Досліджено вплив поверхнево-активних речовин на механізм утворення газових гідратів метану. Визначено значення критичної концентрації міцелоутворення (ККМ) розчинів дібутілфенола, обробленого окисом етилену (ДБ), а також синтанолів (ДС-10, ДС-20). Виявлено, що завдяки процесу солюбілізації відбувається утворення мікрогетерогенних наночасток, які призводять до зміни складу газогідратів і швидкості утворення

Ключові слова: газогідрати метану, міцелоутворення, поверхневий натяг, міжфазовий електричний потенціал, швидкість утворення

Исследовано влияние поверхностно-активных веществ на механизм образования газовых гидратов метана. Определены значения критической концентрации мицеллообразования (ККМ) растворов дибутилфенола, обработанного окисью этилену (ДБ), а также синтанолов (ДС-10, ДС-20). Обнаружено, что благодаря процессу солюбилизации происходит образование микрогетерогенных наночастиц, которые приводят к изменению состава газогидратов и скорости образования

Ключевые слова: газогидраты метана, мицеллообразование, поверхностное натяжение, межфазный электрический потенциал, скорость образования

STUDY OF THE FORMATION MECHANISM OF GAS HYDRATES OF METHANE IN THE PRESENCE OF SURFACE-ACTIVE SUBSTANCES

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1. Introduction

Recent years have seen a worldwide trend towards ever-increasing consumption of fuel and energy resources, with a significantly growing interest in non-traditional ways of production of various sources of energy [1–3]. For Ukraine, this question is particularly relevant because the price of natural gas supplied from abroad grows each year, which adversely affects the economy. Thus, it is obvious that there is the need to modernize the structure of coal and oil and gas complexes of the state and to improve a development mechanism of the country's energy sector, which is possible through the introduction and application of advanced gas hydrate technologies that would enable the possibility of obtaining additional energy resource.

The main directions of scientific and practical research into gas hydrates (GH) are the extraction and development of gas hydrate deposits. On the other hand, with the purpose of disposal and storage of methane from the coal mines in Ukraine, a method for converting them into the gas-hydrate state can be used. The application of GH for storage or transportation has not been industrially exploited so far. However, they constitute one of the most promising directions in the development of hydrate technologies for modern industry [4–6].

An interest in GH is associated with the possibility of their practical application: fuel volumes in the form of GH represent about $2\times10^{16}\,\text{m}^3$, which exceeds the amount of hydrocarbon fuels in all other forms on our planet [7–9]. In connection with the reduction of world oil reserves, searching for methods of using such compounds as a source of energy is particularly relevant [10–12]. Only three deposits of GH are currently being developed in the world industrially – in Canada, Japan, and Russia. Extraction of fuel from such structures is associated, in particular, with the need for safe and effective release of gas from the hydrate [13–16].

Ukraine occupies eighth place in the world by reserves of coal methane, which amounts to 8 trillion m^3, and fourth in the world by the quantity of emissions of this gas in the atmosphere. Given this, there is a problem in Ukraine to dispose of mine methane from degasification wells and ventilation jets, solving which, with the right approach, can save a lot of money for the purchase of natural gas [17]. Methane, which is released into the mines, hampers production of coal, increasing its cost and worsening the safety of miners' labor, which is why obtaining GH from the methane of coal mines is very promising [18]. This method also holds promises for storage and transportation of various gases [19–21], such as carbon dioxide [22]. Using the method became possible due to the fact that methane hydrate is stable at atmospheric

pressure, if it is created below the freezing temperature of water under conditions that are close to adiabatic [21]. Economic efficiency is ensured by the high concentration of gas in hydrate [20] (180 units of volume of natural gas per one unit of volume of hydrate [21]).

From a practical point of view, results of the studies are necessary in order to improve modern technologies of production, transportation and storage of gas, to improve the safety of mining operations, to design new technologies for comprehensive exploration of coal deposits. It can be concluded that studying the mechanism of GH formation appears to be one of the most important and relevant tasks.

