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Synthesis of Natural Gas Hydrates in Water-in-Oil Emulsions

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Abstract

The paper presents the results on the synthesis of natural gas hydrates in a medium of water-in-oil emulsions in a high-pressure cell. Hydrates are generated in emulsions *via* a stepwise mechanism, as established. Its origin is driven by diffusion parameters of natural gas. Hydrate growth from natural gas dissolved in oil occurs in emulsion medium accompanied by concentrating methane, as demonstrated by the study of the composition of the resulting hydrates. Whereas hydrate composition does not depend on a ratio of oil and aqueous components of the emulsion. Hydrate content in emulsions is directly dependent on the amount of water in an emulsion composition and decreases with increasing the water fraction, as demonstrated.

Keywords: natural gas hydrate, water-in-oil (W/O) emulsion, hydrate content

INTRODUCTION

Natural gas hydrates are nonstoichiometric clathrate compounds of water and natural gas. They are generated and stable at low temperatures and high pressures [1]. Hydrating proceeds everywhere with the presence of gas, water, low temperatures, and pressures. Thus, for example, it may occur during the reaction of associated petroleum gas with water emulsified in oil [1–5]. Therefore, low-temperature operating mode of oil and gas condensate fields requires the adoption of certain measures for the prevention and control for gas hydrate plugs. However, if processes of the generation of natural gas hydrates in water and its solutions are well-studied and have a solid fundamental

base, peculiarities of gas hydrate formation process in a multi-component medium of water-in-oil (W/O) emulsions still remain insufficiently clear. As demonstrated by analysis of papers on the study of hydrate formation phenomenon in a medium of W/O emulsion, the majority of them is focused on theoretical and experimental research of thermodynamics and kinetics of growth/dissociation of hydrates of simple gases, for instance, methane, in W/O emulsions of different composition, whereas the majority of natural and associated gases are mixtures and comprise of other hydrocarbons too.

The purpose of the present work was to study the impact of water and oil components of emulsions on peculiarities of the formation process of natural gas hydrates.

EXPERIMENTAL

Samples of W/O emulsions were obtained by mechanical mixing oil from the Irelyakhskoe gas-oil field (Yakutia, Russia) comprising of 1.47 mass % of paraffins, 0.45 mass % of asphaltenes, 12.5 mass % of resins, with a density of 0.855 g/cm³, and distilled water in a mass ratio of 80 : 20, 60 : 40, 40 : 60 and 20 : 80 without the addition of any synthetic surfactants using a household mixer with free blade rotation speed of 11 000 rpm for 30 min. The emulsions prepared in such a way were left for a day to stabilize, after which they were used in subsequent experiments. All the disperse systems obtained are W/O emulsions, or of the reverse type.

Synthesis of natural gas hydrates was carried out using an original setup described in [15] that represented a high-pressure cell (HPC). For that purpose, an aged sample of W/O with a mass of 30 g was placed into a polypropylene capacity that was loaded into the HPC and vacuumed, then natural gas from the Sredne-Vilyuysk gas condensate deposit (Yakutia, Russia) was pumped into the HPC to a pressure of 75 atm. The data of Table 2 cite gas composition. Oil phase saturation with natural gas was carried out at a temperature of 15 °C for one day, afterwards, synthesis of hydrates was performed *via* a method of lowering temperature to -10 °C, with a linear rate of 0.1 °C/min. According to the findings, getting curves were constructed by the ratio: $v = v_0 - v_i$, where v_i is amount of gas in a given time, mol; $v_i = P_i V_{\text{HPC}} / Z(P_i, T_i) RT_i$; P_i is current pressure in the HPC, Pa; V_{HPC} is HPC volume; $Z(P_i, T_i)$ is gas compressibility factor determined by graphical method according to the current values of pseudoreduced pressure and temperature according to [16]; R is gas constant; T_i is current temperature, K; v_0 is the amount of gas in the initial moment of hydrating.

Hydrate content (α_{HPC}) in the studied samples of W/O was calculated according to the ratio:

$$\alpha_{\text{HPC}} = (V_g - r_{\text{oil}} m_{\text{WOE}} n_o) / 164 \cdot 100 \%$$

where V_g is volume of natural gas released during decomposition of W/O emulsion, mL; r_{oil} is oil saturation with natural gas, mL/g, determined experimentally for oil samples with

appropriate mass under similar experimental conditions; moreover, the amount of oil was taken exactly corresponding to its mass in the composition of W/O emulsion; m_{WOE} is mass of W/O emulsion sample, g; n_o is oil fraction in the composition of W/O emulsion; 164 is the maximum volume of methane gas absorbed during hydrating of 1 mL of water [1]. For each composition of the emulsion, the average content of the hydrate was calculated on the basis of 4–5 similar experiments.

