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RESEARCH INTO THERMOBARIC PROCESSES OF METHANE GAS HYDRATES FORMATION

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ABSTRACT

Based on experimental studies, the paper deals with the dynamics of the methane gas hydrates formation, influenced by the organized media, such as surface-active agents (surfactants, SAA), namely, dibutylphenol treated with ethylene oxide, as well as ethoxylated alcohols. The stalagmometric method with automatic photoelectronic drops counting, a conductometric method, a Wheatstone bridge, potentiometer, as well as laboratory setup with varying thermobaric parameters of the hydrate formation process are used. The molecular dynamics method and the Monte Carlo method are applied to the process of methane gas hydrates formation. New experimental dependences of the gas hydrates formation have been determined on thermobaric conditions with and without of organized media. It has been set that under normal conditions of hydrate formation, the hydrate formation thermobaric curve consists of two identical dependences, which is caused by formation of the KS-II structure hydrates with different degrees of filling the crystal lattice cavities: from 275.0 to 279.2 K - small cavities, and above - larger ones. When applying a surfactant, water structuring with formation of immediately large cavities in the gas hydrate crystal lattice are observed, due to which the methane content in the hydrate increases. It has been revealed that the gas hydrates formation process occurs stepwise, by replacing old bonds with new ones with a gradual change in the coordination number of reacting surface atoms. It has been found that surface clustering in the presence of organized media facilitates the gas hydrate formation process by means of micellar catalysis. The dependences have been determined of the gaseous methane amount contained in the cluster upon the temperature in the dissociation of obtained gas hydrate samples. The amount of methane in a unit volume of gas hydrate has been determined: without adding the surfactant at a maximum pressure of 18 MPa - 120 m^3; by adding the surfactant with the same thermobaric parameters - 160 m^3.

Keywords: gas hydrates, thermobaric parameters, formation, methane, dynamics, surface-active agents.

1. INTRODUCTION

Gas hydrates are the objects of supramolecular (permolecular) chemistry - a relatively new science that studies the other, subtler principle of chemical matter organization. This section of chemistry considers the chemical matter in terms of favourable spatial complementarity of reacting components. The supramolecular chemistry methods are applicable even in the case of weak van der Waals interactions in the compounds.

The physical, physical-mechanical, thermodynamic and electromagnetic properties of gas hydrates, as a solid, are similar to ice. Study of cryogenic systems has always been an important aspect both for the conditions of advent and existence of life, and for controlling the speed and mechanisms of biological processes [1] The study of the molecules interaction patterns in gas hydrate systems and the structure of the compounds formed, their thermodynamic stability zones (phase diagrams), the kinetics of formation and decomposition is of great importance for many branches of industry and science [2], [3].

Since gas hydrates belong to the class of non-stoichiometric clathrate compounds and are molecular crystals, the research into the morphology of crystalline hydrates is important and makes it possible to study in depth many of the gas hydrates properties and characteristics [4]-[6]. Undoubtedly, it is also important to consider morphological and geological peculiarities when engineering the gas hydrate deposits development [7], [8], and other types of minerals [9]-[12]. The gas hydrate crystals morphology is influenced by the temperature and pressure of hydrate formation, the composition of the water and gas phases, as well as the velocity of water and gas diffusion to the crystal growth surface. Therefore, an actual scientific direction is to determine the new patterns in the research of the natural gas hydrates morphology depending on the phase state and composition of the water-gas mixture.

The problem of rational use of the existing potential of hydrocarbon gases, in particular methane, remains relevant for coal, oil and gas, as well as for petrochemical industries [13]-[15] and can be successfully solved by applying gas hydrate technologies. This is particularly true for the transportation and storage technologies of natural gas resources [16], [17], coalmine methane [18], methane of drainage boreholes [19], gas of marginal field and marine fields [20] and oil-associated gas [21]. Extraction of additional mineral raw materials, when processing ash from coal enterprises, is also of great interest [22].

The gas hydrate method of storage and transportation of various hydrocarbon gases, for example carbon dioxide, is also considered as a prospect for existing methods (for example, liquefaction) [23]-[25]. The undoubted advantage of obtaining this kind of energy source is the absence of negative impact on the environment, in particular waste accumulation, as in the development of most mineral deposits [26]-[29].

