Intensifying the process of methane gas hydrates crystallization in the presence of surface-activated substances

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Abstract. The crystallization process of gas hydrates during their formation in the presence of surface-active substances (SAS) is studied. The research is conducted in two directions – theoretical and experimental. Experimental data on the crystallization rate of methane gas hydrates formation in the presence of surfactants have been obtained: high-molecular compounds are used on the basis of polymeric quaternary ammonium salts containing side aliphatic radicals of various lengths in the acyl fragment, as well as a number of specific surfactants. The process of methane gas hydrates formation is performed using a laboratory setup of the NPO modification for the gas hydrates creation. To analyse the experimental data, technical and metrological instruments are used: stalagmometric method with automatic photoelectric drop counting, conductometric method, Wheatstone bridge, spectrophotometric titration of amino end-groups, viscometer VPZh-1. It has been substantiated that the crystal formation rate depends on the surfactant concentration. New experimental dependences of the gas hydrates formation on surfactants under thermobaric conditions in the presence of surfactants have been found. It has been revealed that the crystallization process during the methane gas hydrates formation is accelerated in the presence of a surfactant. As a result of their application, the effect of solubilization and catalysis arises with the formation of the so-called “diffusion zone”, the size of which decreases in the presence of surfactants, thereby accelerating the substance transfer to the surface on which crystallization occurs. An increase in the surfactant concentration leads to an increase in the rate of molecular diffusion, and also creates a more intense turbulent diffusion.

1 Introduction

Gas hydrates are solid nonstoichiometric compounds (of variable composition) of the cell type – clathrates (Latin clathratus (clatratus), meaning “with bars, latticed”). For the first time compounds of this type were obtained by Davy in 1811, when saturating water with

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chlorine at $T = 0^\circ C$, this compound was chlorine hydrate (Cl$_2$·5.75 H$_2$O). In 1948 Powell named such compounds “clathrates”.

Clathrate compounds (Fig. 1) in general form are described by the formula $M \cdot n$ H$_2$O ($n \geq 5.67$), where $M$ – gas molecule, $n$ – water molecules number [1].

**Fig. 1.** Gas hydrate structure.

Gas hydrates are formed by including gas molecules (easily volatile liquids) in the cavity of the scaffold (crystal lattice) constructed of H$_2$O molecules under thermodynamic conditions specific for each gas component. In case of their violation, the molecules of “guests”, that is gases retained in the skeletal water scaffold by weak Van der Waals forces leave it, and the hydrate decomposes into gas and fresh water with significant heat absorption [2].

Since gas hydrates belong to the class of nonstoichiometric clathrate compounds and are molecular crystals, research into crystal hydrates morphology is of great importance and gives an ability to study in depth many properties and characteristics of gas hydrates [3, 4]. Undoubtedly, it is important to take into account morphological and geological peculiarities when planning the development of various types of mineral deposits [5, 6]. The morphology of gas hydrate crystals is influenced by the temperature and pressure of hydrate formation, the composition of the water and gas phases, and the rate of water and gas diffusion to the surface of crystal growth. Therefore, the determination of new patterns in the study of the natural gas hydrates morphology depending on the phase state and the water-gas mixture composition is an urgent scientific direction.

The volumes of fuel in gas hydrate form are approximately equal to $2 \cdot 10^{16}$ m$^3$, which significantly exceeds the amount of raw hydrocarbons in all its other types on the Earth [7, 8]. The interest in non-traditional ways of development and production of various energy sources in recent years is directly related to the annual increase in the consumption of fuel and energy resources, as well as their reserves depletion. For this very reason, the intensification of geological exploration work for all types of energy feedstock is undoubtedly relevant both for Ukraine and many other countries around the world [9, 10]. An alternative way for obtaining especially valuable synthesis gas is the technology of underground gasification of coal [11-13], processing of biomass and industrial waste [14]. These technologies are an integral part of the additional energy sources diversification, which is of great importance for Ukraine. The production of additional mineral raw materials during the refinery of ash from coal enterprises [15] and proton-exchange membranes of fuel elements made from natural fillers is also of interest [16].