Component compositions of such gases as natural gas used as the atmosphere in differential scanning calorimetry (DSC) experiments, the gas entered into the composition of hydrates obtained in an HPC; the gas dissolved in oil without hydrating phenomenon were studied by the GC technique using Shimadzu GC-2010 Plus instrument. According to the findings, the component redistribution coefficient in hydrate and hydrate generator gas was calculated: $k_i = c_{i,\text{hydr}} / c_{i,\text{hydr.gas}}$, where k_i is i -th component redistribution in hydrate and hydrate (hydr) hydrate generating gas ($c_{i,\text{hydr}} / c_{i,\text{hydr.gas}}$). Herewith, hydrate generator gas during hydrate synthesis from distilled water is the initial natural gas, while during hydrating in a medium for W/O emulsion – oil-dissolved gas.

RESULTS AND DISCUSSION

During the experiments conducted, there were obtained absorption curves of natural gas by W/O emulsions of various composition. The overall view is presented in Fig. 1. Three intervals, the durations of which differ from composition to composition, can be highlighted in all getting curves of W/O emulsions (Table 1).

TABLE 1
Duration of interval I of getting for W/O emulsions

Oil/water (per mass)	Duration, min
80 : 20	82
60 : 40	232
40 : 60	275
20 : 80	305
Distilled water	295

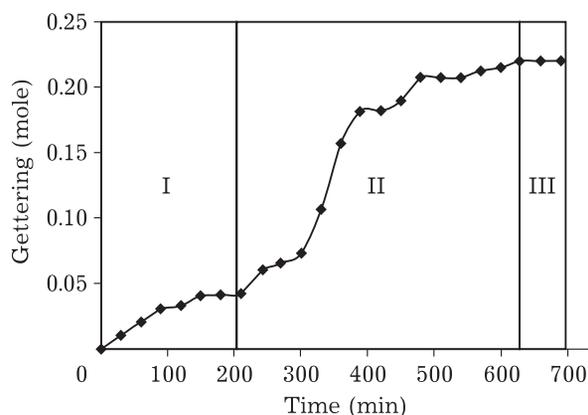


Fig. 1. Intervals on a typical gettinger curve of W/O emulsions (oil and water in a mass ratio of 40 : 60): I – the period of preferential absorption of gas by oil; II – hydrating period; III – the process completion of hydrating

It can be seen that there is no significant gas absorption by emulsions (see Fig. 1, interval I) in the beginning of synthesis during some time range, on reaching which a dramatic increase in gettinger occurs due to hydrating (interval II). This is followed by the transition to a stationary level that is associated with the process completion of hydrating (interval III).

It is established that the process has various durations in the initial period, during which gas dissolution in oil takes place during decreasing HPC temperature (see Table 1). The induction period at high water content is comparable with its duration in distilled water, and with an increase in the water fraction, it becomes longer.

This may attest to a reduction of the induction period at a high content of the oil phase in W/O emulsions, which is probably driven by the presence of water drops of natural surfactants in oil. Thus, for instance, the induction period shortens right up to its disappearance during hydrating from the continuous water phase in the presence of synthetic surfactants, as a layer of surfactant

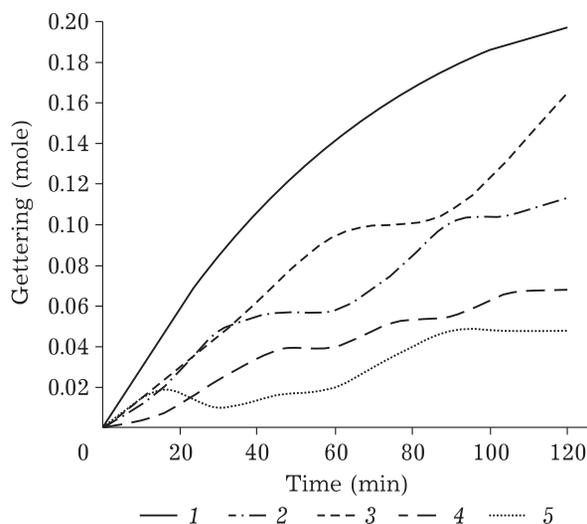


Fig. 2. Gettinger occurs of W/O emulsions due to hydrating (interval II). Compositions of oil and water (per mass) are equal 80 : 20 (1), 60 : 40 (2), 40 : 60 (3), 20 : 80 (4), distilled water (5).

species in water–gas phase section reduces water surface tension and thereby favors to gas dissolution in water [17–19].

