

Effective Self-Preservation of Methane Hydrate Particles in Crude Oils

A. S. Stoporev and A. Yu. Manakov

Abstract—In this work we investigated the behavior of methane hydrates dispersed in crude oils from different fields at temperatures below 0°C. In case of crude oil emulsion the size of water droplets is in the range of 50–100 μm. The size of hydrate particles formed from droplets is the same. The self-preservation is not expected in this field. However, the self-preservation of hydrates with the size of particles 24±18 μm (electron microscopy data) in suspensions is observed. Similar results were obtained for four different kinds of crude oil and model system such as asphaltenes, resins and wax in n-decane. This result can allow developing effective methods to prevent the formation and elimination of gas-hydrate plugs in pipelines under low temperature conditions (e. g. in Eastern Siberia). There is a prospective to use experiment results for working out the technology of associated petroleum gas recovery.

Keywords—Gas hydrate, Gas liberation, Self-preservation, Water-in-oil emulsion.

I. INTRODUCTION

GAS hydrates are inclusion compounds in which the host framework is formed by water molecules while molecules of gases or low boiling liquids are incorporated in the framework cavities [1]. Primarily, the interest in gas hydrates stems from the existence of huge natural gas reserves in the form of gas hydrates in Earth interior [2]. To prevent gas hydrate formation in the oil and natural gas production is also of great practical importance [1], [3]. During oil production and in-field transportation the formation of hydrates generally result from the reaction of emulsified water with associated gas dissolved in oil [3].

Previously, the behavior of gas hydrate suspensions in oil was studied at temperatures above 0°C. However, the decomposition of gas hydrate in the temperature range from –30°C to 0°C is accompanied by covering hydrate particle surfaces with a dense ice crust. As a result, there is a sharp decrease in decomposition rate which allows the hydrate long-term existence in temperature and pressure ranges, where it is thermodynamically metastable [4]–[8]. This phenomenon was called self-preservation of gas hydrates. According to the published data, self-preservation is observed in particles with characteristic sizes of several hundreds of micrometers or greater [9], [10]. For example, Takeya *et al.* [9] observed pronounced self-preservation only for particles larger than

1mm; according to the data [10] characteristic sizes of hydrate particles having effective self-preservation are in the range of 200–300 μm under the pressure of about 0.7MPa.

II. EXPERIMENTAL SECTION

Hydrate suspensions were obtained using water-in-oil emulsions from different crude oils (Table I), n-decane and model solution.

TABLE I
OILS USED IN THE EXPERIMENTS

Characteristic of oil	Oil-1*	Oil-2**	Oil-3***	Oil-4****
Asphaltenes, wt %	-	0.1	2.2	9.9
Paraffins, wt %	-	2.3	5.1	1.1
Resins, wt %	6.4	19.7	5.1	31.1
Freezing point, °C	-	-43	+6	-
Density, kg·m ⁻³	830	858	863	965
Viscosity, mPa·s	-	19.3	25.1	7062.0

*Oil-1 – Yurubcheno – tohomskoe deposit

**Oil-2 – Verkhnechonskoe deposit

***Oil-3 – Gerasimovskoe deposit

****Oil-4 – Usinskoe deposit

The emulsions (1:1 by weight) were stirred with a mixer at 800rpm for 20min at room temperature. They were stable for a prolonged period. The preparation of the hydrate from the emulsion and gaseous methane at pressures from 6 to 9MPa and temperature of 1°C lasted for two months (t). The conversion of water into hydrate (y) was not less than 10%. The autoclave was then frozen up to liquid nitrogen temperature, and the frozen suspension was retrieved into the liquid nitrogen bath. After that a block specimen or a small portion of ground hydrate suspension (0.3 – 0.5g) was placed into a cell at liquid nitrogen temperature, and it allowed the specimen temperature and liberated gas volume (gas liberation curve) to be measured at atmospheric pressure (experimental technique was described in [11]). Furthermore, the suspension was characterized by low-temperature X-ray diffraction and studied with a scanning electron microscope

A. Low-Temperature X-Ray Diffraction

X-ray diffraction experiment was carried out at the 4th station of the VEPP-3 (Siberian Synchrotron and Terahertz Radiation, Institute of Nuclear Physics SB RAS). We applied the Debye-Scherrer scheme using the short synchrotron radiation ($\lambda = 0.3685\text{\AA}$) [12]. Some data were obtained in Lavrentyev Institute of Hydrodynamics of SB RAS with diffractometer Bruker D8 Advance equipped with low-temperature adapter TTK 450 Anton Paar. X-ray powder diffraction patterns were taken in 2 θ scanning mode in the

