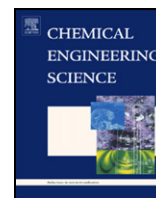




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Evidence of liquid water formation during methane hydrates dissociation below the ice point

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ABSTRACT

Dissociation of small methane hydrate samples formed from water droplets of size 0.25–2.5 mm has been investigated below the ice melting point in the temperature range of 240–273 K, where the self-preservation effect is observed for bulk hydrates. The experiments included optical microscopy observations combined with P – T measurements of the dissociation conditions for the methane hydrates. For the first time, the formation of supercooled liquid water during the hydrate dissociation was reliably detected in the temperature range of 253–273 K. The formation of the liquid phase was visually observed. The induction time of the ice nucleation for the metastable liquid water depended from the dissociation temperature and a size of water droplets formed during the hydrate dissociation. It was found that in the temperature range of 253–273 K values of the dissociation pressure for the small hydrate samples fall on the extension of the water–hydrate–gas equilibrium curve into the metastable region where supercooled water exist. The average molar enthalpy of 51.7 kJ/mol for the dissociation of the small methane hydrate samples in the temperature range of 253–273 K was calculated using Clausius–Clapeyron equation. This value agrees with the enthalpy of dissociation of bulk methane hydrates into water and gas at temperatures above 273 K.

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1. Introduction

Once of the most intriguing results in the study of the kinetics of gas hydrate formation obtained in the recent years is the discovery of the anomalously low dissociation rate of gas hydrates below the ice melting point (Davidson et al., 1986; Yakushev and Istomin, 1992). Under specific conditions, the gas hydrate dissociation rate decreased to zero, so the phenomenon was named self-preservation (Yakushev and Istomin, 1992) or anomalous preservation of gas hydrates (Stern et al., 2001).

It is assumed (Davidson et al., 1986; Yakushev and Istomin, 1992) that the reason for the anomalously low dissociation rate of gas hydrates is the formation on their surface of an ice shell, which prevents the gas from freely leaving the hydrates. The formation of ice upon the hydrate dissociation below the ice point was revealed by X-ray and neutron diffraction techniques (Kufs et al., 2004; Ogienko et al., 2006; Takeya S. et al., 2001, 2005) and using a confocal scanning microscope (Shimada et al., 2005). However, the mechanism of ice formation and development of an impermeable ice shell on the surface of gas hydrates is still poorly understood. Moreover, the simple

formation of ice does not explain the existence of the temperature range of 242–271 K within which the anomalously low dissociation rate of gas hydrates is observed with a minimum at around 268 K (Stern et al., 2001).

Previously we showed (Melnikov et al., 2003; Mel'nikov et al., 2003, 2007), that dissociation of propane hydrates at $T < 273$ K proceeded through the stage of the formation of metastable (supercooled) liquid water, which then converted into ice. Takeya K. et al. (2005) suggested, from ESR data on the activation energy of methyl radical decay in γ -ray irradiated methane hydrate, that methane hydrate dissociation in the temperature range of 235–260 K generated supercooled water instead of ice. However, additional experiments showed that the methyl radical decay was not caused by dissociation of methane hydrate (Takeya et al., 2007). It is worth noting that the dissociation scheme hydrate \rightarrow liquid water \rightarrow ice + gas at temperatures below 273 K was first suggested by Makogon (1961, 1981). Upon dissociation of gas hydrates of natural gas at 238 K and 0.5 MPa, Makogon visually observed appearance of droplets of liquid and their subsequent solidification. However, our thermodynamic estimates showed that the liquid droplets observed by Makogon upon the hydrate dissociation could be condensed components of natural gas, which then converted back into hydrates, but of another composition. Direct visual observation of rapidly freezing water formed during the gas hydrate dissociation below the ice melting point