Gettinger curves of emulsions of various composition versus time in interval II are presented in Fig. 2. Since the process of accelerated gettinger related to hydrating begins in different times of synthesis in the HPC and has different durations, the time scale in Fig. 2 is set to zero and a time interval of synthesis of 2 h is displayed. It can be seen that dependencies of gettinger of W/O emulsions have the appearance of absorption curves, several curves in some cases. Gettinger in oil emulsions is higher compared to gas absorption by distilled water, as demonstrated. The process of hydrate growth in the HPC from the W/O emulsions with a high oil content occurs stepwise – there are plateau periods of a duration to 0.5 h, during which gas diffusion by the hydrate former gas to water drops happens. Thus, hydrating in a

TABLE 2

Composition of natural gas and gas dissolved in oil

Objects	Content c, vol. %				
	CH ₄	C ₂ H ₆	C ₃ H ₈	<i>i</i> -C ₄ H ₁₀	<i>n</i> -C ₄ H ₁₀
Natural gas	92.92	5.25	1.21	0.10	0.12
Gas dissolved in oil	69.36	14.98	11.47	1.40	2.79

TABLE 3

Content (*c*) and rate of the redistribution (*k*) of hydrate-forming components of natural gas in initial gases and hydrates synthesized in W/O emulsions

Oil/Water (per mass)	CH ₄		C ₂ H ₆		C ₃ H ₈		<i>i</i> -C ₄ H ₁₀		<i>n</i> -C ₄ H ₁₀	
	<i>c</i> , vol. %	<i>k</i>	<i>c</i> , vol. %	<i>k</i>	<i>c</i> , vol. %	<i>k</i>	<i>c</i> , vol. %	<i>k</i>	<i>c</i> , vol. %	<i>k</i>
80 : 20	75.88	1.1	11.56	0.8	8.93	0.8	1.46	1.0	2.18	0.8
60 : 40	72.80	1.0	11.31	0.7	10.83	0.9	2.26	1.6	2.79	1.0
40 : 60	82.56	1.2	6.10	0.4	7.78	0.7	1.28	0.9	2.27	0.8
20 : 80	80.85	1.2	9.75	0.6	4.97	0.4	1.55	1.1	2.87	1.0
Distilled water	83.52	0.9	5.75	1.1	9.72	8.0	0.51	5.0	0.52	4.3

thickness W/O emulsions with high oil content is limited by diffusion of gas molecules through the oil phase to hydrate growth areas. Herewith, diffusion role increases with a rise in the fraction of the emulsion oil component.

Distribution coefficients of components of hydrate generators for all W/O emulsions, as demonstrated by analysis of gas after decomposition (Table 2, 3) obtained from W/O emulsion hydrates. Therefore, hydrates generated in a medium of W/O emulsions have similar compositions, regardless of a ratio of oil and aqueous emulsion components. Thus, the average composition of the resulting hydrates in oil emulsion is $0.78\text{CH}_4 \cdot 0.10\text{C}_2\text{H}_6 \cdot 0.08\text{C}_3\text{H}_8 \cdot 0.016i\text{-C}_4\text{H}_{10} \cdot 0.025n\text{-C}_4\text{H}_{10} \cdot 9.1\text{H}_2\text{O}$, where water mole content was calculated according to [21].

It is interesting to note that hydrates with higher methane content than in oil-dissolved gas (redistribution coefficient $k > 1$) are generated. Herewith, the content of heavier components of natural gas in hydrates synthesized in a medium of W/O emulsions is lower than in hydrate growing from distilled water under similar conditions of synthesis: so, ethane concentration is 1.8 times lower, propane – in 11.4 times, *iso*-butane – 4.3 times, *n*-butane – 1.2 times. This fact may be explained, on the one hand, by different diffusion mobility of gas molecules in the oil phase, on the other hand, by the presence of natural oil surfactants in the surface of water drops that selectively let through gas molecules, and the larger hydrate generator molecule is, the harder it is for it to diffuse through the oil thickness to hydrate growth areas simultaneously overcoming the molecular barrier in the surface of water drops. Thus, for instance, papers [22, 23], in which

it is demonstrated that mechanical mixture of hydrates with the prevailing content of methane hydrates, may serve in favor of the assumption about the effect of surfactants on the composition of the hydrates formed. This is related to the presence of a molecular coat in the surface of the gas/liquid interface that selectively let through natural gas components.

Based on the findings, there were constructed dependencies of the average content of hydrates during synthesis in the HPC on the water fraction in the composition of W/O emulsions (Fig. 3). For comparison, the amount of hydrate synthesized from distilled water under similar conditions of synthesis is also indicated in the figure. It was impossible to establish hydrate content during synthesis in the HPC for W/O emulsion composition of 80 : 20 because of a small amount of the sample.