2. Literature review and problem statement

The process of gas hydrates formation consists of the formation of a new phase (solid). Spontaneously occurring processes are caused by the fact that the new state of the system under changed conditions is more stable and has a less reserve of energy.

Formation of inter-phase surfaces and the related surface phenomena is predetermined by the excessive surface energy [23]. This is due to the fact that molecules of the gaseous phase (methane) are in the surface of the interface, they have excessive energy compared to molecules in the volume due to the imbalance in their intermolecular interactions. The resulting noncompensation of intermolecular interactions is caused by a difference in the composition and structure of the contacting phases, which results in the occurrence of surface forces and excess of energy at the interface surface – surface energy.

Almost all hydrophobic gases and volatile liquids the size of molecule of 3.8...9.2 Å can create GH, as well as some hydrophilic compounds that have sufficiently weak interaction with water, which do not prevent clathrate formation [8, 24].

Transportation and application of GH consists of three stages: creation of hydrate; actual transportation; the release of gas at its decomposition. The first stage implies mixing gas and water under necessary conditions. One of the major problems is a small rate of hydrate formation, which hampers industrial application of the method. To resolve this problem, different additives or surface-active substances (SAS), or hydrotropic substances [25], which makes it possible to identify subtle details in the mechanism of the process of gas hydrate formation and its kinetics. As shown in paper [26], a possible direction might be using a solution of sodium dodecyl sulfate with a concentration of 500 particles per million. In this case, the growth rate of GH formation increases by more than 35 times, and its reserve capacity doubles. However, with the addition of SAS, a side effect is often observed, which leads to a decrease in the stability of methane hydrate. As shown in paper [21], this can be avoided by adding a mixture of sodium dodecyl sulfate, xanthan or starch.

The problem of accelerating the process of gas hydrate formation is currently being tackled by scientists from India. They suggest using surface-active substances in order to accelerate the process of nucleation of hydrates, enabling a more active heat transfer and increasing the contact surface between water and gas [27]. Researchers from Iran study effect of the application of nano particles of copper oxide in order to increase the volume of gas absorbed by water, for a better water conversion into hydrate state and for a growth of kinetics of hydrate formation process [28]. Scientists from the

United States have for several years been working on designing a technology of spraying water through the gas phase to increase the contact area between hydrogen and gas phases, leading to the acceleration of the process of gas hydrate formation, especially so when applying the "dry water" [29].

The main condition for effective transportation is ensuring stability of clathrate structure, that is, it is necessary to maintain a certain temperature at atmospheric pressure [30]. To address environmental issues, a method is proposed for substituting methane, bound in the hydrate, with molecules of CO_2. The result is a reliable storage of carbon oxide (IV) with effectively released hydrocarbon [22].

Thus, results of the fundamental research into mechanism of GH formation, as well as data on the influence of chemical additives and SAS on the rate of hydrate formation, can have a significant impact on the technological and economic attractiveness of storing natural gas in the form of GH. Given the difficulties of experimental character, the mechanism of gas hydrate formation has not been studied sufficiently. However, research into mechanism of the GH formation is necessary in order to improve modern technologies for the extraction and transportation of natural gas from gas hydrate deposits, for creating energy-saving technologies, development of hydrocarbon energy generation, and technologies for separating gas mixtures.

3. The aim and objectives of the study

The aim of the studies conducted was to establish influence of SAS on the process of GH formation, as well as to examine kinetic regularities of their formation in the three-phase system "gas" – "water + SAS" → "solid body (GH)".

To achieve the set aim, the following tasks have been formulated:

– to establish a process of micellization in the examined SAS;

– to determine critical micellization concentration (CMC);

– to establish a change in the electrochemical characteristics of the process;

– to determine a constant of GH formation in the presence of SAS.

