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CALORIMETRIC STUDIES OF FORMATION/DECOMPOSITION PROCESSES OF NATURAL GAS HYDRATES IN PARAFFIN OIL/WATER EMULSIONS

Izabella K. Ivanova[a,b*], Matvey E. Semenov[b], Vladilina V. Koryakina[b], Igor I. Rozhin[b]

[a] *Federal State Autonomous Educational Institution of Higher Professional Education Ammosov North-Eastern Federal University, 58, Belinsky str., 677000, Yakutsk, Russia*

[b] *Federal State State-Financed Scientific Establishment Institute of Oil and Gas Problems of the Siberian Branch of the RAS (IPGP SB RAS), 1, Oktyabrskaya str., 677980, Yakutsk, Russia*

Abstract. The paper considers the research results of natural gas (NG) hydrate formation process in systems consisting of paraffin oil and distilled water at various ratios. Thermobaric conditions of hydrates phase transitions in water-oil emulsions were determined by the method of high-pressure differential scanning calorimetry (DSC). It was ascertained that the equilibrium curve in systems under study, compared to the process of hydrate formation of this gas in distilled water, is shifted in the area of low pressures and high temperatures. According to DSC analysis results and volume analysis, it was determined that with increase of the water content in emulsions by more than 40 % of mass, the degree of water conversion into hydrate in emulsions decreases. It was concluded that the degree of water conversion into hydrate in emulsions can be used as an index of its stability.

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[*] Izabella K. Ivanova, *e-mail*: iva-izabella@yandex.ru

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Introduction.

Hydrocarbon gas hydrates are solid compounds in which gas molecules are incorporated in cavities of ice-like structure formed by water molecules by means of hydrogen bonds. Formation of associated gas hydrates in oil wells is the urgent issue at fields development of the Extreme North, as well as Western and Eastern Siberia. The lifted well production fluid is a multiphase mixture comprising associated gas, oil and water (fresh or low-mineralized), in this case oil and water form water-oil emulsions. At appropriate pressures, low formation temperatures and severe climate of these areas create favorable conditions for hydrate formation in these emulsions, as a result, the hydraulic resistance increases in wells, flowlines, and main oil pipelines, and their throughput capacity reduces due to choking by hydrate plugs.[1-8] The model of hydrate plugs formation in such system was proposed by Turner et al.[8] (Figure 1), the mechanism is described by means of 4 processes: water emulsification with oil as a result of their turbulent mixing; hydrate nucleation at the water-oil interphase boundary with the formation of a hydration shell; hydrate particles agglomeration due to capillary attraction forces and the increase of hydrate slurry viscosity; and sedimentation of large hydrate agglomerates on equipment walls with the formation of hydrate plug. A more detailed mechanism developed on the basis of this model is described in ref. 9. It should be noted that the range of hydrates thermodynamic stability also covers positive temperatures (Celsius). Hence, at moderate pressures, the natural gases hydrates exist up to plus 20-25°C.[10] Thus, gas hydrates formation significantly complicates the processes of production, transportation, storage and treatment of oil.

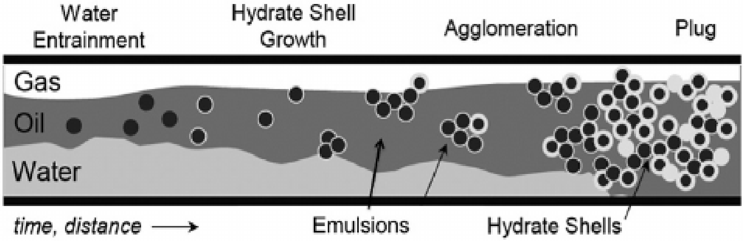


Figure 1. Mechanism of hydrate plug formation in the "gas+oil+water" system.

Analysis of the literature regarding this issue has shown that, both abroad[9, 11-15] and in Russia,[16, 17] the majority of conducted experimental DSC studies of hydrate formation in water-oil emulsions refer to the study of methane hydrate formation, and hydrate formation of complex gas mixtures in oil/water systems was not considered actually.