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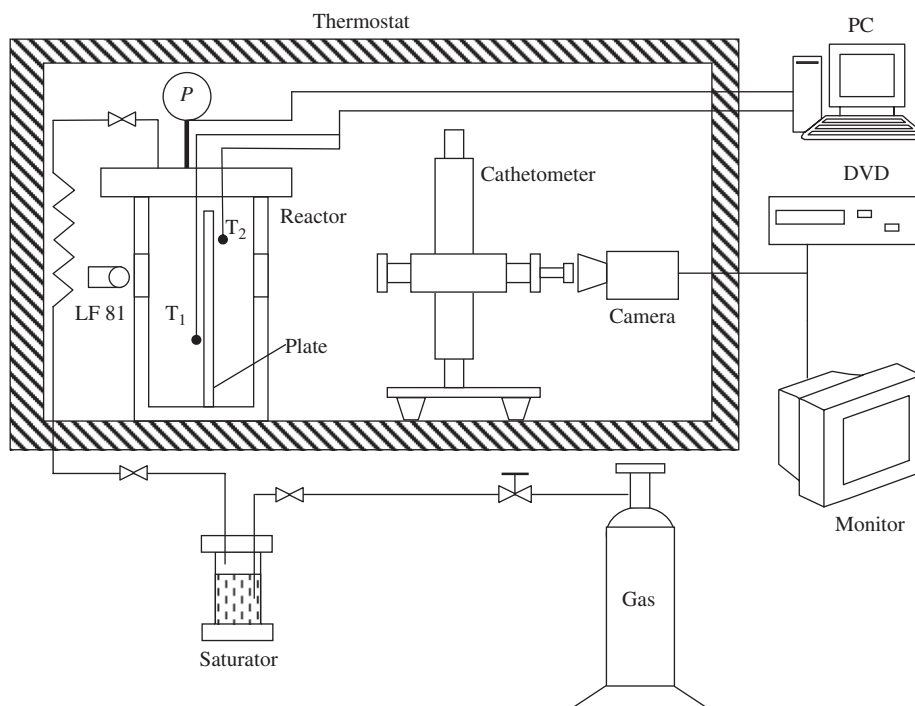


Fig. 1. Scheme of the setup. LF 81 is a light-emitting diode; T_1 and T_2 are thermocouples.

requires a special procedure of hydrate synthesis and dissociation, and it does not always possible. Probably because of this, no convincing evidence is available in the literature for the formation of liquid water during methane hydrate dissociation below 273 K. At the same time the idea of the formation of an intermediate metastable phase may be profitable to explain the bounds for the temperature interval 242–271 K within which the anomalously low dissociation rates of methane hydrates are observed. The temperature about 233 K corresponds to that of the homogeneous nucleation of water (a minimal temperature to which liquid water can be overcooled) (Angell, 1983; Debenedetti, 2003). Ogienko et al. (2006) suggested that the mechanism of the methane hydrate self-preservation is solely associated with the mode of water crystallization. At low temperatures the water, produced during the hydrate dissociation, freezes immediately to form single uniformly sized crystals (also, a direct hydrate to solid ice transition is possible), whereas at higher temperature, the produced water forms a thin liquid film on the hydrate surface and freezes generating an impermeable ice shell. Istomin et al. (2006b) proposed the similar mechanism of the ice shell formation from the metastable liquid water on the hydrate surface. The formation of the contiguous ice cover on the hydrate surface was observed at temperatures above 240 K, while at temperatures below 230–240 K the ice cover was broken up into individual small ice crystallites (Kuks et al., 2004; Shimada et al., 2005).

This work deals with obtaining direct evidence for the formation of metastable (supercooled) water during dissociation of methane hydrates at temperatures below the ice point. For this aim, we used a special procedure of visual observation of dissociation of small methane hydrate samples formed from water droplets combined with measurements of the P – T hydrate dissociation conditions. It is common knowledge that metastable states are detected more often and much more supercooling is achieved upon crystallization for small samples than for bulk liquid (Angell, 1983; Debenedetti, 2003; Skripov, 1974).

2. Experimental section

2.1. Experimental apparatus

The schematic diagram of the experimental apparatus used in the present study is shown in Fig. 1. Its main element is a high-pressure reactor, within which hydrates are formed and dissociate under controlled conditions. The reactor of 100 cm³ useful interior volume was made of stainless steel. The lateral surface of the reactor was equipped with two quartz viewing windows 15 mm in diameter. The reactor was placed in a cool room (air thermostat) with a volume of 8 m³. Two copper–constantan thermocouples were used to monitor the temperature inside the reactor. The layout of the thermocouples is shown in Fig. 1. The temperature inside the reactor was maintained to an accuracy of ± 0.1 K. The pressure in the reactor was measured by a 10 MPa full-scale Wika transducer with an accuracy of 0.5% with respect to the full scale. The pressure and temperature were monitored using an in-house data acquisition equipment and software. A cathetometer was used for optical observation of hydrate formation/dissociation in the reactor. The ocular of the cathetometer telescope was fitted with a digital camera. The image from the camera was displayed in parallel on a screen of a monitor and recorded by a DVD recorder. Image processing and image analysis were performed using the Pinnacle Studio Plus[®] v.10 hardware/software and the PhotoFinish[®] 4.0 software.