4. Materials and methods of research into mechanism of gas hydrate formation of methane in the presence of surface-active substances

4. 1. The essence of the conducted research

When performing experimental part of the study, we employed the following surface-active substances (SAS):

– dibutyl phenol, treated with ethylene oxide (DB);

– oxyethylized alcohols (a mixture of polyethylene glycol ethers with a different number of oxy-ethyl groups and the magnitude of radical).

Micellization in the solutions of SAS was studied in a range of concentrations from 10^{-4} to 10^{-2} mol/l (0.07 %, 0.10 %, 0.15 %, 0.25 %, 2.5 % and 5 % by weight).

We used a stalagmometric method with an automated photoelectron count of the drops (measurement error is 0.1 %). To determine CMC, we applied a conductometric method (conductometer N 5721, Wroclaw: ElBPO). Electrical conductivity was measured using the Wheatson bridge (measurement error is 0.05–0.1 %).

The interphase electric potential was measured by a potentiometric method using the potentiometer PPTV 1.

Based on the data obtained, we plotted dependence charts for $\sigma = f(\lg C)$, the magnitude of CMC was determined by the intersection of two straight lines.

Each solution was tested 7 times, followed by determining the average value.

4. 2. The installation and technique for obtaining gas hydrates of methane in laboratory studies, as well as research into the rate of gas hydrate formation

The study of the mechanism of GH formation in presence of SAS was conducted at the installation created in the laboratory of innovative technologies at the National Mining University (NMU, the city of Dnipro, Ukraine).

4 modifications of the installation were designed over 2009 to 2015 (Fig. 1). It simulates the thermobaric conditions similar to those natural. The installation also enables conducting studies into fast retrieval of GH of methane under mild conditions at temperatures from 281 to 274 K and at a pressure of less than 7 MPa [31].

The installation consists of two units: one experimental and one cooling. The climatic chamber "ILKA" KTK-3000 (Germany) is used as a cooling unit. It makes it possible to maintain and control temperature and humidity.

The experimental unit is used to feed gas and water, to measuring their flow rate, as well as to create the required pressure in the system. Basic operational characteristics of the chamber are given in Table 1.
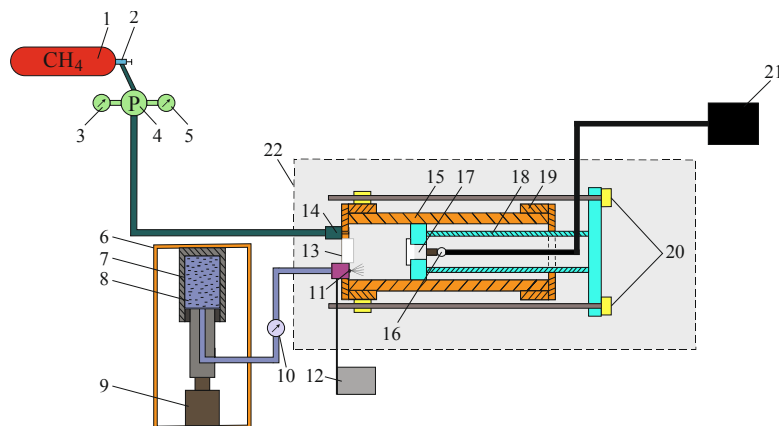
Table 1

Basic characteristics of climatic chamber "ILKA" KTK-3000

Chamber volume, m³	3
Dimensions (H×W×D), mm	2100×2300×2150
Dimensions of useful volume (H×W×D), mm	1200×1500×1650
Thermal insulation thickness, mm	100
Temperature range, ˚C	−30...+100
Discreteness of temperature setting, ºC	1
Permissible temperature deviation, ºC	0.2
Relative humidity, %	10–100
Power, kW	19
Voltage, V	380
Refrigerant, Freon number	22
Cooling of capacitors	water/air
Water flow rate, m³/h	0.6
Permissible load, kg/m²	400
Weight, kg	1650