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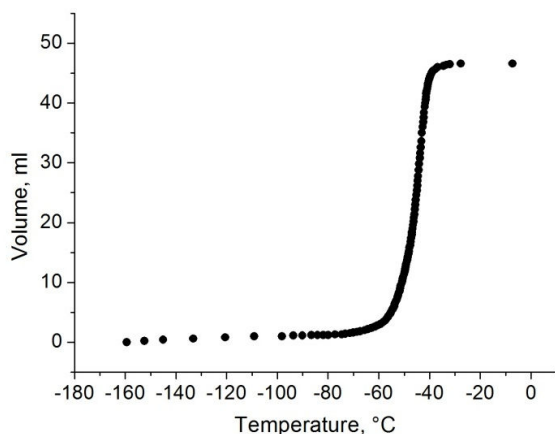
range of 5-45 degrees with step of 0.02 degree. Samples were placed into the holder previously cooled to -120°C .

B. Scanning Electron Microscopy

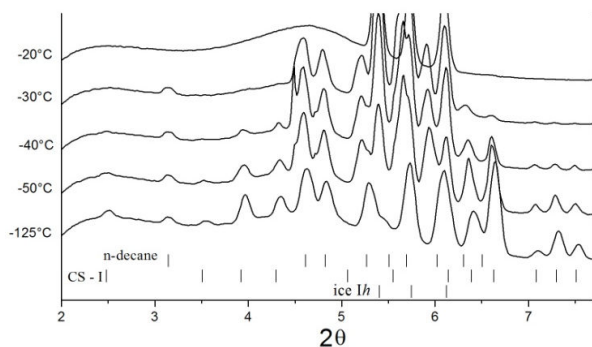
The scanning electron microscope is TM-1000, Hitachi; the specimens were placed on a metal disc located in the microscope vacuum chamber and cooled to liquid nitrogen temperature, which allowed images to be obtained without specimen decomposition.

III. RESULTS AND DISCUSSION

In all cases low-temperature X-ray diagrams corresponded to those expected for the mixture of cubic structure I of methane hydrate (CS-I) and ice *Ih* (there is solid decane if the dispersion medium is n-decane (Fig. 1 (b)) In the case of methane hydrate obtained from the water-in-n-decane emulsion ($y \approx 75\%$, $t = 1$ day) the curve of evolved gas from the sample corresponds to curves obtained for pure methane hydrates (Fig. 1 (a)). Hydrate decomposition occurs at temperature above -70°C . Deviation of methane hydrate decomposition temperature from the equilibrium value is due to the delay of the temperature rise in the sample compared with the temperature of the sample holder's wall.



(a)



(b)

Fig. 1 (a) Gas liberation curve of methane hydrate suspended in n-decane; (b) Diffraction patterns of methane hydrate suspended in n-decane

Behavior of methane hydrate suspended in the oils had distinctive features. Typical gas liberation curves are presented in Fig. 2 ($y \approx 85\%$, $t = 24$ days).

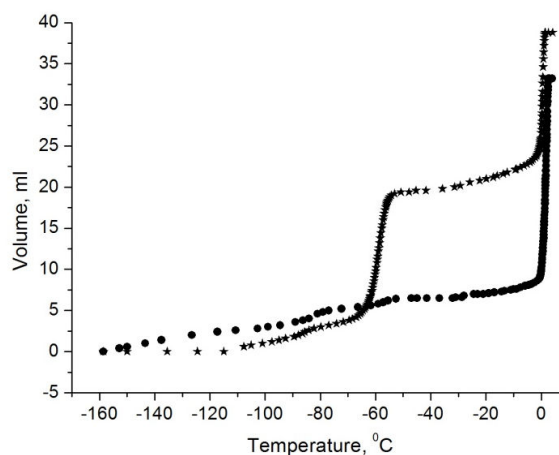


Fig. 2 The volume of gas evolved from frozen samples of a methane hydrate suspension in oil-2 as a function of temperature: (stars) powdered sample (fraction $< 0.25\text{mm}$), (circles) block sample (approximately 3mm)

We found out that gas liberation curves obtained for bulk and powdered specimens had qualitative differences. In case with the frozen suspension having the characteristic size of 3mm heated at $1 - 3\text{Kmin}^{-1}$ rate the gas liberation occurred at about 0°C . The exposure of such specimens at -20°C for 4 – 5 hours resulted in 2.5 – 4.5% gas loss from specimens. Taking into account that the equilibrium temperature of methane hydrate under atmospheric pressure is -80°C and the melting point of the oil emulsion component is -43°C , the self-preservation is the most likely reason for the observed behavior. Earlier it was reported in works [9], [10] if the size of gas hydrate particles is less than 1mm the self-preservation phenomenon will not occur. In our case gas hydrate particle size was $24 \pm 18\mu\text{m}$ (Fig. 3 (b)); it significantly increases in comparison with the size of water particles in the initial emulsion ($18 \pm 10\mu\text{m}$, Fig. 3 (a)).