2.2. Experimental procedure

Pure methane (99.9 mol%) and distilled water were used for hydrate formation. The procedure to produce the hydrate samples was as follows. Water in an amount of 1.5–2.5 g was sprayed on a transparent Plexiglas plate previously cooled to 253 K to form frozen droplets (ice particles) of size 0.25–2.5 mm and about 0.3 mm thick. The plate with the frozen droplets was mounted vertically inside the

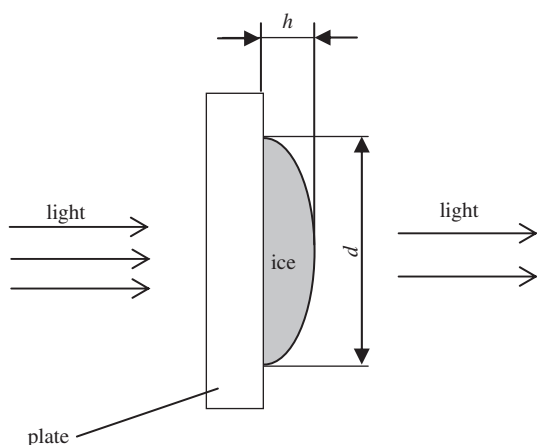


Fig. 2. Scheme of disposition of a frozen water droplet (ice) at the plate in the reactor. $d = 0.25\text{--}2.5\text{ mm}$ and $h = 0.3\text{ mm}$.

reactor between the viewing windows, Fig. 2. Then the reactor was evacuated and charged with methane at a pressure of 5–8 MPa. All activities related to the assembly of the reactor, its evacuation and charging with gas were carried out in the cool room at temperatures of 258–263 K. To initiate rapid hydrate formation and growth, the reactor with pressurized gas and the frozen water droplets was heated slowly above the ice melting point. It is known that slow melting of the ice facilitates the hydrate forming reaction (Hwang et al., 1990; Stern et al., 1996). It should be noted that our numerous attempts to synthesize methane hydrate directly from fresh water droplets (without freezing–thawing) failed. In the experiments with methane and fresh water droplets, hydrates were not formed within 48 h at 8 MPa and 273.5 K.

Hydrates, ice and water on the monitor screen were distinguished by the degree of roughness of their surface and the color. The sample history and P – T conditions within the reactor were taken into account in addition to visual observation to identify the different phases observed upon hydrate formation/dissociation. Only the ice is presented in Fig. 3(a), where $P = 0$ and $T = 259\text{ K}$ (just before the reactor was charged with methane). In Fig. 3(c), the observed solid at 5 MPa and 274 K can be only the hydrate. Because hydrate nucleation has a stochastic nature (Englezos, 1996), hydrates were not formed at a time on different droplets. We observed that the induction time for hydrate nucleation on the different droplets changed from a few hours to tens of hours even in the same experiment, Fig. 3(b). At thermobaric conditions of hydrate formation from ice, the chemical potential of water in the hydrate is lower than the chemical potential of water in the ice. In this case the equilibrium water vapor pressure over ice is higher than one over hydrate, and diffusion transfer of water molecules from ice to hydrate through the gas phase is possible. In other words, when ice and hydrate particles are present inside the reactor at the conditions of hydrate formation, ice will sublime, whereas the hydrate will grow. This fact can explain disappearance of the some small solid particles in Figs. 3(b) and (c), which is observed in Fig 3(a) as the ice particles.

Hydrates shown in Fig. 3 (particularly in Fig. 3(b)) are most likely to be a hydrate shell, and unreacted water (ice) can exist under the shell. Because we used a small amount of water within the reactor, the pressure drop during the gas hydrate formation was insufficient to estimate reliably the amount of water converted into hydrate. The freezing/melting procedure (cooling of the reactor with the hydrate samples to 250 K and its heating to 274 K) was repeated 2–3 times to provide the additional water conversion into gas hydrates. It takes about 3 h to cool the reactor from 274 to 250 K and about 5 h for