Fig. 1. Laboratory installation NPO-5 for obtaining gas hydrates:
1 — cylinder with methane; 2 — cylinder valve; 3 — high pressure manometer;
4 — adjustable reducer; 5 — low pressure manometer; 6 — rigid frame;
7 — device to create water pressure; 8 — water; 9 — hydraulic jack;
10 — water pressure gauge; 11 — input water nozzle with electric drive;
12 — pulse generator for nozzle; 13 — transparent window of reactor;
14 — gas inlet fitting; 15 — reactor of hydrate formation; 16 — LED unit;
17 — transparent window of rod; 18 — rod; 19 — guide flange;
20 — tightening bolts with nuts; 21 — power accumulator; 22 — cooling chamber

The chamber enables conducting research under different temperature modes with varying humidity. Design of the climatic chamber consists of four main parts: working volume, automatic control panel, cooling unit and the steam generator. The working volume is implemented in the form of a cabinet with inside heat exchangers to provide laboratory testing regimes. The chamber has a door with a window and a system of protection against frosting. The chamber's body is mounted on a rigid wheelbase frame made of steel profile.

To prevent the inadvertent movement of the chamber during work, the wheels are equipped with brake pads.

Cooling unit is placed on a removable mounting plate inside the frame. Outside, the unit is closed with housings, providing free access of air in order to cool devices of the refrigeration machine. Next to the door that opens the chamber, that is, on its working volume, is an automatic control panel, which contains main electrical equipment and automation elements. Experiments are conducted as follows: a special device for the formation of gas hydrates is placed inside the refrigeration chamber.

The rate of methane hydrate formation is determined using a kinetic method by the initial speed of formation of an icy crust, and then we determined the amount of methane per unit volume (C_m) at different content of SAS.

Measuring the volume of methane from GH is possible in two ways:

– first, by measuring the volume of gas incoming to reactor at high pressure, but this technique is rather difficult because there are no counters to measure a small amount of passing gas under high pressure;

– second, by measuring the amount of gas leaving the reactor during hydrate decomposition; in this case, the pressure is low, which allows the use of household gas counters, operating at a pressure of less than 1 MPa.

Fig. 2 shows the experimental installation, designed at the laboratory of innovative technologies at NMU, intended for the formation of gas hydrates of various composition under different conditions of their formation and for further studies of the obtained samples.

The following procedure was devised for determining C_m:

1. Upon completion of the process of obtaining GH (all water reacted), we reduced the temperature in the climatic chamber and, accordingly, in the reactor for hydrate forma-

tion from 274 to 263–258 K. The hydrate formation process in the reactor was observed through a window in the chamber and reactor.

2. The valves on the cylinder with gas and on the adjustable reducer were cut off.

3. A high-pressure hose was disconnected from the reducer and connected to the gas counter.

4. We opened the valve of the reactor and raised the temperature in the chamber and reactor up to room temperature.

5. Methane hydrate starts to decompose. The released methane passes through a gas meter and thus its amount is determined.
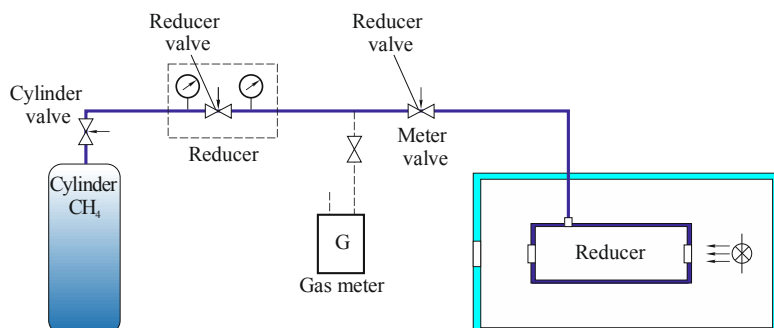

Fig. 2. Schematic of the experimental installation

Knowing the magnitude of the released gas and the volume of water poured into reactor volume, we determined the magnitude of C_m. Then the gas pressure in the reactor was reduced to 1 MPa and we repeated measurements.

