Methane hydrate self-preservation features in oil suspensions

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Abstract. Features of methane hydrate self-preservation in the dispersions prepared from water in oil emulsions from two deposits in East Siberia were studied. Under experimental conditions, substantial self-preservation of the hydrate is observed in the dispersion based on oil 1, while the effect is weakened in the dispersions based on oil 2. It is demonstrated that the observed difference is connected with the presence of Span 80 surfactant in water in oil 2 emulsion.

1. Introduction

The structure of gas hydrates is a framework composed of hydrogen-bonded water molecules with the polyhedral cavities of molecular size, in which the guest molecules are included [1]. Clathrate hydrates are interesting from the scientific and practical viewpoints. Due to the ability to accumulate large amounts of gas, they are considered as promising materials for the storage and transportation of such gases as hydrogen and methane (for example, see [2, 3]). The ability of gas hydrates to include guest molecules only of definite size into cavities of the framework found application for the separation of gas mixtures [4], utilization of carbon dioxide [5, 6] and its extraction from exhaust gases [7, 8]. Gas hydrate technologies for concentrating the diluted aqueous solutions are extensively developing (in fact, these are the technologies of water freshening/purification) [9], air conditioning systems involving hydrate suspension as the coolant are under development [10, 11]. It has been known for a long time that gas hydrates are the reason of plug formation in producing wells and field pipelines [12], so much effort is made in gas and oil industry to take measures against hydrate formation [13]. During the recent decade, special attention is given to the problems connected with the prevention of hydrate formation in oil production. The properties of hydrate in oil dispersions are under intense investigation [14-17]. At the same time, problems connected with self-preservation of methane hydrate obtained from oil emulsions remain only poorly studied yet. It was demonstrated previously [18, 19] that the joint deposits of hydrates and oil components may exist for a long time under the conditions of negative Celsius temperatures due to self-preservation. The phenomena may manifest themselves in the production and pipeline transportation of oil in the regions with cold climate, which makes the investigation of the phenomenon especially urgent for the conditions existing in Russia. In the present work we studied the new features of methane hydrate formation and decomposition that has undergone self-preservation in water/oil emulsions taking into account layer thickness and the presence or absence of surfactants during the preparation of the emulsion.
2. Experimental section

Table 1. Composition and properties of the crude oils used in this work.

| Property                          | O1=Mamontovskaya | O2=Snezhnaya |
|----------------------------------|------------------|--------------|
| content of asphaltenes, wt%      | 0.10             | 0.67         |
| content of paraffines, wt%       | 2.30             | 4.39         |
| content of resins, wt%           | 19.70            | 5.07         |
| content of saturates + aromatics, wt% | -               | 94.26        |
| pour point, °C                   | -43.0            | -10.4        |
| density, kg/m³                   | 0.858            | 0.835        |
| viscosity, mPa.s (20°C)          | 19.3             | 7.29         |

Figure 1. Scheme of an autoclave with 8 sample holders: a steel cup with a cover-obturator with two sealed thermocouples. 8 sample holders are attached to the obturator through the guide bolt. The pressure monitoring and recording system is also attached to the obturator.