Thus, in this paper, we present our first findings on the formation of natural gas hydrates (NGH) in paraffin oil-water emulsions of Irelyakh gas and oil field (GOF). This work is the extension of the research regarding the matter of NG hydrate formation in different systems.[18, 19]

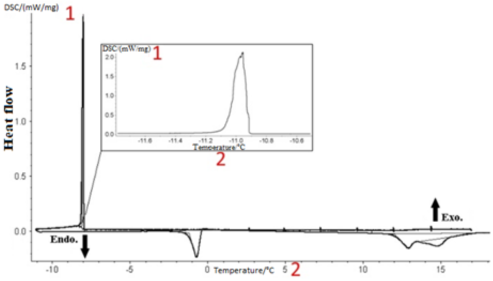
Results and Discussion

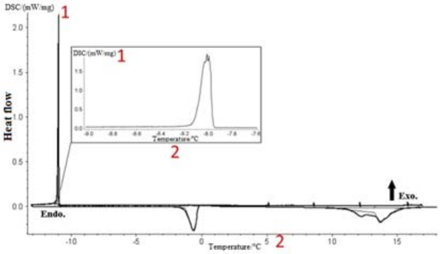
Figure 2 and Table 1 represent the DSC analysis data obtained after two experiments in NGH formation/decomposition in Oil/H_2O samples. All obtained thermal images consist of two segments: one cooling segment and one heating segment, with obtaining forming exotherms and melting endotherms for ice and hydrate. It is obvious that thermal images of samples No. 1, No. 3 and No. 4 have identical nature. So, one asymmetric exotherm effect is observed at cooling of these samples, unlike sample No. 2, which has two or more peaks in the crystallization exotherm, values of these exothermic effects differ and have lower values at lower temperatures. In the melting endotherms of all samples, two endothermic effects were registered: ice melting and hydrate decomposition. It should be noted that for sample No. 1 (experiment 1 and 2) and in experiment 1 for samples No. 2 (the peak with the highest exothermic effect) and No. 3, the crystallization peaks have a common base, but several peaks. In works,[20, 21] it is shown, that the DSC method can be used for studying water-oil emulsions, and, by the form of exothermic effects, we can judge about dispersion ability of the freezing phase. Thus, the asymmetric exothermic peak with the sharp start and extended end is typical for continuous phase freeze. A large number of small exothermic peaks is the evidence of large drops freeze of disperse phase. Exothermic peaks similar by shape to a Gaussian curve are typical for freeze of finely dispersed emulsions samples wherein freeze of each drop occurs independently from other drops. With use this approach, the analysis of the obtained results regarding NG hydrates formation in water-oil emulsions shows that the curve shapes of samples No. 1, No. 3 and No. 4 is intermediate between freeze of the bulk phase and the finely dispersed emulsion. In curves of sample No. 2 the exothermic peaks have asymmetric shape which is typical for freeze of the bulk phase in emulsions, and the presence of little effects provides evidence for large drops freezing of the dispersed phase. The authors of work[22] ascertained that the greater the asymmetry of DSC exothermic peak is, the greater is the tendency of hydrate particles to agglomerate within the studied water-oil emulsion. The maximum exothermic peak asymmetry indicates the least stable emulsion, and vice versa. In our case, the largest asymmetry of freezing peaks is observed in samples No. 1 and No. 2, and these samples are characterized by the highest degree of water conversion into hydrate, which amounts up to ~70 % of mass (Table 1) in both cases, while for samples No. 3 and No. 4, this index is 48% and 29% respectively, which is the evidence of the stability of samples with Oil/H_2O components ratio of 40/60 and 20/80, i.e. with the increase of the water content for more than 40% of mass (Table 1), the degree of water conversion into hydrate decreases, and the stability of these emulsions increases. These results are well correlated with works[23-25] wherein it is shown that the most resistant water-oil emulsions are "chocolate mousse" type emulsions with the water content of about 80-85%. Stability of these emulsions is explained by the presence of gel-emulsion specific structure, which is formed when the water content in the initial water-oil mixture exceeds ~40%.[23, 24]