The gas hydrate technologies application is directly related, first of all, to the search for both optimal technologies for the gas hydrate deposits development [30]-[32] and the production of gas hydrates to use them when transporting the raw hydrocarbons [33]. The hydrate formation process, which is the key one, requires intensive binding of significant gas volumes into the gas-hydrate form. Its efficiency determines the economic performance of the technology and the quality of the final product.

Thus, the relevance of this work is to create reliable methods for predicting hydrate formation processes, which requires a detailed research into the thermobaric conditions.

2. LITERATURE REVIEW AND PROBLEM FORMULATION

Gas hydrates are molecular unstable compounds belonging to the class of non-stoichiometric clathrate compounds, for which it is very difficult to determine their structure and practical gas content. The conducted experimental studies reveal that the developed methodologies are suitable for the artificial production of various structural and morphological gas-hydrate types [34]. However, at this stage of the science development, there is no a perfect mechanism for producing gas hydrates from liquid phases of various compositions, as well as from dispersed media containing finely ground and monolithic ice pieces > 2 cm in size.

In the work [35], an attempt is made to experimentally study the behaviour of certain gas hydrates (methane, propane, and carbon dioxide) at temperatures below 273 K and pressures below the “ice - hydrate - gas” equilibrium pressure. In these conditions, ice is the stable phase. It is assumed that the supercooled (metastable) water, resulting from the hydrates dissociation, is an intermediate product. As evidence, the authors measure the hydrates dissociation pressure onto supercooled water and gas in the temperature range of 253-273 K for methane hydrates, 263-273 K for propane hydrates and 249-273 K for hydrates of CO_2. As a result of this work, it has been determined that in the thermobaric area, hydrates can exist for a long time in a metastable state. However, this occurs only in the area bounded on the phase diagram by the lines of equilibrium “ice - hydrate - gas” and metastable equilibrium “supercooled water - hydrate - gas”.

It is known, that the process of gas hydrates formation is in the formation of a new phase (solid). This is uncontrolled processes proceeding, at which the new state of the system under the changed conditions should be more stable and has a lower energy reserve [36]. As in most disperse processes, the formation of interphase surfaces and associated surface phenomena is conditioned by the excess surface energy [37], [38]. This is due to the fact that the molecules of the gaseous phase (methane) are in the interface surface and have an excess energy in comparison with the molecules in the volume because of their uncompensated intermolecular interactions. The emerging uncompensated state of intermolecular interactions is caused by the difference in the composition and structure of the contacting phases, and this leads to the occurrence of surface forces and an excess of energy – surface energy, on the interface surface.

The higher the molecular weight of a gas or gas mixture, the lower the pressure required to form a hydrate at a constant temperature. The presence of acid gases in the mixture increases the risk of hydrate formation process. Hydrate formation occurs at the “gas - water” boundary when the natural (associated) gas is totally saturated with moisture [39].

Hydrates are actively formed in the volume of water with the presence of crystallization centres [40]. Dissolved gas is partially converted into hydrate. For active hydrate formation, it is necessary that water vapour is condensed on the pipe wall or on paraffin deposits in the form of a drop or film. The hydrate formation mechanism includes the stages of crystallizing nucleus formation and the sorption growth of crystalline hydrate around the nuclei. The nucleus occurs on the surface of the “gas - water” contact. Hydrate can further grow both in the volume of gas and in the volume of water.

The maximum gas molecules number is at the surface of the aqueous phase, that is, in the area of “water – gas” contact. Thus, in the place of a contact there is a transition layer in which water and gas are in a supersaturated state. Here, the nuclei are formed at certain pressure and temperature, caused by the fixation of the water and gas molecules position in the dodecahedron. The hydrate formation process occurs until complete covering the free water surface. Hydrates are formed on the surface from the concentrated film water [41].

It has been studied the gas hydrates formation peculiarities influenced by mechanochemical activation of samples with varying degrees of grinding to increase the contact surface area of heterogeneous phases [42]. In the course of research, it has been found that the formation of gas hydrates on activated aluminum silicates leads to the cryochemical synthesis of hydrocarbons. This is caused by the formation of additional reaction centres created during activation. This indicates a change in the mechanism of formation, as well as acceleration of the gas hydrates formation. The effect of mechanical activation is also often used to intensify the hardening of binding substances [43], [44].

