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Unusual examples of methane hydrate nucleation in bilayer water–oil systems

Andrey Yu. Manakov,[*a,b] **Tatyana P. Adamova**[a] **and Andrey S. Stoporev**[a,b]

[a] *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*
[b] *Novosibirsk State University, 630090 Novosibirsk, Russian Federation*

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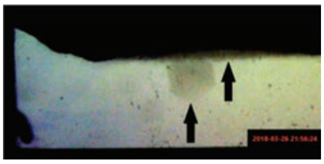
Visual investigation of the nucleation and growth of methane hydrate in a bilayer system of water and oil revealed hydrate nucleation to proceed not only on the water–oil contact surface but also beyond this boundary on the contact surface of water with glass.



Crystalline gas hydrates can contain up to 170 gas volumes in a hydrate volume.[1] According to estimations, naturally occurring methane hydrates contain $10^{14}–10^{16}$ m^3 of gas;[2–4] hence, they are a promising hydrocarbon source.[5] Gas hydrates play important roles in many technological processes.[6] The formation of hydrate plugs is a problem for the production and field pipeline transport of oil and natural gas in subsea systems and in regions with cold climate.[7] The most unusual application of hydrates is their use in pharmaceutics.[8] The development of hydrate prevention methods for oil production requires data on hydrate formation and decomposition in oil.[7,9,10] The behavior of oil disperse systems depends on the presence of an adsorption layer of heavy oil components at the interface.[11] According to current concepts, a hydrate is formed in oil disperse systems as a film at the water–oil boundary.[7,9,10] Gas hydrate nucleation proceeds at the boundary of water with a phase rich in the hydrate-forming component (a hydrate-forming gas, a solution of the hydrate-forming gas in organic liquid, *etc*.).[12–19] Further growth of the hydrate can proceed both in a water phase and in a phase rich in the hydrate-forming component, and it is limited by the diffusion of reagents (gas or water, respectively) through the hydrate shell. The presence of an adsorption layer affects hydrate nucleation in heterogeneous systems.[20] Nucleation is slowed down substantially on the adsorption of oil components.[21] Here, we report on unusual examples of methane hydrate nucleation observed experimentally in two-layer water–oil–methane systems in a glass cell. Primary nucleation and growth of the hydrate occured on the water–cuvette wall boundary; hydrate grow at the water–oil surface was observed only after the front of the growing hydrate touched this surface.

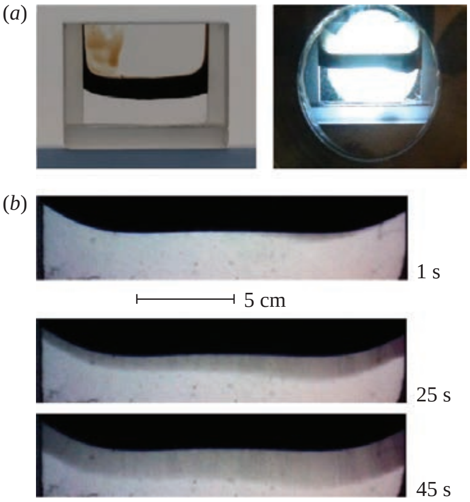


Figure 1 (*a*) Left, the cuvette with water and oil; right, the cuvette loaded into the apparatus. (*b*) Different stages of growth of needle-like crystals in the nucleation and growth of a hydrate at the water–oil interface. The dark field above is oil, the light below is water. The growing darkened zone corresponds to the needle-like crystals of the hydrate growing from the water–oil boundary to the bottom of the cuvette.

We experimentally studied gas hydrate nucleation and growth in a two-layer water–oil system (Figure 1).[†] In approximately 70% of the experiments, hydrate nucleation proceeded near the water–oil boundary. Note that, in the experiments with pure water and a two-layer water–decane system, nucleation occurred in this region in 100% cases. Figure 1(*b*) illustrates typical hydrate formation and growth in the two-layer water–oil system in the case of nucleation near the water–oil boundary. A thin hydrate film at the boundary is not seen with the magnification used in this work; however, hydrate growth manifests itself as the ingrowth of its needle crystals not more than 0.05 mm thick towards the normal to the surface of water–oil contact. We speculate that these crystals are formed from the methane dissolved in water and their growth rate is limited by methane diffusion through the