Reagents used: methane (purity 99.98%), distilled water, two crude oils (table 1), surfactant Span 80 (Sigma-Aldrich). Emulsions of water in oil (50 mass %) were used in the work. The emulsions were prepared from weighted amounts of water and oil by stirring with a mixer (800 r.p.m.) for 20 min. The emulsion of water in oil O1 oil was prepared without using any additives. The emulsion of water in oil O2 decomposed rapidly, so it was stabilized by adding Span-80 surfactant (1 mass % of the amount of oil). Thus prepared emulsions were stable for a long time (several months). The kinetics of decomposition of methane hydrate that had undergone self-preservation was studied in autoclaves with 1 or 8 plate holders for emulsion samples; the amounts of emulsion were the same in both cases. A scheme of the autoclave with eight holders is shown in figure 1. The experiment proceeded as follows. Sample holders with the weighted portions of the emulsion under study (1 or 8 holders) were placed in a high-pressure cell (figure 1). The autoclave was washed with methane, then gas pressure was set at 125±5 bar at room temperature. After that, the autoclave was placed in a thermostat maintaining the temperature of 1°C, and kept until pressure stabilization, which is the evidence of the completion of hydrate formation (4-20 days, depending on the number of holders and the amount of emulsion under study). Decomposition was carried out in the same cell. After the completion of the synthesis, the autoclave, with methane hydrate formed in it, was cooled to the chosen experimental temperature (-5 – -20°C). After cell cooling, the pressure was released to the level close to the equilibrium for methane hydrate (about 20-25 bar, depending on chosen temperature) for maximal oil degassing in order to prevent sample from escaping out of the holder because of airing (foaming). Then pressure was sharply unloaded to 0.2-0.4 MPa, and then valve was closed immediately. Then, at the same temperature (-5 – -20°C), methane hydrate decomposition was followed by recording the dependence of pressure on time (for at least 300-400 minutes since the complete pressure release). Then the autoclave was heated at room temperature at a rate of (~3,3°C/hour), and the dependence of pressure on time was recorded.
To prepare the samples of hydrate suspension in O2 oil without surfactants, the powders of frozen hydrate and ground oil were mixed at the liquid nitrogen temperature, loaded into the autoclave at this temperature, then methane pressure was set in the autoclave, and the autoclave was heated to slightly positive temperature (the conditions of hydrate stability were maintained). Then the autoclave was again cooled to the temperature of liquid nitrogen, and the sample of suspension was taken out from the autoclave. Thus homogeneous samples of the suspensions of methane hydrate in oil were prepared successfully, with oil kinds in which stable water emulsions are not formed. X-ray studies of the samples of quenched methane hydrate obtained from water/oil emulsions were carried out using a Bruker D8 Advance powder diffractometer equipped with a low-temperature attachment TTK 450 AntonPaar. Thermovolumetric studies of the hydrates were carried out with a set-up assembled at the laboratory of clathrate compounds of the Institute of Inorganic Chemistry SB RAS. The principle circuit diagram and a detailed description were presented in [20].

3. Results and discussion

![Figure 2](image)

Figure 2. (a) Typical for the process of formation and decomposition of methane hydrate from oil emulsion temperature and pressure dependence on time; (b) Steps 5 and 6, reflecting the amount of methane hydrate decomposed during experiment.

Now the behavior of pressure and temperature during a typical experiment is to be considered (figure 2a). At stage (1), the autoclave is cooled to 1°C (temperature at which the hydrate is obtained), while pressure decreases due to methane dissolution in the emulsion and due to thermal compression of the gas phase. Stage (2) is characterized by a slow pressure decrease at a constant temperature, which is connected with hydrate formation. Pressure in the autoclave is stabilized after the completion of hydrate formation. At stage (3), the autoclave is cooled to the temperature at which it is planned to study self-preservation of the formed hydrates. Stage (4) involves a stepwise gas release from the autoclave to reach the pressure $P_0 = 0.2-0.4$ MPa. Then, at stage (5), the hydrate was decomposed at a constant temperature and variable pressure; the kinetic curve of hydrate decomposition was recorded. Finally, at stage (6) the sample was heated to room temperature, and the decomposition of self-preserved hydrate occurred. Stage (5) is to be considered in more detail. At first, as a result of the partial decomposition of methane hydrate, a sharp increase in pressure occurs (figure 2b). This region also includes self-preservation of the hydrate (if it is already present). Estimations show that pressure change due to solubility in oil can be neglected for this region. Further on, decomposition rate decreases. In all experiments, here we observed an extended region of the slow hydrate decomposition; this region was used to determine the rate of decomposition of methane hydrate that had undergone self-preservation. In the case if a noticeable part of hydrate underwent self-preservation, pressure jump was observed at stage (6) while crossing the zero (Celsius) temperature. This pressure jump was connected with the decomposition of self-preserved hydrate. The value of this
pressure jump was used to calculate the total amount of hydrate in the sample and to estimate quantitatively the fraction of the hydrate that underwent self-preservation.