Theoretical research on the phase state and properties of gas hydrates are presented in the work [45], as well as the phase diagrams are described, which were obtained as a result of using mathematical modelling. The molecular dynamics method is the basis for calculations by the Monte Carlo method and also includes the energy characteristics calculation on the Lennard-Johnes and Coulomb potentials. The authors considered various water models and determined the boundaries of the phase equilibrium of methane gas hydrates. This method almost always gives overestimated results, and in this case, for the TIP4P/Ice water model, overestimated values of the phase equilibrium boundaries have been obtained. However, for the rest, these data have been underestimated. For the curve of melting, the accuracy of the description is 20 K.

The authors have analysed the modern atomistic models accuracy for water, which is the basis for the gas hydrates formation. The calculation error is the following data: in pressure, tenths of GPa, and in temperature, several tens of degrees.

Gas hydrates and molecular dynamics methods have been of great interest for a long time, since these methods make it possible to study the matter nanoscale level, namely, the dynamics of the gas hydrates formation. The field of mechanical and thermodynamic gas hydrates properties have been studied. The experiments are made in a wide range of temperatures and pressures for various gas hydrates compositions [46], [47]. All this helps to gain knowledge about the processes of crystalline hydrate formation and gas hydrate production.

Thus, the results of basic research on the dynamics of the gas hydrates formation mechanism can significantly influence on the technological and economic appeal of storing natural gas in gas hydrate form. The hydrate formation mechanism is not thoroughly studied due to difficulties of experimental nature. However, it is necessary to study the gas hydrates formation dynamics for improving modern technologies of recovery and transportation of gas from both gas and gas hydrate deposits, as well as to create energy-saving technologies, develop hydrocarbon energy and gas mixture separation technologies.

3. PURPOSE AND OBJECTIVES OF RESEARCH

The research purpose is to study the thermobaric process of the gas hydrates formation and their dissociation with the presence of organized media (surfactants, SAA) both theoretically and practically.

The following tasks are set to achieve the purpose:

- apply the molecular dynamics method to the process of gas hydrates formation in the presence of a surfactant;
- experimentally determine the dependence of the artificial methane gas hydrates formation on pressure and temperature in the presence of organized media.

4. RESEARCH METHODOLOGY

When performing the experimental part of research, the following surfactants are used as organized media:

- dibutylphenol treated with ethylene oxide;
- ethoxylated alcohols (a mixture of polyethylene glycol ethers with a different amount of oxyethyl groups and the radical value – DS-10, DS-20).

The micelle formation in surfactant solutions is studied in the concentration range from 10^{-4} to 10^{-2} mol/l (0.07, 0.10, 0.15, 0.25, 2.5, and 5.0% by weight).

The stalagmometric method with automatic photoelectron drops counting (measurement error 0.1%) is used. To determine the critical concentration of micelle formation (CMC), a conductometric method is used (conductivity meter No. 5721, Wroclaw: ElVRO). The electrical conductivity is measured with a Wheatstone bridge (measurement error 0.05-0.1%).

Interphase electric potential is measured by the potentiometric method using the PPTV1 potentiometer.

Based on the data obtained, the dependency graphs $\sigma = f(\lg C)$ have been plotted, the CMC value has been determined by the intersection of two lines.

Each solution is tested 7 times and the average value is determined.

Research into the gas hydrates formation mechanism using the surfactants has been performed by the authors by the setup, constructed in the laboratory of innovative technologies Dnipro University of Technology (Ukraine), according to the methodology described in the works [42], [48], [49].

The rate of methane hydrate formation is determined by the kinetic method from the initial rate of the ice crust formation, and then the amount of methane per unit volume (C_m) is determined at different surfactant contents.

To determine C_m, the following methodology has been developed:

a) After the process of obtaining gas hydrate (all water has reacted) is completed, the temperature is reduced in the climatic thermal chamber and, accordingly, in the hydrate formation reactor from 274 to 263-258°K. The process of hydrate formation in the reactor can be observed through a window in the chamber and reactor.

b) The valves on the gas cylinder and on the reducer are being blocked.

c) The high-pressure hose should be disconnected from the reducer and connected to the gas meter.

d) The reactor valve is turned and the temperature is raised to room temperature in the chamber and in the reactor.

e) Methane hydrate begins to decompose. The methane evolved passes through the gas meter and its amount is measured.

If to know the amount of the methane evolved and the volume of water poured into the reactor, the value of C_m can be determined. Then the gas pressure in the reactor is reduced by 1 MPa and the calculations should be repeated.