Experiment 1 | **Experiment 2**

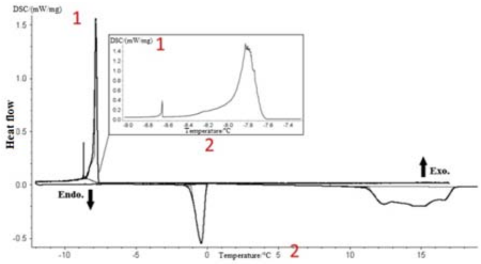
“Oil/H_2O” sample

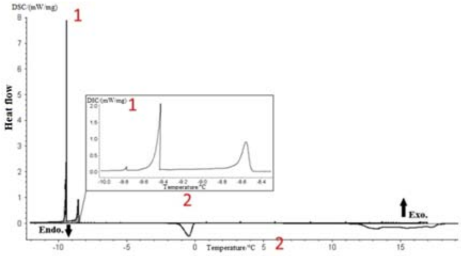
80/20 ratio



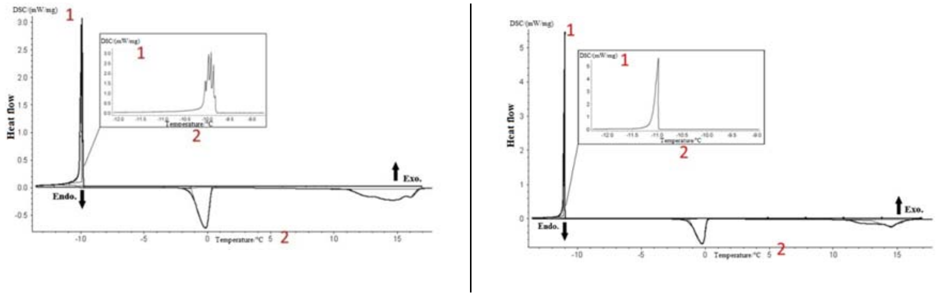


60/40 ratio





40/60 ratio



20/80 ratio

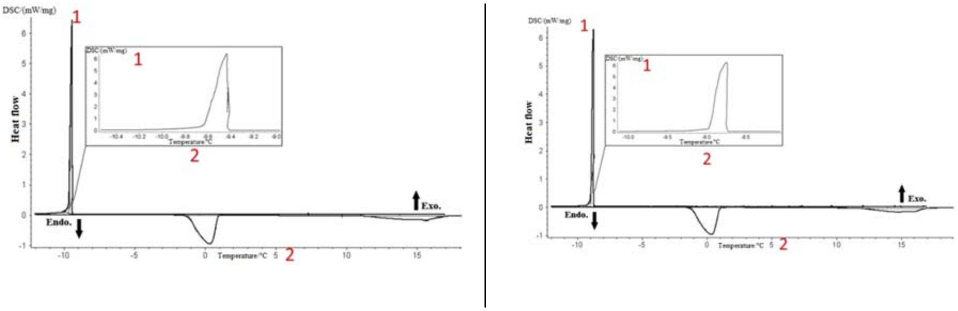


Figure 2. Thermal images of NGH phase transitions in "Oil/H_2O" systems, that are obtained in experiments 1 and 2. Cooling segments are designated "Exo.", heating segments are "Endo."; 1 - DSC/(mW/mg); 2 - Temperature/°C.