Gas hydrates are formed at low temperatures and high pressures, provided that there is a sufficient amount of hydrate-forming gas and water. The thickness of the gas hydrate reservoirs ranges from hundreds of meters to 1 km or more, which is typical for great depths. Currently, three main gas hydrate fields – in Japan, Canada and Russia – are suitable for commercial development. Methods for recovering gas from gas hydrate
Accumulations are based on the use of dissociation – a process during which a substance, in this case the gas hydrate, disintegrates into simpler components [17].

The search and assessment of unconventional hydrocarbon deposits is one of the alternative options for increasing energy capacity. The coal industry of Ukraine, which provides for the extraction and primary processing of bituminous and lignite coal, is one of the main branches of the country's fuel industry. In Ukraine, most of the coal reserves are located in difficult mining-and-geological conditions: low thickness of coal seams, large mining depths, low rock stability, increased water saturation, high gas content of seams [18-20]. In this regard, it became necessary to create new strategies for the country's energy development. The methane reserves in coal seams and interlayers are about 8 trillion m³, while the share of this gas release into the atmosphere due to the highly intensive mining of seams saturated with methane is extremely high. The problem of rational use of the existing hydrocarbon gases potential, in particular methane, remains relevant for both coal and gas-and-oil producing and petrochemical industries. First of all, this relates to the technologies for transportation and storage of natural gas resources [21], coal mine methane [22], methane from methane drainage boreholes [23, 24], gas of marginal and offshore fields [25], and associated petroleum gas. Gas hydrate method of storage and transportation of various hydrocarbon gases, for example, carbon dioxide [26] is also considered as a prospect for existing methods (for example, liquefaction) [27, 28].

The use of gas hydrate technologies is directly related, first of all, to the search for both optimal technologies for the gas hydrate fields development [29, 30], and the gas hydrates production for their use in the transportation of raw hydrocarbons [31]. The hydrate formation process, which is the key one, requires intensive binding of significant gas volumes into gas hydrate form. Its efficiency determines the economic performance of technology and the final product quality. Thus, the relevance of this work is to develop reliable methods for predicting the processes of gas hydrates formation, which requires a detailed thermobaric conditions study.

2 Literature review and problem formulation

The gas hydrates formation process involves a new phase (solid) formation. 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. The formation of interphase surfaces and associated surface phenomena is conditioned by the excessive surface energy. This is due to the fact that the molecules of the gaseous phase (methane) are in the interphase 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 interphase surface [32].

The hydrates nucleation always occurs on the free surface of the “gas – water” contact. In a solution that is insufficiently saturated with gas, the hydrate formation process cannot begin. However, in the case of the crystallization centres formation (on the surface of microbubbles or on the surface of water condensate in the gas volume), the process of hydrate crystals growth can develop with the formation of large hydrate accumulations from a dissolved gas in an undersaturated solution. In the sedimentary rock cover, gas reservoirs are formed only from free gas released from a supersaturated solution with a change in pressure and temperature. Gas hydrate reservoirs can occur and exist stably even under conditions of dissolved gas deficiency in formation waters. It is this property of water (the formation of gas hydrate under conditions of a dissolved gas deficiency in water) that ensures the preservation of free gas huge resources on the Earth in the water space of the World Ocean.
In the work [33], which studies the process of hydrate formation, it has been revealed that frozen “dry water” containing no more than 5 mass % silicon dioxide, is a solid frozen mass with a small admixture of bulking material in the form of a white powder, consisting mainly of ice particles. With an increase in the silicon dioxide concentration of above 5 mass %, the proportion of the bulking fraction in the frozen “dry water” sample increases and reaches 1 at a silicon dioxide concentration of 15 mass %. It is proven that the time of half-transformation of ice into hydrate decreases when the content of silicon dioxide nanoparticles increases in it. Thus, with an increase in the silicon dioxide content from 3-5 to 15 mass %, the half-transformation time decreases by more than 7-15 times, depending on the type of silicon dioxide used to obtain “dry water”. It has been determined that for the crushed ice obtained by crushing ordinary ice with the addition of silicon dioxide nanoparticles, the half-transformation time of ice into natural gas hydrate is reduced by an order of magnitude as compared to ice crushed without such an additive. It is indicated that under the same conditions for water dispersion and ice crushing, the half-transformation time is several times shorter in crushed ice than in frozen “dry water” with the stabilizer nanoparticles content in the studied samples of 5 mass %. With a stabilizer content of 10 mass %, the half-transformation time in frozen “dry water” will be shorter. It has been revealed that the silicon dioxide type used in ice crushing affects the rate of hydrate formation in the resulting crushed ice. Thus, the half-transformation time for crushed ice stabilized with H18 (specific surface area 200 m²/g) is by 3 times less than for crushed ice stabilized with aerosil (specific surface area 100 m²/g), with the same stabilizer content (5 mass %) [33].