5. THE RESEARCH RESULTS OF THE GAS HYDRATES FORMATION DYNAMICS USING THE SURFACTANTS

To accelerate the gas hydrate formation process from 274 to 285°K and at normal pressure, non-ionic surfactants are added to the water in an amount from 10^{-4}

to 10^{-2} mol/l. When using such additives, a surface tension decreases at the phase interface and the interphase surface is concentrated.

As previous studies have revealed [42], the measurement of surface tension makes it possible to determine the critical concentration of surfactant micelle formation. Based on the surface tension parameters of DB, DS-10, and DS-20 aqueous solutions, isotherms have been plotted (Figure-1), according to which the CMC value is calculated.

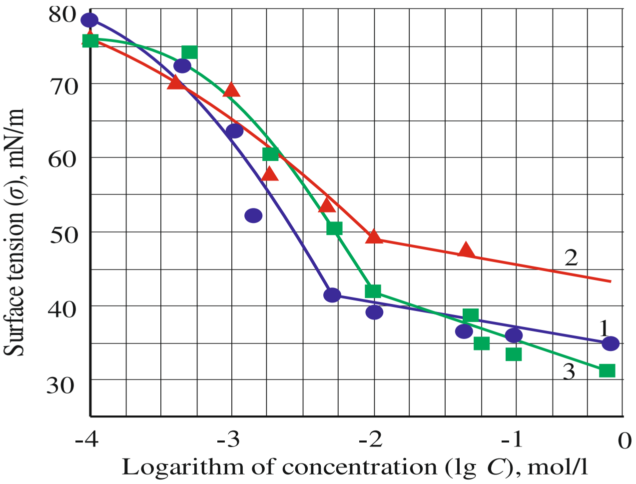

Figure-1. Surface tension isotherm in logarithmic coordinates: determining the critical concentration of micelle formation using the method of surface tension measurement: 1 - DS-10; 2 - DS-20; 3 - DB.

It has been found that with an increase in the surfactants concentration, qualitative changes occur in the system: changeover from macroheterogeneous to microheterogeneous colloidal dispersion (micelle formation process). This change leads to a change in the physical-chemical properties of the system, which is accompanied by arising the characteristic kinks in the dependency curves of some parameters on the surfactants concentration.

The study of the interphase boundary during the hydrate formation reaction is of great interest. For this purpose, research has been conducted for determining the surfactants influence on the change in interphase electric potential at the "liquid - gas" phase interface. In this regard, computational-theoretical research has been conducted, which consist of several stages.

The first task is to study the gas hydrates formation dynamics by the molecular dynamics method. As a rule, the Monte Carlo method or molecular dynamics method with quantum-mechanical computations is used to determine the energy dependence of any process.

For computer experiments, one-dimensional, two-dimensional, and three-dimensional models of dozens of atoms are compiled. Mass, initial coordinates, and type of potential (U_N), describing the interaction of N particles in a solid are specified for each model. This potential is assumed to be a function X_1..., X_i..., X_N, where X_i - a sequence of numbers describing the activated centre position and the orientation of the i-th atom. The U_N approximation by the sum of pair interactions potential energies is sufficiently substantiated:

$$U_N\left(X_1...X_N\right) = \sum_{i<j}\sum U_{ij}\left(X_i, X_j\right). \qquad (1)$$

The forms and parameters of the potential U_{ij} may be different. The simplest and the most convenient are the Lennard-Johnes potentials:

$$U_i\left(r\right) = Ar^{-n} - Br^{-m}, \qquad (2)$$

where A and B – characteristic substance constants; n and m – whole numbers, with $n > m$.

The first term is the repulsion energy and the second term is the attraction energy. The force acting between the particles being crushed in the active surface layer is equal to:

$$U = \frac{dU_i\left(r\right)}{dr} = nAr^{-(n+1)} - mBr^{-(m+1)}, \qquad (3)$$

and becomes zero when the distance between particles becomes equal r_e. In this case, the potential energy is minimal and is equal to $U_i(r_e)$. Excluding A and B, it can be written:

$$U_i\left(r\right) = U_i\left(r_e\right)\frac{1}{m-n}\left[m\left(\frac{r_e}{r}\right)^n - n\left(\left(\frac{r_e}{r}\right)^m\right)\right]. \qquad (4)$$

In the case of polyatomic particles, expressions for determining energy are much more complicated, because orientation should be considered.
One of the simplest and best-case is the potential:

$$U\left(X_i, Y_j\right) = U_i\left(r_{ij}\right) + S\left(r_{ij}\right)U_{EL}\left(X_i, Y_j\right), \qquad (5)$$

where U_{EL} - the interaction potential of two charge massifs (reflecting the distribution of charges in the active layer).