Table 1. Thermobaric conditions of NGH phase transitions in "Oil/H_2O" systems

No.	Sample Experiment No.	Crystallization conditions	Melting conditions		α*,%
			of ice	of hydrate	
1.	Oil/H_2O=80/20 Experiment 1	1 peak: t=-11.0°C; P=43.38 bar; ΔH=-55 J/g	t=-1.25°C; P=41.94 bar; ΔH=31 J/g	t=11.3°C; P=41.14 bar; ΔH= 54 J/g	63.7
	Experiment 2	1-st peak: t=-8.0°C; P=46.56 bar; ΔH=-47 J/g	t=-1.19°C; P=44.96 bar; ΔH= 23 J/g	t=12°C; P=44.38 bar; ΔH= 57 J/g	71.6

Table 1. Continued

2.	Oil/H_2O=60/40 Experiment 1	1 peak: t=-7.83°C; P= 44.73 bar; ΔH=-102 J/g; 2-nd peak: t=-8.66°C; P=44.35 bar; ΔH=-2 J/g	t=-1.15°C; P=42.13 bar; ΔH= 59 J/g	t=11.3°C; P=41.30 bar; ΔH= 132 J/g	69.3
	Experiment 2	1-st peak: t=-8.56°C; P=46.64 bar; ΔH=-32 J/g; 2-nd peak: t=-9.5°C; P=46.25 bar; ΔH=-33 J/g; 3-rd peak: t=-9.77°C; P=46.1 bar; ΔH=-1 J/g	t=-1.15°C; P=44.66 bar; ΔH= 51 J/g	t=11.9°C; P=43.98 bar; ΔH= 133 J/g	72.3
3.	Oil/H_2O=40/60 Experiment 1	1 peak: t=-9.8°C; P=45.43 bar; ΔH=-171 J/g	t=-1.31°C; P=42.92 bar; ΔH= 123 J/g	t=11.2°C; P=42.05 bar; ΔH= 120 J/g	49.4
	Experiment 2	1-st peak: t=-11.0°C; P=44.22 bar; ΔH=-138 J/g	t=-1.20°C; P=42.38 bar; ΔH= 102 J/g	t=11°C; P=41.64 bar; ΔH= 89 J/g	46.1
4.	Oil/H_2O=20/80 Experiment 1	1-st peak: t=-9.44°C; P=44.47 bar; ΔH=-191 J/g	t=-1.2°C; P=42.88 bar; ΔH= 194 J/g	t=11.4°C; P=42.15 bar; ΔH= 82 J/g	29.8
	Experiment 2	1-st peak: t=-8.74°C; P=45.72 bar; ΔH=-208 J/g	t=-1.21°C; P=43.98 bar; ΔH= 203 J/g	t=12.1°C; P=43.33 bar; ΔH= 80 J/g	28.3

α * is the degree of water conversion into hydrate.

Thus, the study of NGH formation/decomposition processes in paraffin Oil/H_2O systems by DSC method has shown that, in those systems, the degree of water conversion into hydrate is within the range of 29-70% against 2.3% hydrate formation rate in distilled water.[18] If melting endotherms of all studied samples are the same (there are melting peaks of ice and hydrates on all endotherms), then crystallization exotherms reflect the mechanism of continuous phase freezing, and the geometry of curves indicates the emulsion stability. Probably, the degree of water conversion into hydrate can also be an index of water-oil emulsion stability, since with the increase of water content by more than 40% of mass the degree of water conversion into hydrate reduces, and the emulsion stability increases.

The next step of work was the study of NGH formation/decomposition in Oil/H_2O systems in the high-pressure reactor. Figure 3 shows the experimental results on formation (a) and decomposition (b) of NG hydrates in the systems above.