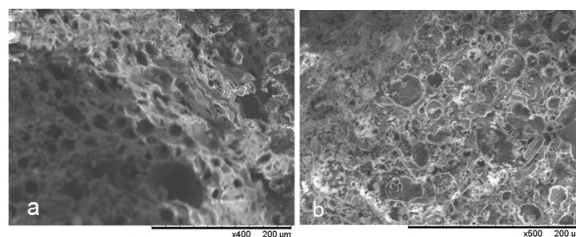


Fig. 3 (a) Microphotograph of frozen sample of initial water-in-oil emulsion from Verkhnechonskoe deposit, (b) Microphotograph of methane hydrate suspension sample in oil from Verkhnechonskoe deposit

The gas liberation curves for the powdered specimens of the frozen suspension (fraction $< 0.25\text{mm}$) had two steps, one of which matched the decomposition temperature of pure

methane hydrate (decomposition at a noticeable rate under our experimental conditions started on overheating by 10 – 20°C), whereas the second one was observed at about 0°C.

On carrying out the experiments with block of suspensions, the same phenomenon was observed in all the rest cases (Fig. 4). For oil-1 the parameters were as follows: $y \approx 90\%$, $t = 29$ days.

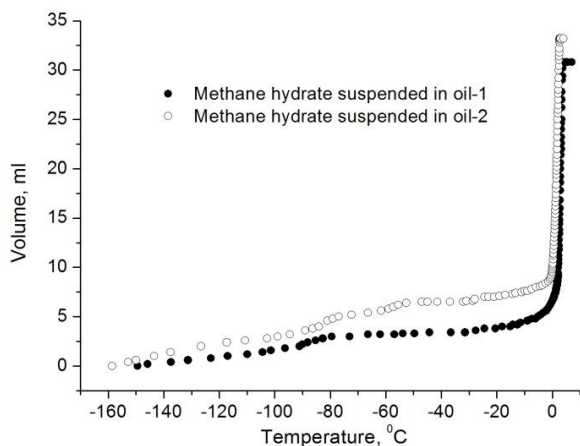


Fig. 4 Gas liberation curves of methane hydrate suspended in oil-1 (2). Block of suspensions with the characteristic size of 2-3mm was used

Fig. 5 shows behavior of methane hydrate dispersed in oil-4. There was the smallest amount of methane hydrate in comparison with all other systems ($y \approx 10\%$, $t = 21$ days). Slow mass transfer in the oil could be explained by significantly high viscosity (7062.0mPa·s).

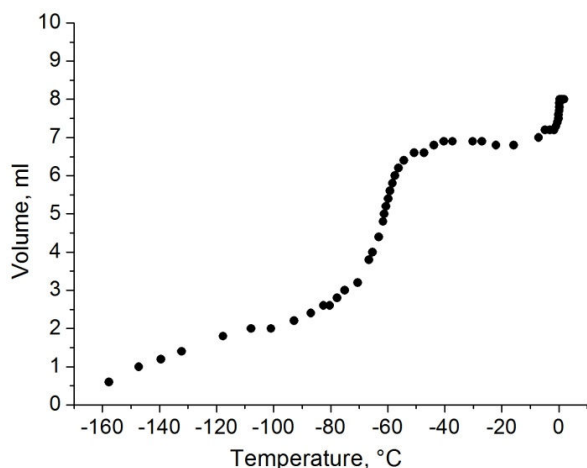


Fig. 5 Gas liberation curve of methane hydrate suspended in oil-4 (powdered sample)

We assumed that the existence of two gas liberation steps for powdered specimens was most likely explained by the fact that only those hydrate particles which directly contact the surface of frozen suspension particles undergo decomposition.

To prove our hypothesis the methane hydrate suspended in oil - 3 was separated into fractions by size. Data obtained for each fraction are illustrated in Fig. 6 ($y \approx 96\%$, $t = 72$ days). Let us assume that (1) all the frozen suspension particles have a spherical shape, (2) the suspension particle diameter is 0.375 mm (the middle of the size range for one fraction studied) and (3) the hydrate is uniformly distributed inside suspension particles. In this case, we can calculate the thickness of the spherical layer containing the amount of gas equal to the fraction of the gas liberated at the first stage (Fig. 6). For the data presented in Fig. 6 (empty circles) 81% of hydrate undergoes to self-preservation effect. The calculated thickness of the spherical layer is 0.025mm, *i.e.* the mean diameter of suspension particles, which does not contradict our assumptions.