The experimental data on thermodynamics (adsorption potentials) and calculation by the Monte Carlo method make possible to suggest a simple correlation connecting the specific dimensionless energy of gas hydrate formation with the number of monomeric particles in the surface cluster:

$$\varepsilon_g = \frac{U_g}{g \cdot L} = 1 - g^{-\frac{1}{4}}, \qquad (6)$$

where ε_g - the ratio of the adsorption potential formation to the potential calculated according to Lennard-Johnes; L - activated layer thickness, g - the number of active particles connected into a cluster.

Figure-2 shows a computational-theoretical graphical interpretation of equation (6), that is, the dependence of the thermodynamic characteristics of the methane gas hydrate formation at relatively small cluster sizes is presented: ε - this is a ratio of the heat of methane gas hydrate formation to the heat of ice vaporization from n - the number of "guest" molecules in the cluster (in dimensionless units).

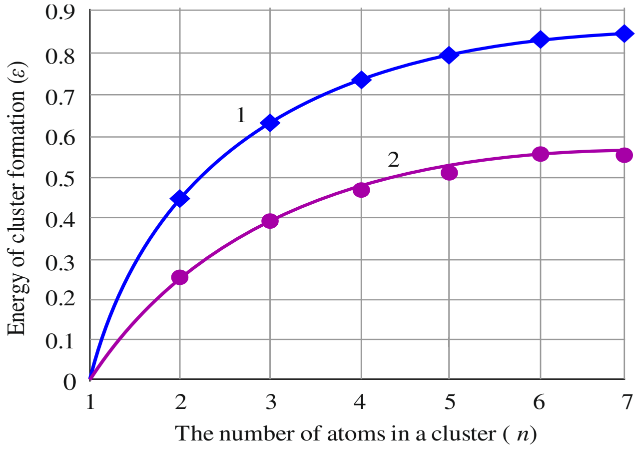

Figure-2. Thermodynamic characteristics of cluster structures: dependence of a ratio (ε) of cluster formation energy on the number of atoms in a cluster (n): 1 - experimental; 2 - theoretical.

Figure-2 shows that the proposed correlation presents a flatter curve (line 2) than experimentally obtained one (line 1). This is conditioned by the fact that the process of gas hydrate formation proceeds, on the one hand, with increasing the number of particles (methane), and, on the other hand, with combining these particles into clusters with the formation of a new phase and a change in the "host" (water) cavities sizes. Thus, the gas hydrates formation dynamics reaches a limiting value, after which the growth occurs slightly, which is caused by a decrease in the temperature and the heat of phase transition, which leads to a change in the gas hydrate structure. Theoretical results have found that phase transition temperatures for a cluster of 16 methane molecules decrease by 67%, and for a cluster of 55 methane molecules - by 50%.

To perform the second task, the thermobaric conditions, similar to natural ones, are simulated. The obtained samples of artificial gas hydrates are studied in order to quickly obtain methane hydrate under mild conditions at temperatures from 274 to 285°K and a pressure of less than 7 MPa.

The hydrates formation begins with an ice film on the water surface. When shaking the reactor, the film is destroyed and a new one is formed in the same place, then they are superimposed over each other, forming a gas hydrate lump. This process occurs until all the water has reacted with the gas. To accelerate the gas hydrate formation process in the reactor, surfactants are added to water in an amount of 0.01 to 0.1% of the water volume.

To determine the thermobaric dependence, the processes of methane gas hydrates formation without additives, as well as in the presence of surfactants have been studied. Figure-3 presents the thermobaric curves of the hydrate formation process obtained during the cryoprocess without adding the surfactants and with them.