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[†] The nucleation and growth of hydrates were studied by continuous video filming in the transmission mode. A custom-made high-pressure apparatus with a cylindrical working chamber (inner diameter, 32 mm; height, 45 mm) was used. A cell of borosilicate optical glass K8 with a thickness of 3 mm and a width of 18 mm with oil and water was put inside the chamber [see Figure 1(*a*)]. Temperature and methane pressure in the chamber were controlled to within ±0.2 °C and ±0.1 MPa, respectively. Before experiments, the cell was washed with methane, and the methane working pressure of 12–13 MPa was set. The sample was kept for 6–12 h to saturate oil and water with methane. Experiments were carried out at –5 °C (supercooling was 19.9–20.5 °C). Methane of 99.98% purity and distilled water were used. The test oil from a deposit of West Siberia had the following characteristics: density, 895 kg m^{-3}; viscosity, 7.3 mPa s; pour point, –10.4 °C; and asphaltene, paraffin and resin contents, 0.67, 4.39 and 5.07 wt%, respectively.

water phase. On heating, these crystals did not decompose at a temperature up to 14 °C, which proves their hydrate nature.

An unexpected result of these experiments was hydrate nucleation at a boundary between water and the cell wall, which was detected in approximately 30% of cases. This was observed as the sudden emergence of a growing blackout region in the water phase. In many cases, at the beginning of growth, this region had a regular shape (square, triangle). The growth of this region could start directly at an arbitrary point on cell wall (without touching the water–oil contact surface, Figure 2) or from the sidewall or bottom of the cell (Figure 3). The growth of needle-like crystals in the normal direction to the water–oil contact surface, characteristic of hydrate nucleation and growth on this surface, started after the blackout region touched the surface of water–oil contact [*cf*. Figure 1(*b*) and Figures 2, 3]. The blackout region continued growing. The resulting crystals and the blackout region at the cell wall did not disappear up to 14 °C, which corresponds to the equilibrium temperature of methane hydrate at the experimental pressure. Thus, the formed substance is methane hydrate. We interpret the observed phenomena as a result of the primary nucleation of the hydrate on the surface of water–glass contact and the secondary nucleation of the hydrate on the surface of water–oil contact when this surface is touched by the hydrate growing at the cell wall. Therefore, the visible blackout region is a layer of methane hydrate growing over the cell wall. The regular shape of this region, observed in the majority of cases, allows us to assume that this is a single crystal. Indeed, the most common gas hydrate structures are cubic in symmetry; hence, the projections of their crystals may be rectangular or triangular,[22] which corresponds to the shape of the growing blackout regions (hydrate). The linear growth rate of the sides of blackout figure varied within a range of 0.035–0.046 mm s^{-1}.

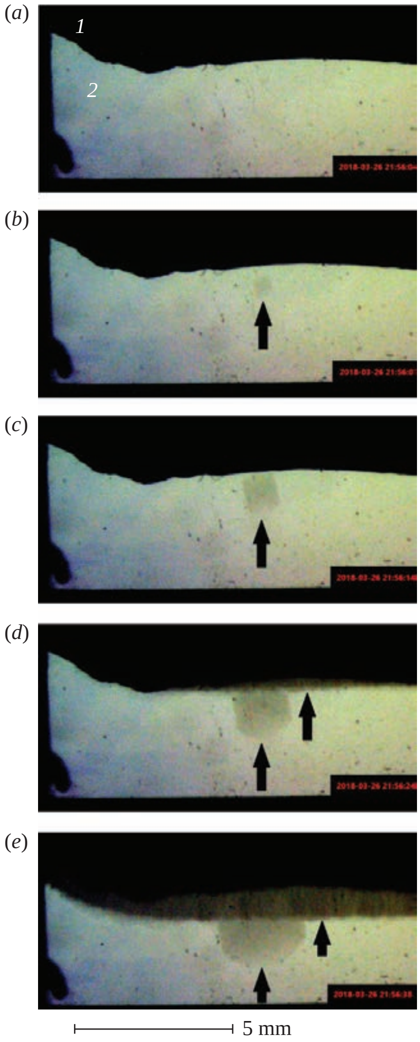

Figure 2 Nucleation and growth of methane hydrate crystal on the surface of the contact between water and the cuvette wall; (*1*) oil, (2) water. The crystal of the hydrate on the wall of the cuvette and the growing needle hydrate crystals are indicated by arrows. (*a*) View before the crystal appearance; time, 0 s. (*b*) The appearance of a square crystal on the cell wall (darkened square); time, 3 s. (*c*) Growth of the square crystal hydrate, the moment just before it comes into contact with the water–oil boundary; time, 10 s. (*d*) The growing hydrate crystal touched the water–oil boundary, the hydrate film on the water–oil surface and needle hydrate crystals began to grow; time, 17 s. (*e*) Further growth of the hydrate; time, 31 s.