Scientists from India are currently working on the problem of accelerating the hydrate formation process. They propose to use surfactants for accelerating the hydrate nucleation process, provide more active heat transfer and increase the water and gas contact surface [34]. Scientists from Iran study the effect of using copper oxide nanoparticles to increase the volume of gas absorbed by water, for better water conversion into a hydrated state and an increase in the kinetics of the hydrate formation process [35].

For several years, scientists from the USA have been working on the development of a technology for spraying water through the gas phase to increase the contact area of the hydrogen and gas phases, which leads to an acceleration of the hydrate formation process, especially when using “dry water” [36].

The work [37] describes the kinetic curves of methane hydrate formation in distilled water and water containing inhibitors (the concentration of salts is up to 5 mass %). Based on the traditional concepts of formal kinetics, a mechanism is proposed for the process, which includes the stages of gas dissolution, the formation of a metastable hydrate cluster, and the growth of a gas hydrate particle. The potential reversibility of each process stage is taken into account, and a general kinetic equation is proposed. The pressure of the hydrate forming gas is not maintained during the process. The methane absorption rate is calculated from the pressure drop in the experimental cell.

In this work, the peculiarities of gas hydrates formation influenced by mechanochemical activation of samples with varying degree of grinding to increase the contact surface area of heterogeneous phases are studied [38]. In the course of research, it has been found that the formation of gas hydrates on activated aluminium silicates leads to cryochemical synthesis of hydrocarbons caused by additional reaction centres formed 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 [39].

The transportation and use of gas hydrates includes three stages: hydrate creation; transportation proper; release of gas during its decomposition. The first stage involves mixing of gas with water under the necessary conditions. One serious problem is the low hydrate formation rate, inhibiting the industrial application of the method. Surfactants and hydrotropic
substances are often used to solve this problem [40], which makes it possible to reveal finer points of the mechanism of the hydrate formation process and its kinetics. However, when adding surfactants, a side effect is often observed that leads to a decrease in the methane hydrate stability. As indicated in the work [41], this can be avoided by adding a mixture of sodium dodecyl sulphate, xanthan, or starch. Thus, the results of fundamental research into the mechanism of gas hydrates formation, as well as data on the effect of chemical additives and surfactants on the rate of hydrate formation, can significantly influence on the technological and economic attractiveness of storing natural gas in gas hydrate form.

A new direction in the gas hydrates formation is their production in the presence of polyelectrolytes and surface-active substances (SAS) [42]. Polyelectrolytes are widely used in various branches of technology as flocculants and coagulates of dispersed systems, for example, for clearing exhaust and turbid water, for structuring soils from radioactive elements [43], as well as for stabilizing colloids, in particular emulsions and foams, which is especially important in obtaining gas hydrates. Moreover, it is known that polyelectrolytes affect the hydrodynamic properties of ecosystems.

3 Purpose and objectives of research

The purpose of the research is to determine the influence of surfactants on the gas hydrates crystallization process.