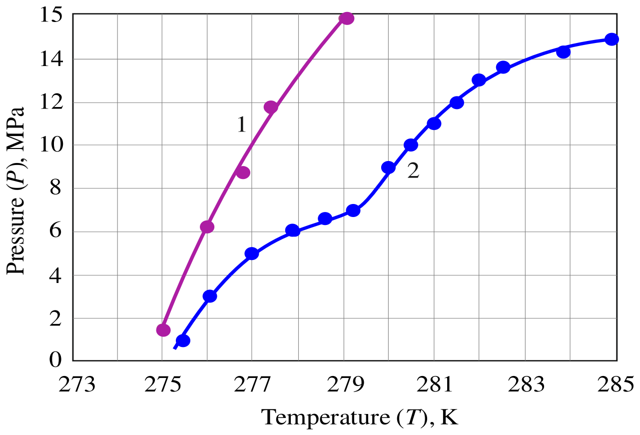

Figure-3. Thermobaric parameters for obtaining methane gas hydrates: 1- by adding the surfactant; 2- without adding the surfactant.

The thermobaric curve for methane hydrates without surfactants, as can be seen from Figure-3 (curve 2), has an inflection point in the temperature range of 279.0-279.5°K and consists of two identical curves. This proves that during the gas hydrate formation, the processes related to structure formation occur, that is, changeover from one structure to another. Thus, a changeover is observed of methane gas hydrate from the KS-I structure to the KS-II structure with various degrees of filling the cavities: from 275.0 to 279.2 K - small cavities, and above - larger ones.

The peculiarity of the methane gas hydrate formation in the presence of organized media (surfactants, SAA) is that, on the one hand, the reaction proceeds according to the solubilization mechanism. On the other hand, water is structured and large cavities are formed in the lattice, due to which the methane content in gas hydrate increases. This is facilitated by the formation of intramolecular salt bridges and hydrogen bonds, leading to the compact structures formation and the crystal lattice cavities expansion. The thermobaric curve of hydrate formation in the presence of a surfactant (Figure-3, curve 1) indicates that there is no inflection from 274 to 279 K. The cavities in the lattice are initially larger than during the study of the methane hydrate formation without adding a surfactant.

Experimental data testify that the gas hydrate formation begins in 5-10 minutes after the pressure is supplied to the reactor. Methane gas hydrate is formed by laminating one ice layer over another, which can clearly be observed visually [42], [45]. This process occurs until all the water has reacted with the gas.

At the same time, a necessity arises to determine the amount of methane per unit volume of gas hydrate (more than C_m) not approximately, but accurately, as well as determine the dependence of C_m on pressure and temperature of its formation. If to know the amount of gas evolved and the volume of water poured into the reactor, the value C_m can be determined.

Then the gas pressure in the reactor is reduced by 1 MPa, and everything is repeated. The studies of C_m are conducted in the pressure range from 18 to 4 MPa and a temperature of 274 K. At the same time, the hydrate formation process is monitored.

It has been found experimentally that the formation and dissociation of methane gas hydrates at pressures less than 4 MPa is problematic, because it occurs in metastable areas of gas hydrate existence. This complicates the process of its production and determining the methane volume.

When studying the thermobaric peculiarities of the gas hydrates formation at 274 K, the following assumptions have been made:

- the hydrate formation reaction or the limiting stage of the process is monomolecular;
- the first occurrence of a hydrate formation crystal is determined visually.

The methane gas hydrate formation, as indicated above, begins in 5-10 minutes after the pressure is supplied to the reactor. The time of occurrence of the first methane gas hydrate crystals depends on the gas pressure and temperature. It also has a transition point, which indicates to the structural changes occurring in gas hydrate. The higher the pressure, the faster the process begins, the higher the temperature, the process slows down by 5-10% for each degree (as theoretical calculations testified).

To accelerate the gas hydrate formation process from 274 to 285°K and at normal pressure, non-ionic surfactants have been added to the water in an amount from 10^{-4} to 10^{-2} mol/l. It has been revealed that when using such additives, a decrease occurs in surface tension at the phase interface and concentration of the interphase surface. The surfactants influence on the hydrate formation process was studied, as a result of which it has been found that the gas hydrates formation occurs by two mechanisms:

- as a result of the inverse microgas emulsions formation. Such microgas emulsions, according to Plato, occur during hydrate formation of the "methane + surfactant + water" system;
- as a result of the surfactants influence on the crystallization process.

Figure-4 presents the dependences of the gaseous methane content in a cluster on the temperature under the dissociation of gas hydrate samples, formed by adding and without adding surfactants.