5. Results of experimental research into the mechanism of GH formation in the presence of SAS

To speed up the process of gas hydrate formation, at 274 to 281 K and under normal pressure, we added a nonionic SAS to water in the amount of 10^{-4} to 10^{-2} mol/l. When employing such additives, there occurs a decrease in the surface tension at the phase interface and a concentration of the interphase surface.

The first task was to study SAS: measurement of surface tension makes it possible to determine a critical micelle concentration (CMC). Applying the indicators for the surface tension of aqueous solutions of DB, DC-10 and DC-20 (Table 2), we plotted isotherms of surface tension in logarithmic coordinates $\sigma - \lg C_{SAS}$.

Experimental data are given in Table 2.

Based on the measurements of surface tension (Table 2), we plotted isotherms (Fig. 3), which were applied to calculated the magnitude of CMC.

Fig. 3 and Table 2 show that an increase in the concentration of SAS in the system results in the occurrence of qualitative changes: transition from macro heterogeneous to micro heterogeneous colloidal dispersion (by micellization process).

This change leads to the alteration of physical-chemical properties of the system, accompanied by the appearance of characteristic kinks on the curves of dependences of certain parameters on the concentration of SAS.

It is interesting to study the interphase boundary in the course of hydrate formation reaction. For this purpose, we carried out research into determining the effect of SAS on a change in the interphase electrical potential at the interface

of phases of liquid-gas. Fig. 4 shows dependence of change in the potential and electric resistance in the system on the amount of introduced SAS. The process of micellization is stepwise in character and is implemented through a number of structures whose properties are registered on the potentiometric curves (Fig. 4).
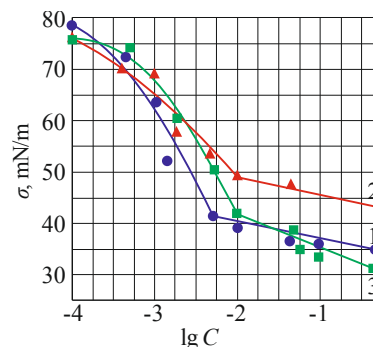

Fig. 3. Isotherm of surface tension (σ) in logarithmic coordinates ($\lg C$): determining of critical micelle concentration by the method of measuring surface tension: 1 — DS-10; 2 — DS-20; 3 — DB

Table 2

Dependence of surface tension (mN/m) on the concentration of SAS

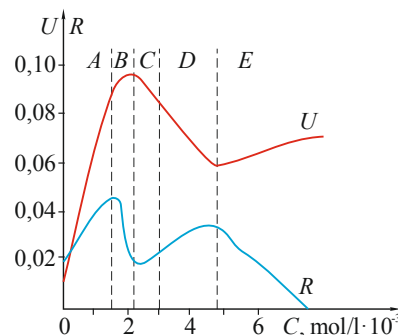| Sample No.	$C_{SAS} \times 10^{-4}$	$\lg C_{SAS}$	Surface tension σ_{SAS}, mN/m		
			σ_{DC-10}	σ_{DS-20}	σ_{DB}
1	1.0	−4.00	75.33	75.00	75.44
2	5.0	−3.30	70.12	72.76	74.33
3	10.0	−3.00	64.70	69.45	59.88
4	15.0	−2.80	51.10	56.75	50.56
5	17.5	−2.75	41.55	54.98	43.76
6	20.0	−2.70	39.71	49.17	38.48
7	25.0	−2.60	37.50	47.78	36.76
8	30.0	−2.50	37.00	46.55	34.01
9	35.0	−2.46	36.00	44.31	33.77
Decrease relative to water, %	–	–	82	54	96

Fig. 4. Change in potential and electric resistance of the system on the amount of introduced SAS

Region (A) characterizes the process of formation of micelles of variable composition, accompanied by a sharp increase in the potential, binding the molecules of SAS, which

leads to increased electrical resistivity of the medium. In the zone (in) Micellization takes place in region (B); the shape of micelles changes in region C. A full transformation into the most robust micelles (plastic, with sharply expressed asymmetry) corresponds to region (D).