To achieve this purpose, the objective is set to experimentally study the influence of surfactants on the mechanism of artificial gas hydrates formation with different content of a “guest” depending on the rate of hydrates crystallization.

4 Materials and research methods

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

– dibutylphenol treated with ethylene oxide;
– oxyethylated alcohols (a mixture of polyethylene glycol ethers with different amounts of oxyethyl groups and the radical value).

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 mass). The stalagmometric method with automatic photoelectron drops counting (measurement error 0.1%) is used. To determine the critical concentration of micelle formation, a conductometric method is used (conductivity meter No. 5721, Wroclaw: EIVRO). 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.

The mechanism of gas hydrates formation with the use of surfactants is conducted on a setup constructed in the laboratory of innovative technologies Dnipro University of Technology (Ukraine). From 2009 to 2015, four modifications of the setup were built, in which thermobaric conditions similar to natural are simulated. The setup also makes possible to perform a research on the rapid production of methane hydrates under mild conditions at temperatures from 274 to 281°K and a pressure of less than 7 MPa [44, 45].

The setup consists of two blocks: experimental and cooling. A climatic chamber “ILKA” KTK-3000 (Germany) is used as a cooling block. It enables to maintain and regulate temperature and humidity. The chamber allows to conduct research in different temperature conditions and with different humidity. Structurally, four main parts can be distinguished in the climatic chamber: the working space, the automatic operating panel, the cooling unit and the steam generator. The working space is designed in the form of a cabinet with heat exchangers placed inside to ensure the modes of laboratory tests. The
chamber has a door with an observation window and an anti-freeze system. The chamber body is mounted on a rigid steel profile wheel frame. To prevent spontaneous movement of the chamber during operation, there are brake pads on the wheels.

The cooling unit is made on a removable mounting base inside the frame. Outside, the unit is covered with shells that provide free air access for cooling the refrigerating machine devices. Near the opening door of a chamber, namely, on its working space, an automatic operating panel is set, in which the main electrical equipment and automation elements are located. The experiments are conducted as follows: a special device for the gas hydrates formation is placed in the cooling chamber.

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

The volume of methane from a gas hydrate can be measured in two methods:

- the first, by measuring the volume of gas supplied to the reactor at high pressure, but this method is very difficult, since there are no counters that measure a small amount of passing gas at high pressure;
- the second, by measuring the volume of gas outgoing from the reactor when the hydrate decomposes; in this case, the pressure is low, which allows the use of domestic gas meter operating at a pressure of less than 1 MPa.

The method for determining \( C_m \) is described in detail in previous works [38, 46].

For structuring the medium during the hydrate formation process, the following compounds are used:

1. 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 interphase and the interphase surface energy is concentrated.

2. Use of high-molecular weight compounds and surfactants. When studying the kinetic peculiarities of the gas hydrates formation at 274 K, the following assumptions can be made:
   - the hydrate formation reaction or the limiting stage of the process is monomolecular;
   - the first occurrence of a hydrate formation crystal during crystallization.

5 The research results of the crystallization process during the gas hydrates formation in the presence of surfactants

As it is known [47], the hydration shell around ions and molecules and on the surface of crystals hinders crystallization, therefore, in the process of producing gas hydrates, crystallization will proceed at low rates. However, when using the surfactants, the effect of solubilization and micellar catalysis arises [38, 46] with the formation of the so-called “diffusion zone”, the presence of which without the use of a surfactant also reduces the rate of crystal growth, since the substance is transferred through this zone by means of slow molecular diffusion process.

When using surfactants, the dimensions of the “diffusion zone” decrease and the substance transfer to the surface on which crystallization occurs is accelerated. An increase in surfactant concentration leads to an increase in the rate of molecular diffusion, and also creates a more intense turbulent diffusion. In addition, with the use of surfactants, the solution viscosity changes and more favourable conditions are created for the elimination of the hydration shell and the reduction of the disjoining pressure of the intermediate layer.