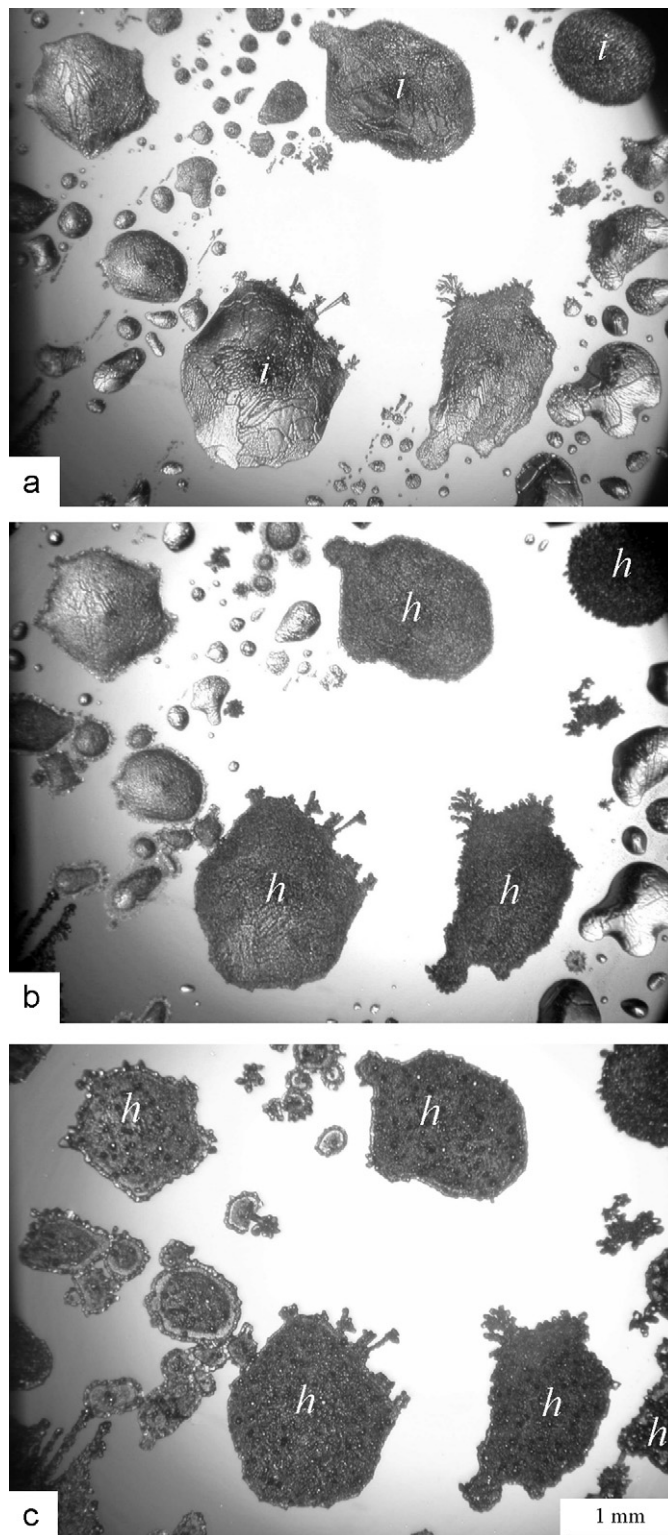


Fig. 3. Methane hydrates formation from frozen water droplets upon heating. (a) Time = 0 (just before pressurization), $P = 0$, $T = 259\text{ K}$; (b) time = 9 h, $P = 5\text{ MPa}$, $T = 270\text{ K}$; (c) time = 24 h, $P = 5\text{ MPa}$, $T = 274\text{ K}$. i is ice, h is hydrate.

its succeeding heating to 274 K. Before the each freezing/melting procedure the reactor with the hydrate samples was held at 274 K and 5.5–9.5 MPa no less than 16 h. The hydrate formation runs, as a rule, were carried out continuously in aggregate for 60–72 h.

Table 1
Dissociation pressure of methane hydrate formed from water droplets

T (K)	P (MPa)
240 K < T < 253 K	
240.2	0.45
243.2	0.57
248.5	0.77
249.7	0.65
253 K < T < 273 K	
253.2	0.39
254.2	0.44
256.2	0.51
257.9	0.61
259.2	0.69
262.0	0.89
263.2	1.00
264.8	1.20
266.1	1.34
268.0	1.63
268.2	1.61
269.4	1.87
270.9	2.10
272.3	2.34
T > 273 K	
273.5	2.74
274.0	2.88
274.6	3.04
274.9	3.12
276.2	3.53
277.0	3.79
279.0	4.73

After the synthesis, a specified temperature was set in the cool room and the reactor with the hydrate samples was kept at this temperature for another 2 h. Then, methane pressure was lowered with the rate about 0.15–0.2 MPa/min to values just above the water(ice)–hydrate–gas equilibrium boundary by venting gas from the reactor. The phase equilibrium data were taken from Sloan and Koh (2007). Once the pressure was lowered, the samples temperature re-equilibrated with the cool room temperature during the next hour, then a pressure in the reactor was lowered with the rate of 0.02 MPa/min. No temperature change was detected in the reactor for this rate of the pressure lowering. The dissociation of the hydrates was judged from the visually observed collapse of the rough surface of the hydrates, the appearance of smooth islands of the liquid phase on hydrate particles, and evolution of gas bubbles from the liquid. The pressure at which the first changes in hydrate particles were visually observed was taken as the methane hydrate dissociation pressure P_d at the given temperature. Once the hydrates began to dissociate, the venting valve was closed and the pressure drop in the reactor was stopped.