Experimental data are consistent with the thermodynamic equilibrium in the transition of one form of micelles into another one, shown in Fig. 5.
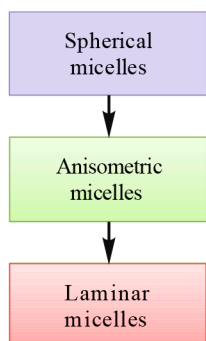

Fig. 5. Transition scheme of the shape of micelles: spherical shape — purple color; anisometric ellipsoidal — green color; laminar micelles with sharply expressed asymmetry — red color

The results obtained (Fig. 4, 5) correspond to the notions of T. Alty on the double electric layer at the interphase boundary, which is due to the orientation of molecules of water by oxygen atoms into the gas phase, and by hydrogen atoms into liquid.

Experimental data demonstrate that the formation of hydrate starts in 5–10 minutes after pressure is fed to the reactor. GH forms by layering one ice layer over the other one. This process proceeds until all the water has reacted with gas (Fig. 6).

An important feature of micellar solutions of colloidal SAS in water is their ability to solubilization (colloidal dissolution) of substances that are practically insoluble in water. During solubilization, there occurs a spontaneous dissolution by the micellar phase of SAS of substances that are virtually insoluble under normal conditions in a disperse medium, with the formation of thermodynamically stable isotropic solution. Thus, for example, solubility of octane in water is very low (only 0.0015 %), but it grows by thousand times in a 10 % solution of sodium oleate. Solubility of many gases, including O_2 and CO_2, in the micellar solutions of SAS is markedly higher than that in water.

Kinetic equation of the process of hydrate formation under condition of constancy of one of the parameters (pressure, temperature) takes the following form:

$$\tau = \ln(V_m / (V_m - V_9)) \qquad (1)$$

or

$$V_0 = V_m(1 - e^{-k\tau}), \qquad (2)$$

where k is the rate constant for hydrate formation; τ is the time of hydrate formation; V_0 and V_m is the initial and maximally achievable volume of methane in GH. Due to the fact that GH belong to clathrate compounds, in order to determine V_{max}, we use only the initial part of the curve. Under condition $2\tau_1 = \tau_2$, it is possible to derive V_{max} from equation (2):

$$V_{max} = \frac{V_1^2}{2V_1 - V_2} . \qquad (3)$$

Rate constant (k) was determined by the least square method, processing experimental data in the $\ln(1 - V/V_{max})_x - \tau$ coordinates.

The hydrate formation process was monitored also through the transparent window of the reactor, Fig. 1 (symbol 13). Time of the occurrence of the first crystals of ice crust is 20 minutes; the hydrate formation process proceeds for 4 hours in total. The amount of methane (C_m) in GH was determined according to the described procedure (Fig. 2).

Fig. 7 shows a dependence of change in the number of moles of methane in GH (n) on the concentration of SAS, and without the SAS application in the course of reaction for 20 minutes.

The shape of curve in Fig. 7 is similar to dependence of relative solubilization (S) on the concentration of DB. Thus, during formation of GH of methane in the presence of DB there occurs the process of solubilization.

Fig. 8 shows dependence of the content of the amount of gaseous methane per unit volume of methane hydrate on the time of hydrate formation at T=274 K in the presence of 1.75×10^{-3} mol/l DB, and without SAS.

