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Self-preservation behaviour of methane hydrate particles in oil suspensions

Andrey S. Stoporev,[a,b] Andrey Yu. Manakov,*[a,b] Lubov K. Altunina[c] and Andrey V. Bogoslovsky[c]

[a] *Department of Natural Sciences, Novosibirsk State University, 630090 Novosibirsk, Russian Federation*
[b] *A. V. Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation. Fax: +7 383 330 9489; e-mail: manakov@niic.nsc.ru*
[c] *Institute of Petroleum Chemistry, Siberian Branch of the Russian Academy of Sciences, 634021 Tomsk, Russian Federation*

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The efficient self-preservation of a methane gas hydrate has been described for the first time for small (less than 42 μm) ice-hydrate particles suspended in oil.

Gas hydrates are clathrate compounds in which the host framework is formed by water molecules, while the molecules of gases or highly volatile liquids are incorporated in the framework cavities.[1] Interest in gas hydrates primarily stems from the existence of huge natural gas reserves in a gas hydrate form in Earth's interior.[2] The prevention of gas hydrate formation in the production of oil and natural gas is also of great practical importance.[1,3,4] In oil production and in-field transportation, the formation of hydrates generally results from the reaction of emulsified water with associated gas dissolved in oil.[3,4]

Previously, the behaviour of gas hydrate suspensions in oil was studied at temperatures above 0 °C. However, the decomposition of gas hydrates in a temperature range from –30 to 0 °C is accompanied by the covering of hydrate particle surfaces by a dense ice crust. It results in an abrupt decrease in the decomposition rate, which enables the long-term existence of the hydrate intemperature and pressure ranges where it is thermodynamically metastable.[5–9] This phenomenon was called the self-preservation of gas hydrates. According to published data, self-preservation is observed in particles with a characteristic size of several hundreds of micrometers or greater. For example, Takeya *et al.*[10] observed pronounced self-preservation only for particles larger than 1 mm. In this work, we report experimental data to demonstrate that self-preservation occurs for a methane hydrate suspension in oil with a particle size smaller than 42 μm. The observed self-preservation is of importance for the prediction of the behaviour of hydrate suspensions in oil.

Hydrate suspensions were obtained using an emulsion of water in oil from the Verkhnechonskoe field (oil contained 0.1 wt% asphaltenes, 2.3 wt% paraffins, and 19.7 wt% oil resins; freezing point, –43 °C; specific density, 858 kg m^{-3}; and viscosity, 19.3 mPa s). The emulsion (1:1 by weight) was stirred with a mixer at 800 rpm for 20 min at room temperature. The emulsion had a density of 919 kg m^{-3} and a viscosity of 184.9 mPa s, and it was stable for a prolonged period. The preparation of the hydrate from the emulsion and gaseous methane at a pressure of 6.8 MPa and a temperature of 1 °C lasted two weeks. The conversion of water into hydrate was no smaller than 65%. The autoclave was then frozen to liquid nitrogen temperature, and the frozen suspension was retrieved into a liquid nitrogen bath. After that, a block specimen or a small portion of ground hydrate suspension (0.3–0.5 g) was placed at liquid nitrogen temperature in a cell that allowed the specimen temperature and liberated gas volume (gas liberation curve) to be measured at atmospheric pressure. Furthermore, the suspension was characterized by low-temperature powder X-ray diffraction and studied with a scanning electron microscope (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 the images to be obtained without decomposition of the specimens).

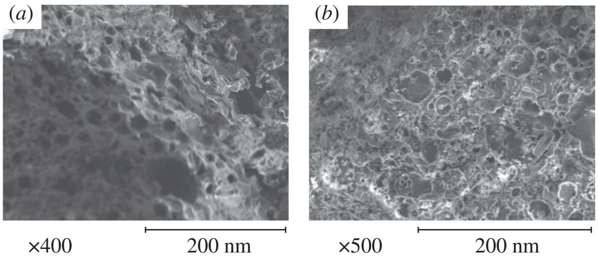

Figure 1 (*a*) Micrograph of a frozen specimen of the original water emulsion in oil from the Verkhnechonskoe field; (*b*) micrograph of a frozen specimen of a methane hydrate suspension in the oil.

As shown by electron microscopy, the size of ice-hydrate particles suspended in the oil matrix is 24±18 μm [Figure 1(*a*)], which is slightly larger than the size of water particles in the emulsion [18±10 μm, Figure 1(*b*)]. The low-temperature powder X-ray diagrams matched those expected for a mixture of methane hydrate (cubic structure I) and ice. Typical gas liberation curves are presented in Figure 2.

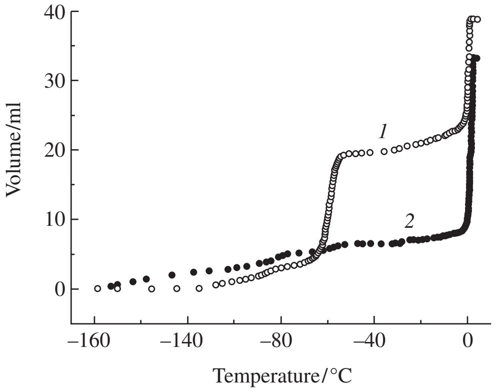

Figure 2 The volume of gas evolved from frozen specimens of a methane hydrate suspension in oil as a function of temperature: (*1*) powdered specimen (fraction < 0.25 mm), (*2*) block specimen (approximately 3 mm).

We found that the gas liberation curves obtained for bulk and powdered specimens had qualitative differences. In the frozen suspension with a characteristic size of 3 mm heated at a rate of 1–3 K min^{-1}, gas liberation occurred at about 0 °C. The exposure of such specimens at –20 °C for 4–5 h resulted in the loss of 2.5–4.5% gas from the specimen. 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 of hydrate particles is the most likely reason for the observed behaviour. The gas liberation curves for the powdered specimen of the frozen suspension (fraction of <0.25 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. We assumed that the most likely explanation for the existence of two gas liberation steps for the powdered specimens is that only those hydrate particles which directly contact the surface of the frozen suspension particles undergo decomposition. Let us assume that (1) all the frozen suspension particles have a spherical shape, (2) the particle diameter is 0.125 mm (the middle of the size range for the fraction studied) and (3) the hydrate is uniformly distributed inside the 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 (Figure 2). For the data provided in Figure 2, 47.2% of the entire gas liberated during the experiment was liberated at the first stage. The calculated thickness of the spherical layer is 0.024 mm, *i.e.* the mean diameter of the suspension particles, which does not contradict our assumptions.

Thus, we described the efficient self-preservation of small (<42 μm) gas hydrate particles suspended in an oil matrix. Apparently, the size limitation for self-preservation of gas hydrate particles in oil suspensions is less pronounced in comparison with conventional samples of gas hydrates (at least for the oil grade studied).

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