Natural gas hydrates in distilled water are poorly generated under these conditions of synthesis, and with a decrease in the water

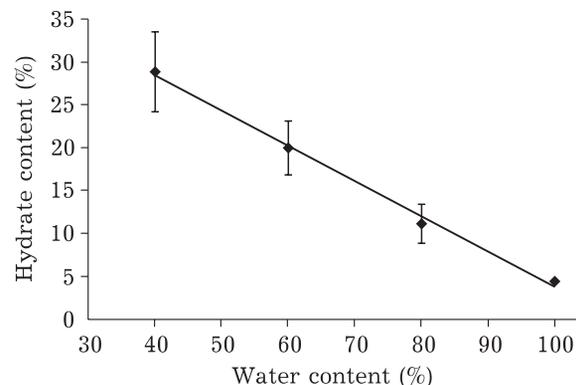


Fig. 3. Hydrate content in W/O emulsions synthesized in high-pressure cells (HPC).

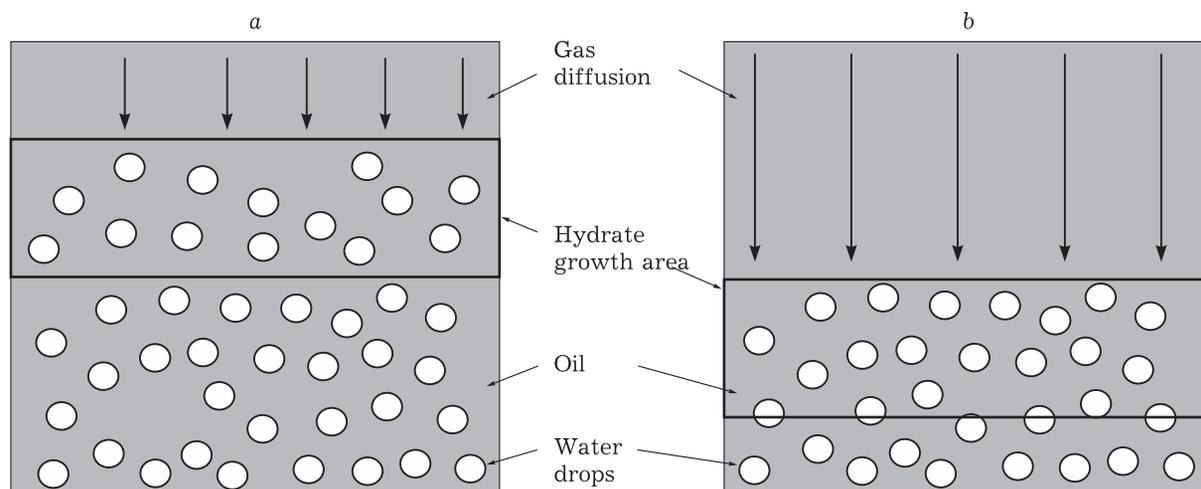


Fig. 4. Scheme for spatial hydrate growth in W/O emulsions of various composition: with large (a) and small (b) water content.

fraction in W/O emulsions, hydrate content increases. Considering that hydrate content, a ratio of hydrate mass to water mass in W/O emulsion composition, hydrating in terms of W/O emulsion sample will be 10, 12, and 12 % for compositions of emulsions containing 80, 60, and 40 mass % H_2O , respectively. With equal emulsion sample mass, the weight of the hydrate formed will increase to a certain maximum value with increasing the water fraction, which is driven by the presence of hydrating front (Fig. 4). Thus, hydrate content is dictated by not peculiarities of the hydrating process but the vessel geometry and water phase amount in an emulsion composition.

CONCLUSION

Thus, the research has been carried out on the peculiarities of the growth, composition, and the content of natural gas hydrates in emulsions of oil disperse systems. It is established that the growth process of hydrates in a medium of W/O emulsions flows in spurts: the growth of hydrates flows fast, with the exhaustion of the hydrate former gas dissolved in an oil matrix, after which saturation of growth areas of hydrates occurs with gas through diffusion of its components.

Unlike synthesis of hydrates from distilled water, during hydrating in emulsion medium, there happens redistribution of natural gas components accompanied by enriching hydrate

with methane. This is related to differences in the diffusion mobility in oil and penetration quality of various components of natural gas through a layer of surfactants. It is demonstrated that hydrates are mainly generated in a limited area, *i.e.* the hydrating front, and the growing hydrate mass is driven by peculiarities of vessel geometry and the amount of aqueous phase in emulsion composition.

Thus, diffusion parameters of gas molecules, in other words, mobility in oil and their penetration quality through a layer of surfactants are limiting factors of hydrating in a medium of W/O emulsions. Herewith, the role of emulsion composition (ratio of oil and aqueous components) is not so significant.

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