The presence of a surfactant in the crystallizing solution can have a significant influence on the result of the crystallization process as a heterogeneous process. Surfactants, being adsorbed on the surface of crystals, can change the rates of formation and growth of crystals, both as a result of a change in the interphase surface energy, and as a result of
inhibition of the mass transfer process to the crystal surface, which is caused by additional resistance of the surfactant adsorption layer. Surfactants, being adsorbed selectively on the faces of crystals with different indices, cause a change in the crystal habit.

Finally, in real crystallization processes, surfactants can passivate active foreign solid impurities in the solution, which, in their absence, would serve as crystallization centres.

Most of the works studying the surfactants influence on the crystallization process are devoted to only one manifestation of their action – a change in the crystal habit in the presence of surfactants.

Taking into account the limited information on the influence of surfactant additives on the quality of crystals obtained by mass crystallization from aqueous solutions, a set of works have been conducted to identify new cases of the surfactants influence, as well as to search for patterns of this influence.

For this purpose, the following surfactants were used as research objects:

– monomeric: sulphonate, sulphanol, OKN azolate, “clarified Petrov contact”;
– polymeric: polyvinyl alcohol, polyglycerol phthalate ether, urea-formaldehyde resin, polyoxyacetylene sorbitly laurate, polyethylene glycol, gelatin, polyvinylamine, polyacrylimide and its derivatives – polymethacrylate hydrazide, polyvinylpyridolidone, polyvinylaminopropyl carboxylic acid, polyacrylimide amino-derivative, polyacrylimide sulfo-derivative, novolac resin, VRS resin, polyvinyl acetate pyridinium, Pluronic T-707, Pluronic F-168, sodium polyphosphate, sodium hexametaphosphate, sodium tripolyphosphate, Sterox CD, Renex 25.

Crystallized substances are selected so that it is possible to check the links between the degree of surfactant action and the properties of crystallized substances. The following substances, such as ammonium chloride, potassium chloride, potassium fluoride, potassium bromide, potassium iodide, potassium sulphate, are taken as the object of research for crystallization. The hydrodynamic properties of polyelectrolytes are largely determined by the intra- and intermolecular electrostatic interaction of the charged sections of the chain, which leads to the formation of stretched conformations.

On the other hand, the presence of hydrophobic groups, the possibility of the formation of intramolecular salt bridges and hydrogen bonds leads to the formation of compact structures. In general, the conformational state of a polyelectrolyte macromolecule is determined by the ratio of the forces of electrostatic and non-electrostatic interactions, which can be assessed by the intrinsic viscosity values. A sharp increase in the reduced viscosity in the area of low polymer concentrations does not allow determining the intrinsic viscosity by extrapolating to zero concentration. Therefore, the viscosimetric data are linearized in the coordinates of the Fuoss and Yuan-Dougherty-Steval equations. The values of intrinsic viscosities for fully ionized and fully non-ionized states are calculated by extrapolation to the zero abscissa.

Obviously, the ratio of these values will characterize the change in the volume of the macromolecular coil when the degree of polion dissociation changes from 0 to 1. All calculated parameters for aqueous and mixed solvents show that the intrinsic viscosity for a fully ionized polymer decreases significantly with lengthening of the side alkyl radicals. This is obviously caused by the hydrophobic interactions that stabilize the compact structure of the macromolecule. A decrease in the swelling parameter $\alpha$ is a consequence of this, as indicated in the work [48].

The value of the true intrinsic viscosity at an infinitely high ionic force of the solution is obtained by the isoionic dilution method. The constancy of the solution ionic force during the dilution process leads to obtaining a linear dependence of the reduced viscosity on the polymer concentration (Fig. 2). This enables to determine the intrinsic viscosity at a given ionic force of the solution, and using the Fuoss-Strauss equation, the intrinsic viscosity at infinite ionic force can be found.
Experimental data show that the hydrate formation begins in 5-10 minutes after the pressure is supplied to the reactor. Hydrate is formed by laminating one ice layer over another. This process occurs until all the water has reacted with the gas. 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. In addition, to accelerate the hydrate formation process, surfactants and high-molecular weight compounds (HMCs) are added in optimal concentrations to create organized media. In this case, the hydrodynamic characteristics of the process, in particular the viscosity, changes.

