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Effect of reactor wall material on the nucleation of methane hydrate in water-in-oil emulsions

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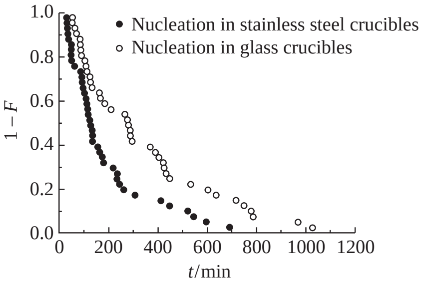
The material of container walls may have a substantial effect on the rate of methane hydrate nucleation in a water-in-oil emulsion in this container, though the wall–emulsion contact surface is more than two orders of magnitude smaller than the surface of contacts between water and oil in this emulsion. The data obtained allow the efficiency of gas hydrate nucleation on various types of surfaces formed during the production and transportation of oil at oil and gas deposits to be evaluated.



Gas hydrates are inclusion compounds with a host framework formed by water molecules, while guest components (gases or low-boiling liquids) occupy the cavities of this framework.[1] The thermodynamic conditions for the stability of gas hydrates were studied.[1–4] The prevention of hydrate formation during oil production and the transportation of multiphase oil–gas–reservoir brine flows is a problem of considerable current interest.[5,6] Hydrate formation results from the reaction of oil-dissolved associated petroleum gas with water emulsified in oil.[5,6] The nucleation of gas hydrates in these systems occurs at the water–oil interface.[7–10] This is evidenced by the large water–oil contact areas in emulsions[10] and the reported effect of oil composition on the formation of hydrates and their plugs in oil systems.[3,9,11,12] It is well known that the nucleation of gas hydrates may be affected by the presence of nucleation centers, such as microparticles and solid surfaces.[13–17] The nucleation of gas mixture hydrates (90 mol% methane and 10 mol% propane) in the presence of either water–gas–stainless steel or water–gas–glass three-phase contact lines in the systems was described.[16] The rates of hydrate nucleation determined in these systems and normalized to the lengths of three-phase lines were close to each other, and this fact indicated that nucleation proceeds at the three-phase contact lines.[16] Note that hydrate nucleation was not observed at the other contact lines such as water–*n*-decane–Teflon, water–*n*-heptane–polycarbonate and water–gas–Teflon.[8,18,19] In these cases, nucleation took place only at the interface between water and an organic phase or water and gas. To the best of our knowledge, the effect of a reactor wall material on the nucleation of gas hydrates in both regular and reverse emulsions has not been reported so far. Here, we present the first results on the effect of a reactor wall material on the nucleation of methane hydrate in water-in-oil emulsion.

The experiments were performed in crucibles with stainless steel or glass walls under static conditions.[†] To describe nucleation processes, the survival function 1 – *F* is often used. This function depicts the time dependence of the fraction of samples in which crystallization did not occur at a given point in time.[9,16,17] For every moment of time, the value 1 – *F* corresponds to a ratio between the number of experiments in which nucleation did not occur and the total number of experiments. As a rule, the nucleation of gas hydrates occurs at the gas–water and liquid

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[†] The methane hydrate nucleation in the emulsion of water in oil from the Kazan deposit (KazM; density, 0.845 g cm^{-3}; viscosity, 6.0 mPa s; asphaltenes, 3.5 wt%; resins, 10.2 wt%; and paraffins, 4.8 wt%) was studied by thermal analysis at 12.5 MPa and –5 °C (the supercooling value ΔT was 19.7 °C). The water-in-oil emulsion (50 wt%) was prepared by stirring a mixture of water and oil at 800 rpm and room temperature for 20 min. The emulsion was stable for several months. Four samples of the emulsion were loaded into glass (~70 wt% SiO_2, ~2 wt% Al_2O_3, ~10 wt% CaO + MgO, and ~15 wt% Na_2O + K_2O) or stainless steel (Russian analogue of AISI 321) crucibles inserted into a sample holder made of aluminum. The contact area between the emulsion and crucible walls was 0.47×10^{-3} m^2, and the area of the water–oil interface was 0.15 m^2 (calculated from droplet size distribution measured based on microscopic images). The geometry of the crucibles and sample mass were the same in all experiments. Then, the sample holder was put into an autoclave with a chromel–alumel thermocouple introduced into the sample. The autoclave was purged with methane; then, the necessary pressure was set, and the sample was saturated with the gas at 20 °C for 15 h. After that, the high-pressure apparatus was placed in a thermostat and cooled at a rate of 0.84 K min^{-1}. The time from the transition of the system into a metastable state to the moment when the required supercooling (19.7 °C) was reached was 24 min. Then, the autoclave was kept at this temperature for 22 h. The measurement procedure was described in detail elsewhere.[9] After each particular experiment, the crucibles were washed with *n*-pentane and THF and dried; then, the experimental run was repeated with a new portion of the emulsion. Experiments with 40 emulsion samples were carried out for each test system (10 experiments with 4 samples in each case).