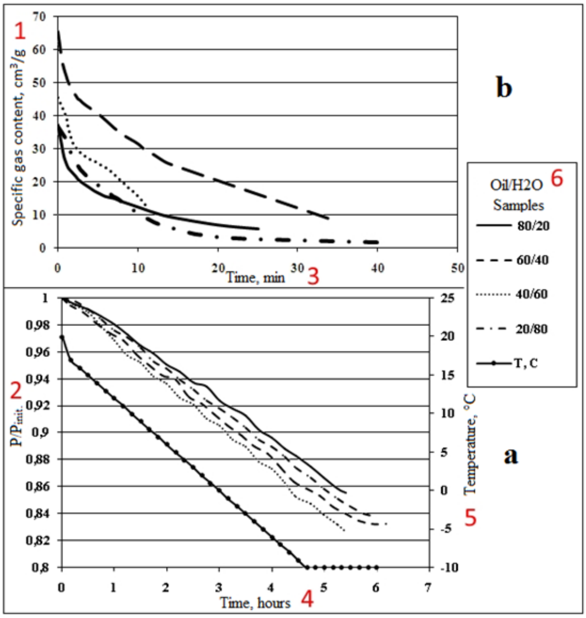


Figure 3. Pressure change (A) when NGH formation in Oil/H_2O systems in the temperature range from +20 to-10°C and change of their specific gas content (B) during decomposition; 1 - specific gas content, cm^3/g; 2 - P/P_{init}; 3 - time, min; 4 - time, hours; 5 - temperature, °C; 6 - Oil/H_2O samples.

It is seen (Figure 3a) that the curve of pressure drop is smooth and steps that correspond to the stage of saturation with gas and hydrate formation in oil and water systems are not separated. Curves with similar forms were obtained in works[16] wherein the research results of methane hydrates formation in water emulsions of oil from Verkhnechonskoe, Gerasimovskoe and Usinskoe fields are given, and in ref. 19 wherein the processes of this NG hydrate formation in the systems consisting of paraffin sediments and water are studied.

The results of decomposition analysis are presented in Figure 3b and in Table 2.

Table 2. Gas content of NGH synthesized in Oil/H_2O systems.

System	**Oil/H_2O**			
Ratio	80/20	60/40	40/60	20/80
Escaped gas volume, cm^3	20	1130	640	380
Specific gas content, cm^3/g	4	94	34	15
Degree of water conversion into hydrate, %	~3	57	21	9

Table 2 shows that the hydrate synthesized in the Oil/H_2O sample with 80/20 components ratio has the lowest gas content, therefore the degree of water conversion into hydrate, in this case, is the lowest and does not exceed 3%. The highest amount of escaped gas is detected for the Oil/H_2O sample with 60/40 components ratio - the degree of water conversion into hydrate is 57%, which gradually decreases and reaches 9% when water content increases up to 80% of mass in the sample. Since the hydrate formation process depends on distribution and size of water drops in samples, we carried out the studies of parameters of drops in emulsions. Micro-photographs (Figure 4) show the studied samples before (a) synthesis and after (b) decomposition of hydrates. It is seen that the hydrate formation entails the enlargement of water drops in the samples, apparently it is related to agglomeration of hydrate particles. This fact agrees with works[19] and[26] where, respectively, drop sizes were studied in the systems of asphalt-resin-paraffin sediments (ARPS) and water before synthesis and after decomposition of utilized NG hydrates, as well as in water-oil emulsions before synthesis and after decomposition of methane hydrate. Quantitative analysis of obtained micro-photographs allowed the ascertainment that distribution of water drops in all samples before hydrate synthesis has poly-disperse nature, and the drop size varies from 8 up to 35 μm (Figure 5a), except for the sample with the Oil/H_2O component ratio of 60/40, for which the peak of water distribution by volume falls on drops of 27 μm in diameter, for the rest of samples, it falls on drops with diameter of 23 μm. During hydrates decomposition, the peak is displaced toward the drops with a larger diameter (Figure 5b). For Oil/H_2O sample with a component ratio 40/60 the maximum of water distribution falls on drops with the diameter of 33 μm, and 35 μm for the rest of samples. Based on the size and amount of dispersed water drops in samples, their specific surface areas were calculated (m^2/g) and graphs of their dependence on the gas content in samples (Figure 5c) were plotted according to hydrate decomposition data obtained as a result of DSC-analysis and volumetric analysis in reactor chambers. It is apparent that the dependencies revealed according to two methods have similar nature. With reduction of the water content in samples with 80 to 40% of mass (points 1-3), the specific surface area of drops increases which leads to an increase of hydrate gas content in emulsions. In Oil/H_2O sample with component ratio of 80/20 (point 4), notwithstanding that drops in the emulsion have the largest specific surface area, the gas content decreases, and even has a minimum value according to volumetric analysis results. The obtained data can be explained by the fact that this sample, in comparison with other ones, contains the minimum amount of water, i.e. 20% of mass, which has the effect on its lower gas content. Thus, increase in the water content in samples entails decrease in the specific surface area of drops in emulsions, and the dependence of sample gas content on specific area of drops has the nonlinear nature, and according to results of two methods: DSC and volumetric analysis, the maximum of this curve falls on sample 60/40 Oil to H_2O ratio.