When studying the thermobaric characteristics in the organized media, the volume of methane per volume of water ($C_m$) is determined from the pressure and temperature of its formation by the amount of gas released and the volume of water poured into the reactor. $C_m$ is studied in the pressure range from 18.0 to 4.0 MPa and a temperature of 274 K. The hydrate formation begins in 5-10 minutes after the pressure is supplied to the reactor. This time depends on the gas pressure and temperature. 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, a magnetic field is created in the reactor and surfactants are added to water in an amount of 0.01 to 0.1% of the water volume.

The results of research into the gas hydrate decomposition are presented in Table 1.

**Table 1.** Experimental data on the determination of the “methane-water” ratio depending on the pressure.

| $P$, MPa | 4.0 | 6.0 | 8.0 | 10.0 | 12.0 | 14.0 | 16.0 | 18.0 |
|----------|-----|-----|-----|------|------|------|------|------|
| $C_m$, m$^3$/m$^3$ | 75  | 85  | 97  | 107  | 130  | 140  | 155  | 160  |

As a result, the following dependence has been obtained, shown in Fig. 3. Analysing the data obtained as a result of the studies performed with the use of a $1.75 \times 10^{-3}$ mol/l solution of dibutylphenol treated with ethylene oxide and an HMCs concentration of 0.01 kg/m$^3$, the following conclusions can be drawn:
– the methane hydrate formation at pressures less than 4.0 MPa is problematic and occurs in 100 or more hours;
– the dependence between $P$ and $C_m$ in the pressure range from 4.0 to 14.0 MPa is close to straight-line and is described by the equation: $y = 6.5298 x + 46.798$;
– in the presence of organized media, the crystallization process increases in direct proportion.

![Graph](https://via.placeholder.com/150)

**Fig. 3.** Dependence of the gas hydrate composition in the presence of organized media on pressure at $1.75 \times 10^{-3}$ mol/l of a dibutylphenol solution treated with ethylene oxide, and an HMCs concentration of 0.01 kg/m$^3$.

The obtained dependences, presented in Figs. 2 and 3, are characteristic of quasistationary equilibria. The direct proportional thermobaric dependence indicates that the hydrate formation process in the presence of organized media changes for a nonequilibrium surface on which an exothermic reaction takes place. In this case, the energy released in an elementary act does not have time to dissipate, and the surface is “overheated”. This leads to a sharp increase in the degree and rate of clustering.

This takes place when the hydrate formation process is catalysed by organized media. The reason for such an extensive reactional restructuring is not only that the reaction promotes an increase in the surface, but also that the surface clustering promotes a decrease in the cryoreaction activation energy.

Thus, “dissolution” or “gasification” of supercooled water occurs due to the surfactants or HMCs concentration and means the formation of new bonds, mainly hydrogen (nucleation). When comparing the energy curves of the hydrate formation process, it becomes obvious that the changeover from bonds in the initial components to the final ones (with chemical additives, that is organized media) must occur with an insurmountably high energy barrier. However, it occurs stepwise, with the gradual replacement of old bonds with new ones. The path of such a reaction is longer, but more smooth. There is a gradual decrease in the coordination number of reacting surface atoms. This explains the difference of the results obtained experimentally and theoretically (Fig. 3).

### 6 Conclusions

1. An experimental thermobaric dependence of the hydrate formation crystallization process has been obtained: with increasing pressure $P$ in the presence of a surfactant, the “gas-water” ratio in the gas hydrate increases in direct proportion.
2. In the presence of organized media, the crystallization rate during the methane hydrates formation is directly proportional to the dependence of the composition on the pressure in the system.

3. The crystallization process during the methane hydrates formation includes the opening of some chemical bonds and the formation of other hydrogen bonds (nucleation), which entails differences in energy consumed for the gas hydrate crystal formation. Therefore, due to the organized media, the surface clustering occurs, which reduces the activation barrier.

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