The recorded thermobaric curves were used to calculate the number of moles of the gas evolved/absorbed at different stages of the experiment. It was assumed that the degree of water transformation into hydrate was equal to 100%, and in all cases methane hydrate having the composition CH₄·6H₂O is formed from the emulsions of water in oil [20,21]. Methane (Nₘethane, mol) under experimental conditions could be present in 4 phases: (1): methane in the gas phase (N₁, mol); methane dissolved in oil (Nₒ, mol); methane dissolved in water (Nₜ, mol); methane in the form of hydrate (Nₘ, mol).

\[ N_{methane} = N₁ + Nₒ + Nₜ + Nₘ. \]  

(1)

The amount of methane in the gas phase is calculated using equation 2:

\[ N₁ = \frac{P V}{Z RT}. \]

(2)

Here \( Z = \frac{PV_m}{RT} \) – is compressibility factor which is determined from Peng-Robinson gas equation of state. To determine the amount of gas evolved during the decomposition of methane hydrate, we used equation (3) in which indexes \( i \) and \( f \) stand for the initial and current state of the system.

\[ Nₘ = \Delta N₁ = \frac{V}{R} \left( \frac{P_i}{Z_i T_i} - \frac{P_f}{Z_f T_f} \right). \]

(3)

Self-preservation of hydrate was studies directly at stage (5) (figure 2b); the moment of pressure release to the minimum is designated as \( t₀ \). The rates of decomposition of self-preserved methane hydrate were calculated at the initial stage (5 points starting from moment \( t₀ \), an hour later and 5 hours later, after pressure release (table 2). Calculating the amount of methane at stage (5) we neglected the changes in methane solubility in oil and in water because estimations showed that these values are small in comparison with the gas evolved from the hydrate (less than 1%). So, pressure increase at stage (5) was due only to methane hydrate decomposition.

### Table 2. Decomposition rates.

| Experiment       | \( T_{decomp} \) °C | \( v_0^{decomp} \) mol/min | \( v_1^{decomp} \) mol/min | \( \alpha_1^{selfpres} \) % | \( v_2^{decomp} \) mol/min | \( \alpha_2^{selfpres} \) % |
|------------------|----------------------|----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| O1/8p2gmin10     | -10.1                | 0.00525                    | 16.2·10⁻⁵                   | 51.27                       | 3.9·10⁻³                    | 26.32                       |
| O2/8p1gmin5      | -4.8                 | 0.01090                    | 1.9·10⁻⁵                   | 2.95                        | -                           | -                           |
| O2/8p1gmin10     | -10.2                | 0.00428                    | 8.3·10⁻⁵                   | 20.26                       | 0.94·10⁻⁵                  | 1.69                        |
| O2/8p1gmin19     | -18.8                | 0.01873                    | 7.3·10⁻⁵                   | 13.53                       | 0.14·10⁻⁵                  | 2.87                        |
| O2/1p8gmin11     | -10.8                | 0.00304                    | 3.0·10⁻⁵                   | 3.56                        | -                           | le-                         |

\( a \) Initial decomposition rate (0-5 points from \( t₀ \).

\( b \) Decomposition rate at \( n^{th} \) hour.

\( c \) Relative amount of remaining hydrate at \( n^{th} \) hour.

The data shown in table 2 are to be considered in more detail. Each sample is encoded as L/xpygmnz. Here L means the kind of oil used (table 1), x is the number of holders; y is the mass of the portion of emulsion per one holder; z is round temperature at which the self-preservation of methane hydrate was studied. One can see in the data presented in table 2 that hydrate sample O1/8p2g min10 has undergone self-preservation; the rate of its decomposition was rapidly decreasing with time. At a moment 5 hours later than the start of decomposition, more than 26% of initial hydrate was still present in the sample. In general, this picture corresponds completely to the situation expected for the sample that has undergone self-preservation. At the same time, all samples of the O2/8p1minz series have been decomposed almost completely by this moment of time. The observed decrease in decomposition rate in this case is connected with the exhaustion of hydrate in the sample. This result confirms that decelerated hydrate decomposition in experiment O1/8p2gmin10 is connected exactly with self-preservation rather than hindered heat and mass transfer because the conditions of heat and mass transfer were close in all experiments. It should be stressed that in
different experiments hydrate decomposition in this series proceeded in different manners, and we did not observe any close correlation between experimental conditions and decomposition rates. The maximal initial decomposition rate was observed in experiment \( \text{O2/8p1min19} \) which was carried out at minimal temperature. In experiment \( \text{O2/1p8gmin11} \), the thickest suspension layer was used, so one might expect the slowest hydrate decomposition. Indeed, the initial decomposition rate is minimal in this experiment (table 2). However, hydrate had decomposed almost completely within one hour after the start of the experiment. Parameters \( \nu^1 \) and \( \alpha^1 \) allow us to state that a thicker emulsion layer and lower temperatures do not ensure more efficient self-preservation and even its occurrence (in experiments \( \text{O2/1p8gmin11} \) and \( \text{O2/8p1min5} \) self-preservation was almost absent). In general, self-preservation is only weakly pronounced in hydrate dispersions based on \( \text{O1} \) oil; most likely, self-preservation here depends on small variations and pre-history of samples. Analysis of the results showed that the most probable reason of so different efficiencies of self-preservation of hydrate suspensions in oil \( \text{O1} \) and \( \text{O2} \) may be the presence of surfactants in suspensions based on \( \text{O2} \) oil. It should be stressed that hydrate self-preservation in oil dispersions described in [18,19] proceeded after preliminary deep (to liquid nitrogen temperature) freezing of the dispersion.