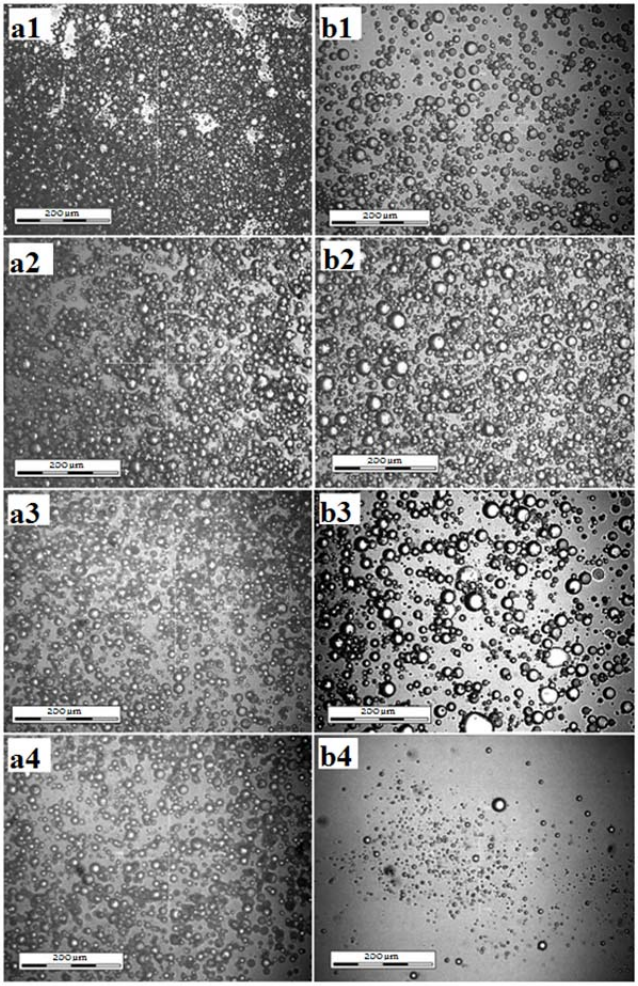


Figure 4. Micro-photographs of "Oil/H_2O" samples before (**a**) and after (**b**) hydrate formation, scale interval 200 µm: **a1**, **b1** - "Oil/H_2O" sample with component ratio 80/20; **a2**, **b2** - "Oil/H_2O" sample - 60/40; **a3**, **b3** - "Oil/H_2O" sample - 40/60; **a4**, **b4** - "Oil/H_2O" sample with component ratio 20/80.

