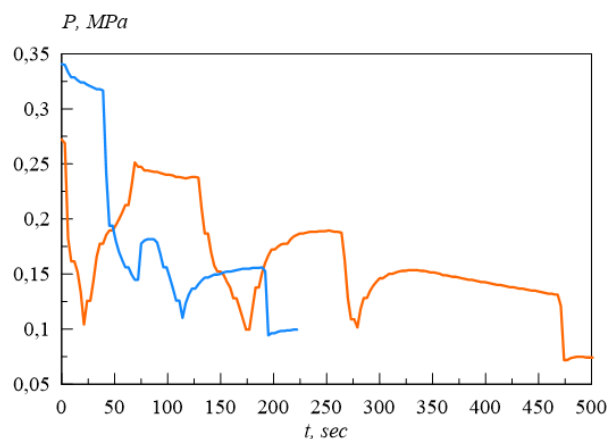


Fig. 3. Pressure change in the system during the process of explosive boiling of liquefied gas for SDS concentrations of 0 ppm (blue line) and 1500 ppm (orange line).

Fig. 4 shows the change in pressure in the system during the process of explosive boiling of liquefied gas for SDS concentrations of 0 ppm and 1500 ppm. As can be seen from both graphs, the release of pressure is accompanied by cooling of the medium at the initial moment of time. However, for the case with a solution of water and SDS, then a sharp increase in temperature occurs. This is due to the intensive growth of hydrate in the area of contact between water and gas.

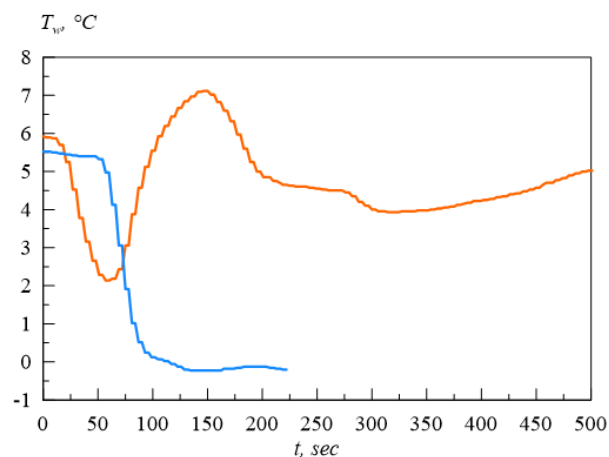


Fig. 4. Temperature change in the system during the process of explosive boiling of liquefied gas for SDS concentrations of 0 ppm (blue line) and 1500 ppm (orange line).

The results obtained are presented in Fig. 5 and Table 1. It can be seen that the concentration of SDS has a significant effect on the process of hydrate formation in the method under study. At the same time, after 750 ppm, the water conversion values practically do not change. This result was obtained due to the fact that SDS makes the resulting hydrate porous, as a result of which the growing hydration shell on the surface of the bubble has less effect on the diffusion of gas into water, unlike

pure water, and foaming of the solution occurs during discharge, creating additional interfacial surface between water and gas.

Table 1. Water conversion in gas hydrate.

Csds, ppm	0	250	500	750	1000	1250	1500
Kw, %	22,4	36,4	54,6	72,1	76,8	79,2	78,6

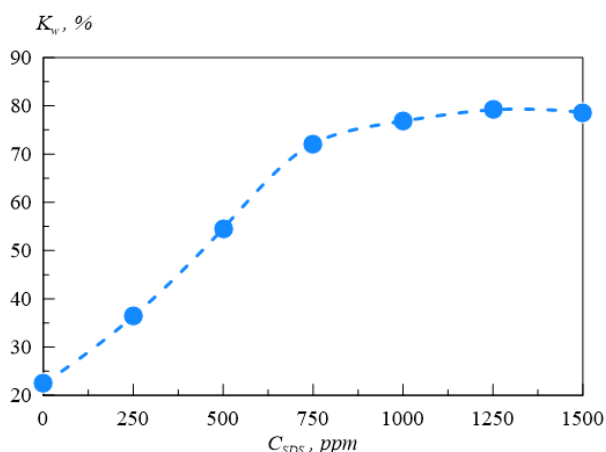


Fig. 5. Water to gas hydrate conversion for various SDS concentrations: 0, 250, 500, 750, 1000, 1250 and 1500 ppm.