To test this assumption, we carried out experiments in which the efficiencies of methane hydrate self-preservation were compared by means of thermovolumetry for hydrate dispersions in \( \text{O2} \) oil in the presence and in the absence of Span 80 surfactant. First of all, dispersions prepared according to the above-described procedure in sample holders with thin and thick emulsion layers were studied. For this purpose, after stage (2) (figure 2a), the autoclaves under pressure were rapidly frozen to the temperature of liquid nitrogen boiling. The resulting hydrate samples were taken out, averaged and studied by means of X-ray powder diffraction (figure 3) and thermovolumetry (figure 4).

![Figure 3. Methane hydrate X-ray diffraction patterns obtained from water/O2 emulsion. Positions of the corresponding phases reflexes are marked by vertical risks; * – paraffins crystalline phase reflexes positions [22]. Both diffractograms are recorded at -100 °C.](image)

One can see in figure 3 that for hydrate samples obtained from water/O2 emulsion in both cases we observe reflections corresponding to methane hydrate sI (the major phase) and the crystalline phase of paraffins [22]. Reflections corresponding to the phase of hexagonal ice Ih can hardly be distinguished. This fact confirms that the degree of water transformation into hydrate is close to the maximal possible one in all our experiments.
Figure 4. Methane hydrate gas emission curves obtained from water/O2 emulsion. ■ – 2 grams/holder; □ – 8 grams/holder; ■ – pure methane hydrate mixed with O2 (1: 1 by weight); □ – pure methane hydrate mixed with O2 (1: 1 by weight, 1% Span 80 per weight of oil).

Thermovolumetric data show that the samples are gradually decomposed within temperature range -50 to 0°C (figure 4). The equilibrium temperature of methane hydrate decomposition is -75°C; in thermovolumetric experiments in the absence of self-preservation it always decomposes within temperature range -75 - -60°C [18]. So, thermovolumetric data are in good agreement with the above-driven conclusion concerning weak manifestation of self-preservation in dispersions based on O2 oil. One can see in figure 4 that due to self-preservation curves ■ and □ do not have a step of methane hydrate decomposition under equilibrium conditions. At the same time, for samples ■ and □, intense decomposition starts at -45 – 40°C, which we suppose to be connected with the presence of Span 80 surfactant in the initial emulsion (1 mass % with respect to oil mass). The curves of gas evolution ■ and □ have a bend within temperature range -20 to -10°C (within this temperature range, decomposition of self-preserved methane kind of decelerates, which agrees with the data shown in table 2). So, self-preservation of methane hydrate occurs indeed, but one can hardly call it efficient. For comparison, experiments were carried out in which the dispersions of methane hydrate in O2 oil were prepared by mixing hydrate powder with the powder of frozen oil (see Experimental section). One of the dispersions was prepared using pure O2 oil, while another one was prepared by adding 1 mass % solution of Span-80 surfactant to the sample kind of oil. The results of thermovolumetric experiment with methane hydrate mixed with O2 oil (1:1 by mass, points ■) are shown in figure 4. At -70°C, partial decomposition of methane hydrate occurs; the formed ice preserves the major part of hydrate efficiently (the major amount of gas evolves at the point of ice melting). In the experiment with methane hydrate mixed with O2 oil + Span 80 surfactant, the results different substantially (figure 4, □). One can see that here the behavior of the curve coincides with that for the samples of suspensions obtained from water/O2 oil emulsion (■ and □). So, the decisive contribution into the efficiency of self-preservation is made by the presence or absence of a surfactant in the initial oil emulsion. In addition, the data obtained demonstrate that self-preservation may manifest itself for the samples of hydrate suspensions in oil that had not been preliminarily exposed to deep freezing.

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