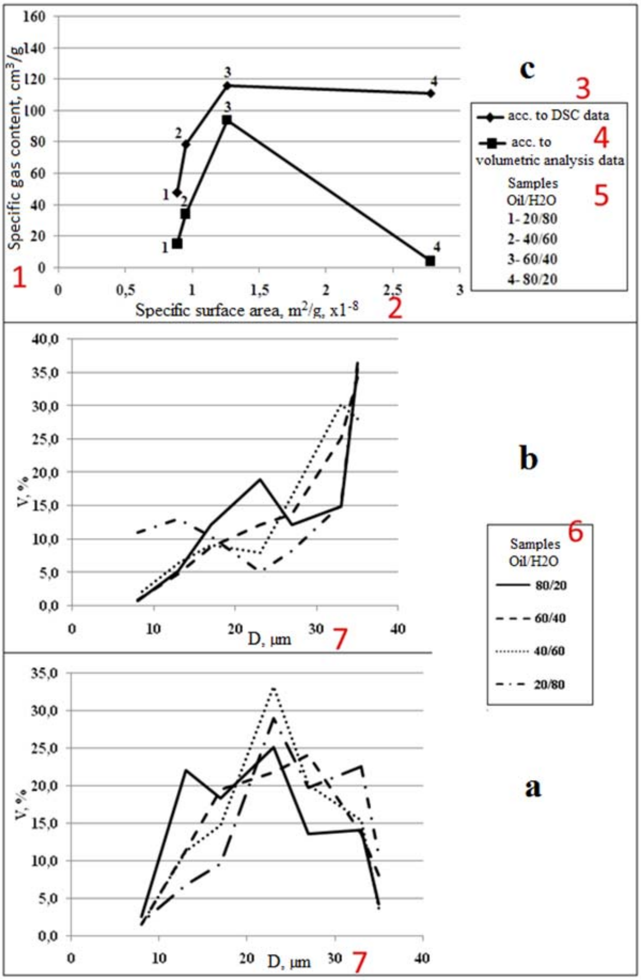


Figure 5. Distribution by water volume in dispersed drops of Oil/H_2O samples before (**a**) and after (**b**) hydrate formation. Dependence of the specific gas content of Oil/H_2O samples (**c**) on their specific surface area according to the results of DSC and volumetric analysis; 1 - specific gas content, cm^3/g; 2 - specific surface area, m^2/g, $x10^{-8}$; 3 - according to DSC data; 4 - according to volumetric analysis data; 5,6 - Oil/H_2O samples; 7 - D, µm.

The experimental data obtained in this work was correlated with the equilibrium conditions of used NG hydrate formation, that were calculated by the procedure elaborated by E. Dendy Sloan (Figure 6).[27] As a comparison, the figure shows the results of the study of this NG hydrate formation in systems based on distilled water (points 1-4) and in systems that consist of paraffin and water (points 13-18), that were published in ref. 18 and 19 respectively. It is shown in these studies that the calculated and experimental data on equilibrium conditions of NG hydrate formation with the specified composition are well correlated,[18] and, in systems consisting of paraffin ARPS and water, the curve of hydrate formation equilibrium conditions is shifted to the area of high pressures and low temperatures.[19]

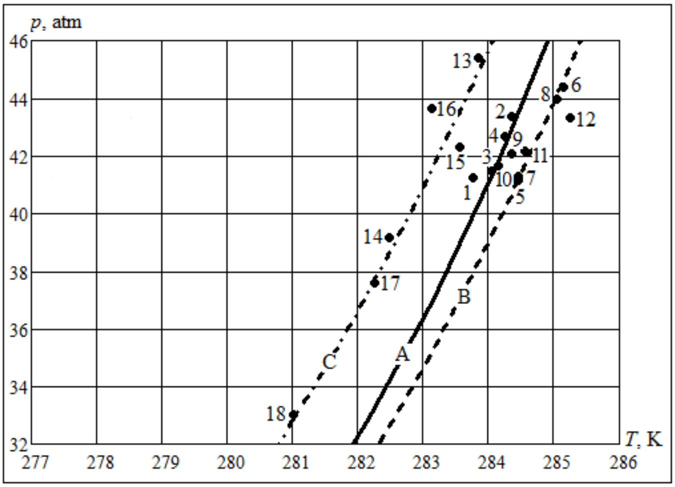


Figure 6.Comparison of calculated (curves) hydrate formation conditions to experimental (points) ones of the natural gas of Sredneviluyskoe field for systems: 1 - distilled water; 2 - distilled water + sand; 3 - water with thermal history; 4 - water with thermal history + sand; 5, 6 - Oil/H_2O with 80/20 component ratio; 7, 8 - Oil/H_2O - 60/40; 9, 10 - Oil/H_2O - 40/60; 11, 12 - Oil/H_2O - 20/80; 13, 14 - ARPS/H_2O - 40/60; 15, 16 - ARPS/H_2O - 60/40; 17, 18 - ARPS/H_2O - 80/20; A - equilibrium curve for natural gas; B - approximation of conditions for water-oil systems (points 5-12); C - approximation of conditions for ARPS/H_2O systems (points 13-18).