Similar results were obtained when examining the mechanism of selective flotation of Au, Pt [32] on polymeric matrices with the formation of clusters.
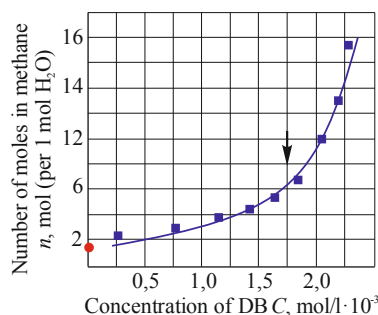

Fig. 6. Gas hydrates obtained in the experimental studies under laboratory conditions: *a* — condensed gas hydrate; *b* — gas hydrate crystals in the reactor of a laboratory installation; *c, d* — loose gas hydrate

Fig. 7. Dependence of the concentration of GH on the concentration of DB in 20 minutes after the start of the reaction of gas hydrate formation: arrow indicates CMC; red dot — n without SAS
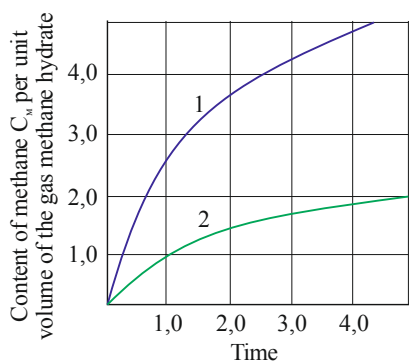

Fig. 8. Dependence of the content of the amount of gaseous methane content per unit volume of methane hydrate on the time of hydrate formation at $T=274$ K in the presence of 1.75×10^{-3} mol/l DB (1), and without SAS (2)

To determine the energy of bond formation in clusters and internal energy, we applied a simplified method by Butler-Polanyi.

Assuming that $A=10^{13}$ s^{-1} and by measuring the magnitude of k at the temperature of the experiment, we calculated energy as $D=E=R \times T \times \ln(10^{13}/k)$. Note that, as a result of the deviation in pre-exponential in expression for the rate constant, there may occur errors in a given method (about 5 kcal).

Table 3 gives results of the calculation of kinetic curves and internal energy U, which was spent to form GH of methane in our installation.

Table 3

Results of calculation of kinetic curves and internal energy U

Time, min	Internal energy U, cal/mol	Content of gaseous methane per unit volume of its hydrate	Formation constant k, min^{-1}
0.00	10000.00	0.0	0.00
0.01	16940.32	0.4	2.34
10.00	21452.58	0.8	$1.06 \cdot 10^{-2}$
20.00	24176.02	1.1	$1.09 \cdot 10^{-2}$
30.00	24127.38	1.5	$1.17 \cdot 10^{-2}$
40.00	24038.93	2.0	$1.32 \cdot 10^{-2}$
50.00	23949.53	2.3	$1.50 \cdot 10^{-2}$
60.00	23833.10	2.5	$1.78 \cdot 10^{-2}$
120.00	24328.36	3.6	$8.77 \cdot 10^{-3}$
180.00	24226.68	4.2	$1.02 \cdot 10^{-2}$
240.00	24368.87	4.9	$8.28 \cdot 10^{-3}$

The formation of GH mostly occurs over the first 20 30 minutes, this is also confirmed by data on the calculated internal energy (Table 3).

From minute 20, an energetically stable process begins, which is probably associated with the formation of clusters with stable bonds, so there is only a slight decrease in energy.

Of interest is the activation effect that allows us to assume that, as a result of GH formation in presence of SAS, there occurs a micellar catalysis.

6. Discussion of results of research into the mechanism of formation of gas hydrates in the presence of SAS

One of the main problems for accelerating the process of hydrate formation at present is the low rate of the process of GH formation, which hinders their industrial production, transportation, and application. To resolve this task, various additives or surface-active substances (SAS) are employed, which accelerate this process on the one hand, while, on the other hand, reduce the stability of GH (a side effect).

This necessitates exploring the mechanism of the process of hydrate formation and its kinetics at a temperature of 274 K. It was found that exactly under such conditions, when SAS reach a certain concentration in the volume of water, the aggregates of molecules start to form spontaneously. This ability to self-organization makes it possible to obtain ultra-micro heterogeneous organized media that contain molecules-receptors, which possess rigid internal cavities in space.