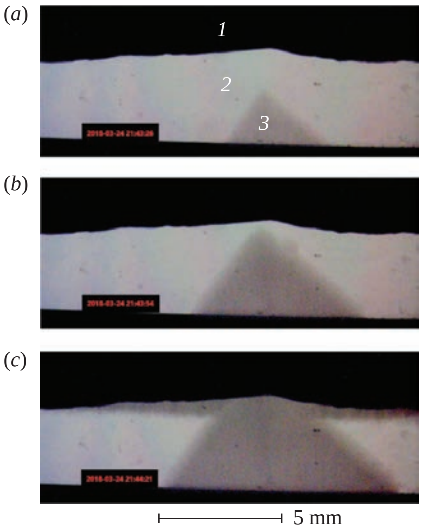

Figure 3 Nucleation and growth of methane hydrate crystal on the surface of the contact between the water and the bottom of the cuvette; (*1*) oil, (*2*) water, (*3*) hydrate crystal. Different stages of growth of the triangular crystal of hydrate from the bottom of the cuvette: (*a*) 25 and (*b*) 53 s. (*c*) The growing crystal of the hydrate was in contact with the water–oil boundary, the growth of the hydrate film over the water–oil surface and the growth of the filamentous hydrate crystals towards the bottom began. Time, 80 s.

The growing blackout regions of the hydrate were localized at cell walls at a distance of 0.5 to 3 mm from the water–oil boundary, so their growth could proceed only from methane dissolved in water. According to published data,[23,24] methane solubility in water at –5°C and 12 MPa in equilibrium with the hydrate and in the absence of the hydrate can be estimated at 7.1×10^{-4} and 6.0×10^{-3} (the molar fractions of gas in water), respectively. The simplest recalculation, for a cell thickness of 3 mm, shows that this dissolved gas amount is sufficient for the formation of a hydrate layer 0.12 mm thick on one of the water–glass contact surfaces. The thickness of well visible needle-like hydrate crystals [Figure 1(*b*)] is approximately two times smaller, and the amount of methane in the aqueous solution is sufficient for the formation of the observed hydrate amount. The reasons for hydrate nucleation beyond the water–oil contact surface are considered below. First, note that there is no principal prohibition of hydrate nucleation at any point of the water–oil–gas system because the thermodynamic activities of the components of this system in equilibrium (and, hence, the driving force of hydrate formation) are the same. This consideration is well illustrated by the possibility of hydrate formation from a homogeneous aqueous solution of gas under natural conditions.[25] In terms of mass transfer, the most favorable conditions for hydrate growth occur near the surface of water contact with a phase rich in the hydrate-forming agent. Correspondingly, for the sufficiently high rate of hydrate nucleation at the surface of water contact with the phase rich in the hydrate-forming agent or at the line of contact water–phase rich in the hydrate-forming agent–the wall of the reaction vessel, noticeable amounts of the hydrate will be formed exactly in this region. This situation was observed in the experiments described previously.[12–17] It is known that the rates of methane hydrate nucleation at the water–oil boundary can decrease by several orders of magnitude in comparison with the nucleation rates at water–methane boundary and at the boundary of water with decane saturated with methane.[21] Under these conditions, the presence of active hydrate nucleation centers at the surfaces in the system, other than the surface of water contact with the phase rich in the hydrate-forming agent, can cause rapid hydrate formation at these centers, which was experimentally observed in this work. Note that the growth of methane hydrate crystals on the wall of the glass cell above the oil phase is similar to the epitaxial hydrate growth reported previously.[26] We assumed that one of the faces of methane hydrate crystals has affinity to the glass surface used in this work. In this case, an increased activity of the glass as a promoter of hydrate formation may be expected.

Thus, the nucleation and growth of methane hydrate beyond the water–oil contact surface was demonstrated experimentally for the first time in the water–oil–gaseous hydrate-forming agent systems. The results obtained demonstrate the importance of the gas hydrate nucleation and growth in multicomponent systems with a large number of different interfaces and the necessity to take into account the behavior of these test systems in the analysis of hydrate formation in real systems.

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