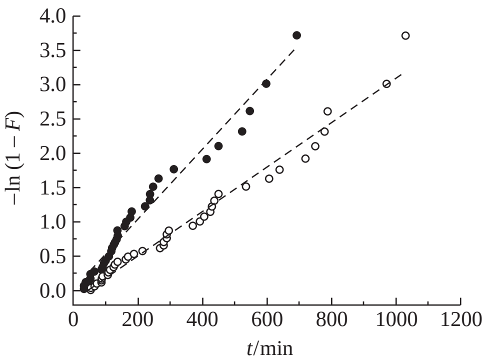

Figure 1 Survival curves for the liquid phase (water) in semilogarithmic coordinates (the nucleation of methane hydrate): (●) emulsion of water in KazM oil–stainless steel and (○) – emulsion of water in KazM oil–glass; dash lines are the approximation.

hydrocarbon–water interfaces or on a solid substrate rather than in the bulk of liquid, and the time dependence of 1 – *F* can be described by the following equation:[14]

$$-\ln(1 - F) = J(t - t_0) = \textstyle\sum_i X_i J_i(t - t_0),\ \ X_i = s_j,\, l_k,\, m_n. \qquad (1)$$

Here, t_0 is the moment of time starting from which the sample cools below the equilibrium temperature and becomes metastable, J_i is the rate of nucleation at an interface with area s_j, a line of three-phase contact with a length of l_k[16] or mineral particles with concentration m_n. Therefore, the nucleation of a new phase in the sample may proceed along different competing routes. In our case, identical samples were loaded into the cells. A difference between two series of experiments was only in the material of crucibles (stainless steel and glass). Figure 1 shows the resulting survival curves in semilogarithmic coordinates. According to equation (1), the slope angle is equal to the sum of the products of specific nucleation rates of methane hydrate at the contact surfaces/lines or nucleation centers and the amount (number) of the corresponding surfaces/lines/centers. The total rate of hydrate nucleation in a sample for the steel crucibles is higher than that for glass crucibles (5.14×10^{-3} and 3.24×10^{-3} min^{-1}, respectively). The first events of the appearance of methane hydrate in steel and glass cells were recorded 32.7 and 55.3 min later, respectively, after the system passed into the metastable state.

As considered above, the observed nucleation rate may be the sum of the rates of nucleation on the centers of different types. The emulsion samples were taken from the same vessel after thorough mixing; thus, the areas of water–oil interfaces and the sets of suspended solid particles in our samples were identical. Therefore, the difference in the observed nucleation rates can be only due to differences in the materials of crucible walls. For the hydrate formation, a contact between the aqueous phase and the hydrate-forming agent rich phase is necessary; in our case, the latter is oil saturated with methane. Therefore, the processes responsible for different observable nucleation rates in our experiments can occur at the three-phase contact lines of crucible wall–water–oil and at the two-phase water–oil interface. The effect of crucible walls can be caused by the facts that (i) different materials of crucible walls possess different nucleation activity; (ii) different materials bear separate regions possessing high nucleation activity or these regions are formed in the interaction of wall materials with oil components; and (iii) the length of the contact boundary at which nucleation occurs is substantially different for different materials. Note that the length of the contacts of water–stainless steel–oil and water–glass–oil should be dependent on the wettability of crucible walls with the emulsion components.

Therefore, it was found that the material of reactor walls has a substantial effect on the nucleation of gas hydrates in emulsions. This result is unexpected because the contact area between the emulsion and the walls in our experiments was smaller by a factor of 318 than the water–oil contact area in the emulsion. Note that the active role of container walls in hydrate nucleation on contact surfaces between water and organic liquid saturated with gas has not been reported yet; as a rule, the hydrate formation was observed at an arbitrary point of the interface.[8,18,19] Based on the experimental data obtained in this work, gas hydrate nucleation on different types of surfaces in multiphase oil–gas–reservoir brine flows during the production and transportation of oil at oil and gas deposits can be relatively estimated. These results are of practical interest for the prediction of hydrate formation under field conditions. It may be assumed that the materials of pipelines and devices may have a substantial effect on the dynamics of hydrate formation in these systems.

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