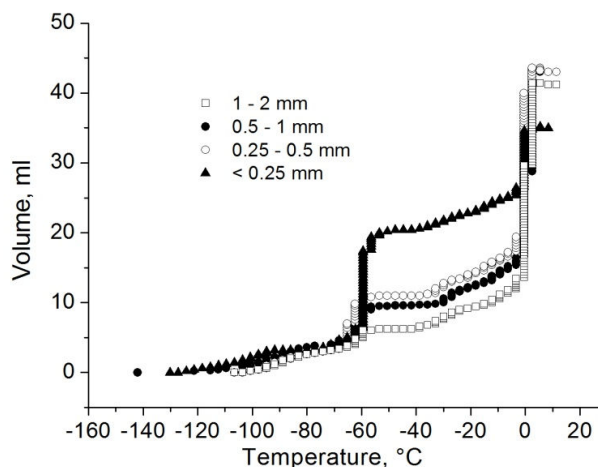


Fig. 6 Gas liberation curves of methane hydrate suspended in oil-3 (size ranges for fractions are indicated on the picture)

Self-preservation of hydrate particles suspended in oil with sizes less than 40 μm is undoubtedly caused by ice (decomposition takes place at 0°C). However, self-preservation of such small hydrate particles might be due to the sorbed film of heavy hydrophobic-hydrophilic oil components (asphaltenes, naphthenic acids etc.) on the surface of hydrate particles. The particles with a destroyed sorbed film are decomposed without any self-preservation. Further investigations in this area will be aimed at understanding the role of oil components. At present experiments with methane hydrate formed from water-in-solution of asphaltenes, resins and paraffins in n-decane emulsion were carried out (the amount of these components in solution equals to the one in oil-3; $y \approx 95\%$, $t = 59$ days). The technique of sample preparation does not differ from the one used for oils. The results of the sample analysis so obtained are shown in Fig. 7.

The similarity in the decomposition character of methane hydrate samples suspended in model and natural dispersion media up to -40°C is clearly observed (the solution with above components and oil-3, respectively). At the temperature higher than -40°C the hydrate in a model system begins to

decompose, but it partly retains up to the ice melting point. These data match those of X-ray powder diffractometry. The phases of n-decane, methane hydrate CS-I and ice I_h were found in the sample. This confirms our hypothesis that compounds sorbing on the hydrate surface influence self-preservation.

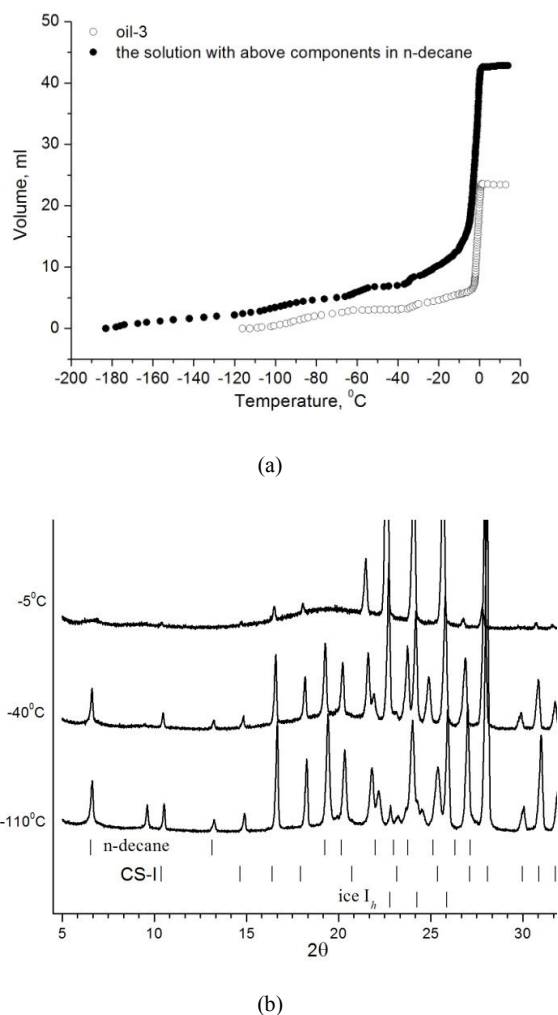


Fig. 4 Comparison of gas liberation curves of methane hydrate samples; Dispersion media are indicated on the (a) and diffraction patterns of methane hydrate suspended in the solution with above components - on the (b)

IV. CONCLUSIONS

Thus, we have described the efficient self-preservation of small ($< 42\mu\text{m}$) gas hydrate particles suspended in the oil matrix. Apparently, the size limitation for self-preservation of gas hydrate particles in oil suspensions is less pronounced than the one in conventional samples of gas hydrates.

The results can be applied for developing offshore and Eastern Siberian deposits. In addition, the data can be used to prevent hydrate plugs in oil recovery systems and eliminate the formation of gas hydrate block.

ACKNOWLEDGMENT

This study was supported by the Siberian Branch of the Russian Academy of Sciences (Integration project no. 19 for 2012 – 2014).

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