According to the experimental data (points 5-12) it is possible to emphasize the thermobaric area of NG hydrates existence in paraffin Oil/H_2O systems. It is obvious that the hydrate formation curve in systems under study is displaced to the area of low pressures and high temperatures. Therefore, hydrate formation in the emulsions of paraffin oils compared to this process in the bulk water (curve A) and in ARPS/H_2O system (curve

C), does not require high pressures, and, other things being equal, leads to the preferred hydrate formation.

Experimental

As a model of associated oil hydrating gas, we used the natural gas of Srednevilyuiskoe gas condensate field (GCF) with high methane content (92.9 % of vol.).[18]

Targets of the research were hydrates of this gas, synthesized in oil systems of Irelyakh gas and oil field (GOF) - oil composition is given in ref. 28, and distilled water in various mass ratios:

- No.1 Oil/H_2O components ratio 80/20;
- No.2 Oil/H_2O components ratio 60/40;
- No.3 Oil/H_2O components ratio 40/60;
- No.4 Oil/H_2O components ratio 20/80.

Samples were prepared at the room temperature, using a domestic electric mixer (blades rotation velocity of 11,000 rpm), during 30 minutes without adding synthetic surfactants. Using technical scales with accuracy of up to 0.001 g, we prepared oil and water sample weights and stirred them in the mixer bowl. Being maintained for 2 days in a separatory funnel and, as it was shown, the obtained samples retained their stability.

The size of dispersed water drops in Oil/H_2O systems before and after hydrate forming was determined by photographing under “Olympus BX 51 M” microscope and measuring drop sizes in photographs. According to drops size, calculations of drops distribution depending on their volume (V, %) were carried out and specific surface areas of the samples (m^2/g) were determined.

Determination of thermodynamic characteristics of hydrate phase transitions was conducted using the DSC 204 HP Phoenix high-pressure differential scanning calorimeter of Netzsch company (Germany). The relative error of enthalpy measurement was of ±3%, temperature measurement error was of ±3 °C. In the course of experiments, the melting pots of steel were used, which were covered with lids of pierced aluminum. The thermal images were recorded in the mode described in ref. 18. Minimum 2 DSC-grams for each of water-oil emulsions composition were acquired.

The study of NGH formation/decomposition in Oil/H_2O systems was carried out on devices which main component was high-pressure reactor tube. Schematic diagrams of the devices and the modes of NGH synthesis and decomposition in the studied systems are given in ref. 19. Synthesis and decomposition of each sample were performed at least 2 times.

Decomposition of synthesized hydrates was conducted at the temperature of +25 ^{o}C. Specific gas content (cm^3/g) and the degree of water conversion into hydrate in studied samples are determined with volumetric method described in ref. 29 and 30.The method is based on measurement of the gas volume escaping during hydrate heating.

Conclusions

Thus, with the DSC high-pressure method in the calorimeter cell at micro-level we have studied the phase transitions of natural gas hydrates synthesized in paraffin Oil/H_2O systems. In the high pressure reactor chambers, at macro-level, the kinetics of their formation/decomposition was studied. It is shown that in the very Oil/H_2O sample with the water content of 40% of mass, the dispersed water drops have the largest surface area, due to this fact, this sample is characterized with the high degree of water conversion into hydrate and has the highest specific gas content. It was experimentally ascertained that equilibrium conditions of NG hydrate formation in emulsions are different from those in bulk water, and the curve is shifted to the area of low pressures and high temperatures. Probably, the degree of water conversion into hydrate in water-oil emulsions can be the index of its stability. It is possible that the experimental data obtained in this work and published in ref. 18, 19 will provide the basis for developing recommendations to prevent formation of complex hydrate plugs, which are formed during development and exploitation of oil fields located in permafrost rock zones.

Acknowledgments

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