The obtained dependences evidence that the methane content in gas hydrate is being increased, that is, in the presence of a surfactant, methane gas hydrate contains a greater amount of methane. This is conditioned by the presence of hydrophobic groups, which, due to the formation of intramolecular salt bridges and hydrogen bonds, on the one hand, lead to the formation of compact structures, and, on the other hand, to increased dimensions of the "host" cavity, caused by the structuring effect in the presence of organized media.

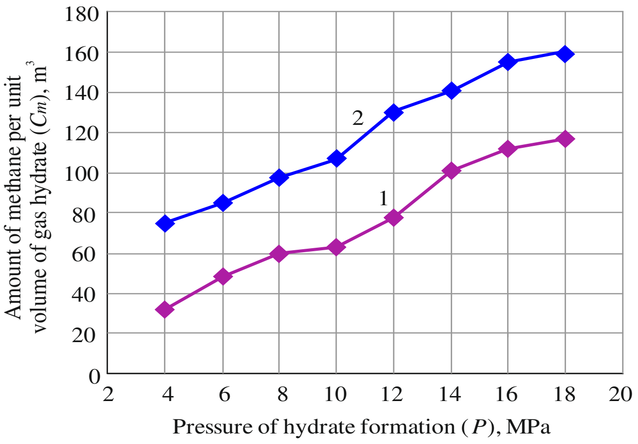

Figure-4. Dependences of the gaseous methane content per unit volume of methane hydrate under dissociation: 1 - sample obtained without adding the surfactant; 2 - sample obtained by adding the surfactant.

Thus, the process of gas hydrates formation from supercooled water occurs due to surfactants and indicates the new structures formation between the "guest" and the "host". If to compare the energy profiles of this process hypothetical paths, it becomes obvious that the changeover from initial to final bonds (with chemical additives) does not occur as a single act with a high energy barrier, but in avalanche manner (stepwise), with the gradual replacement of old bonds with new ones. The path of such a reaction is longer, but more smooth. It has the changes of cavities in the clathrate without transition point, that is, there is a gradual change in the coordination number of reacting surface atoms.

Based on the obtained experimental data, it can be concluded that the mechanism of methane gas hydrates formation in the presence of organized media (surfactants, SAA) passes through the solubilization mechanism, followed by micellar catalysis, which leads to a change in the cavities structures in the clusters with the simultaneous compact structures formation.

The influence of organized media on the methane gas hydrate formation process is as follows:

1 stage - localization, as a result of favourable concentration in the micelle of all three components "methane + surfactant + water". This stage increases the frequency of interaction (collisions) between the reagents;

2 stage - the field medium influence, which leads to mycelial catalysis, under which the reaction proceeds faster.

6. CONCLUSIONS

a) It has been revealed that the process of gas hydrate formation proceeds both by increasing the number of particles (methane), and by combining these particles into clusters with the formation of a new phase and a change in the "host" (water) cavities sizes. The gas hydrates formation dynamics reaches a limiting value, after which the growth occurs slightly. This is caused by a decrease in the temperature and heat of the phase transition, which leads to a change in the gas hydrate structure. Theoretical results have shown that the temperatures of phase transitions for a cluster of 16 methane molecules decrease by 67%, and for a cluster of 55 methane molecules - by 50%.

b) The processes of methane gas hydrates formation without additives, as well as in the presence of organized media, such as surface-active agents (surfactants), have been studied. It has been determined that the thermobaric curve for methane hydrates without surfactants has an inflection point in the temperature range of 279.0-279.5°K and consists of two identical curves. This is conditioned by the changeover from one gas hydrate (KS-I) structure to another (KS-II). On the contrary, adding of a surfactant leads to water structuring and immediate formation of large cavities in the gas hydrate crystal lattice, due to which the methane content in the hydrate increases.

c) The dependences have been determined of the gaseous methane amount contained in the cluster upon the temperature under the dissociation of obtained gas hydrate samples, formed by adding and without adding surfactants. Thus, in the presence of a surfactant, methane gas hydrate contains a greater amount of gas. This is conditioned by the presence of hydrophobic groups, which, due to the formation of intramolecular salt bridges and hydrogen bonds, on the one hand, lead to the formation of compact structures, and, on the other hand, to cavities expansion. The amount of methane in a unit volume of gas hydrate obtained without adding the surfactant at a maximum pressure of 18 MPa is 120 m^3; by adding the surfactant with the same thermobaric parameters is 160 m^3.

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