Conclusions

In this work, the influence of the kinetic promoter sodium dodecyl sulfate (SDS) on the process of hydrate formation by the method under study was determined. It has been shown that the conversion of water to the gas hydrate state is better in the case of a solution with SDS. This is due to the porous structure of the resulting hydrate from a solution of water and SDS and its foaming during pressure relief. In this case, the formation of hydrate from the solution during pressure release is accompanied by heat release, which indicates the possibility of even greater acceleration of the process with more perfect heat removal. The optimal value is 750 ppm and is 72.1%, a further increase does not have a significant effect on the process.

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References

1. S. Misyura, P. Strizhak, A. Meleshkin, V. Morozov, O. Gaidukova, N. Shlegel, M. Shkola, *Energies* **16**, 3318 (2023)
2. R.V. Belosludov, Y.Y. Bozhko, R.K. Zhdanov, O.S. Subbotin, Y. Kawazoe, V.R. Belosludov, *Fluid Ph. Equilibria* **413**, 220 (2016)
3. V.R. Belosludov, Y.Y. Bozhko, *J. Phys.: Conf. Series* **1128**, 012086 (2018)

4. B. Castellani, E. Morini, M. Filipponi, A. Nicolini, M. Palombo, F. Cotana, F. Rossi, *Sustainability* **6** (10), 6815 (2014)
5. S. Choi, J. Park, Y.T. Kang, *Appl. Energy* **242**, 1358 (2019)
6. Y.Y. Bozhko, R.K. Zhdanov, K.V. Gets, O.S. Subbotin, V.R. Belosludov, *J. Engin. Thermophys.* **32**, 62 (2023)
7. V.R. Belosludov, Y.Y. Bozhko, O.S. Subbotin, R.V. Belosludov, R.K. Zhdanov, K.V. Gets, Y. Kawazoe, *Molecules* **23**, 3336 (2018)
8. O.S. Subbotin Y.Y. Bozhko, R.K. Zhdanov, K.V. Gets, V.R. Belosludov, R.V. Belosludov, Y. Kawazoe, *Physical Chemistry Chemical Physics* **20**, 12637 (2018)
9. V.S. Shagapov, N.G. Musakaev, M.K. Khasanov, *Int. J. Heat Mass Transfer* **84**, 1030 (2015)
10. A.K. Sagidullin, A.S. Stoporev, A.Yu. Manakov, *Energy & Fuels* **33**, 3155 (2019)
11. S. Skiba, D. Strukov, A. Sagidullin, T. Adamova, A. Stoporev, L. Svarovskay, L. Strelets, L. Altunina, A. Manakov, *J. Pet. Sci. Eng.* **192**, 107211 (2020)
12. V.A. Shestakov, A.K. Sagidullin, A.S. Stoporev, *J. Mol. Liq.* **318**, 114018 (2020)
13. M.Y. Shumskayte, A.Yu. Manakov, A.K. Sagidullin, V.N. Glinskikh, L.S. Podenko, *Mar. Petrol. Geol.* **129**, 105096 (2021)
14. S.Y. Misyura, *Environ. Pollut.* **265**, 114871 (2020)
15. S.Y. Misyura, A.Y. Manakov, V.S. Morozov, G.S. Nyashina, O.S. Gaidukova, S.S. Skiba, R.S. Volkov, I.S. Voytkov, *J. Nat. Gas Sci. Eng.* **80**, 103396 (2020)
16. S.Y. Misyura, *Energy* **206**, 118120 (2020)
17. O.S. Gaydukova, S.Y. Misyura, P.A. Strizhak, *Combust. Flame* **228**, 78 (2021)
18. S. Y. Misyura, A. Y. Manakov, G. S. Nyashina, O. S. Gaidukova, V. S. Morozov, S. S. Skiba, *Entropy* **22**, 710 (2020)
19. S.Y. Misyura, I.G. Donskoy, A.Y. Manakov, V.S. Morozov, P.A. Strizhak, S.S. Skiba, A.K. Sagidullin, *J. Energy Storage* **44**, 103288 (2021)
20. A.V. Meleshkin, N.V. Marasanov, *J. Engin. Thermophys.* **31**, 696 (2022)
21. A.V. Meleshkin, N.V. Marasanov, *J. Engin. Thermophys.* **30**, 699 (2021)
22. A.V. Meleshkin, A.A. Shkoldina, *J. Engin. Thermophys.* **30**, 693 (2021)