When considering the kinetic characteristics of GH formation at 274 K, the following assumptions were made:
– the reaction of hydrate formation or the limiting stage of the process is monomolecular;
– the first emergence of a hydrate formation crystal was determined visually.

Based on the obtained experimental data, we can conclude that the mechanism of hydration under conditions of a solid phase formation in the presence of SAS proceeds in line with the mechanism of solubilization, with the subsequent micellar catalysis.

The results obtained are a continuation of the research carried out at SHEE "National Mining University" [26].

Based on an analysis of the received isotherms (Fig. 3) by the indicators for surface tension of the aqueous solutions DB, DC-10, and DC-20 (Table 2), we plotted isotherms of surface tension in the logarithmic σ–lgC_{SAS} coordinates. The isotherms demonstrate a curvilinear section in the region of low concentrations, on which, in accordance with the Gibbs equation, adsorption at the interphase boundary increases with an increase in the concentrations. The curvilinear section of the isotherm passes into a straight line; in this case, the adsorption reaches its maximum value. Based on kink of the isotherm, we determined the value of CMC, which corresponds to the concentration of SAS equal to $1.75–2.00 \times 10^{-2}$ mol/l. The addition of SAS leads to a decrease in the magnitude of CMC. Thus, at temperatures close to zero, DB, DS-10, and DS-20 behave as cryoprotectants.

While exploring the mechanism of methane hydrate formation in the presence of SAS it was discovered that the hydrate formation mechanism includes the following stages: micellization and solubilization. However, an increase in the volume of absorbed methane in the presence of SAS (Fig. 8),

as well as the activation effect (Table 3), allow us to assume that the result of micelle formation is the micellar catalysis.

The influence of SAS in the process of hydrate formation consists of the following:

Stage I – localization of SAS as a result of favorable concentration in micelle of all three components "methane+ +SAS+water". This stage increases the frequency of interaction (collisions) between reagents;

Stage II – effect of a field medium (the interphase boundary), which leads to the micellar catalysis, at which the reaction proceeds faster.

A feature of this mechanism is the formation of inverse micro-gas emulsions resulting from the application of SAS. Such micro-gas emulsions, according to Plateau, occur during foam formation of the system "methane+SAS+water". At the interface of three films that belong to three or more contacting bubbles, the Plateau channel is formed. In this case, the bubbles of methane in GH take the shape of a pentagonal dodecahedron. It is necessary to take into account the fact that at concentrations of 10^{-4}–10^{-2} mol/l, at a temperature of 274–281 K, gaseous methane is concentrated inside the pentagonal dodecahedron. This is a result of cryoprotective properties of SAS at the indicated temperatures. The micelles that are being formed are in fact inverse, concentrating gaseous methane.

Thus, the resulting micro-gas emulsions at relatively low temperatures can serve as a "nanoreactor", in which the synthesis of the required substance takes place in the temperature range of 274–281 K. It is possible to synthesize different kinds of nanoparticles in the micro emulsions.

In the further study into the mechanism of GH formation, it is necessary to define the impact of the feed rate of the system "methane+SAS+water" into experimental chamber, as well as diffusion characteristics of the mass transfer process on the rate of GH formation. Experimental studies of such a system require, however, creation of the new installations.

7. Conclusions

1. It is revealed that over the temperature range of 274–281 K the addition of SAS leads to the solubilization and micellization processes, the result of which, during hydrate formation, is the emergence of gas emulsions that contain methane. The amount of methane in such HG is several times higher than in the case of obtaining GH without SAS.

2. We determined CMC values, which correspond to the concentrations of SAS equal to 1.75–2.00×10^{-2} mol/l.

3. It was established that in the process of obtaining GH, adsorption at the interphase boundary increases with a rise in the concentrations, leading to a gradual change in the shape of micelles.

4. We determined a rate constant of the process of hydrate formation and the activation effect, at the expense of micellar catalysis. It was found that at temperatures of 274–281 K the process of micellar catalysis is affected by both electrostatic and geometrical factors.

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