3. Results and discussion

The measured values of the methane hydrate dissociation pressure P_d for different temperatures are summarized in Table 1. Comparison of P_d and the equilibrium pressures of hydrate formation for methane bulk hydrates P_{eq} calculated by the CSMGem program (Sloan and Koh, 2007) is shown in Fig. 4. In semilogarithmic $\ln P - 1/T$ coordinates, the curve of the equilibrium pressure of gas hydrate formation $P_{eq} = P_{eq}(T)$ consists of two intersecting straight lines, over limited temperature ranges, corresponding to water–hydrate–gas and ice–hydrate–gas equilibria. The slope of these lines to the reciprocal temperature axis characterizes the molar enthalpy of hydrate dissociation into water and gas ΔH_{hwg} at $T > 273$ K or into ice and

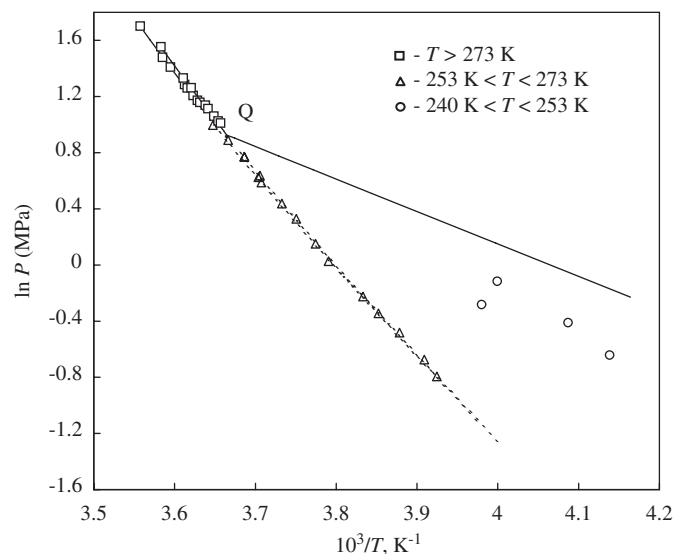


Fig. 4. Comparison of the dissociation pressure of methane hydrates formed from water droplets (symbols) and the equilibrium pressure of hydrate formation for bulk methane hydrates (—) calculated by the CSMGem program (Sloan and Koh, 2007). The dash line is the calculated extension of the water–hydrate–methane gas equilibrium curve into the metastable area of supercooled water (Istomin et al., 2006a). Q is the quadruple point, where ice + water + hydrate + gas coexist.

gas ΔH_{hig} at $T < 273$ K via the Clausius–Clapeyron equation

$$\Delta H_{hwg(hig)} = -zR \frac{d(\ln P_{eq})}{d(1/T)} \quad (1)$$

where z is the compressibility factor for gas and R is the universal gas constant.

The point of intersection of the ice–hydrate–gas and water–hydrate–gas equilibrium curves defines the quadruple point Q, where four phases ice + water + hydrate + gas coexist. For methane hydrate, T_Q is 272.9 K and P_Q is 2.56 MPa (Sloan and Koh, 2007).

At temperatures above T_Q , the values of P_d coincide with the equilibrium pressures of gas hydrate formation P_{eq} (Fig. 4). This demonstrates that the measuring of the dissociation pressure for small hydrate particles at a given temperature can be used to define the equilibrium conditions of hydrate formation above T_Q . Advantages of the “small droplets method” are that much smaller samples and shorter times are required for these measurements in comparison with those for bulk hydrate.

At temperatures below T_Q and up to 253 K, the values of P_d fall on the extension of the water–hydrate–gas equilibrium curve into the metastable region where supercooled water can exist. This extension was calculated by Istomin et al. (2006a). Another method to extend the water–hydrate–gas equilibrium curve into the metastable region of supercooled water is to use Eq. (1) as follows:

$$P = P_Q \exp \left[-\frac{\Delta H_{hwg}}{zR} \left(\frac{1}{T} - \frac{1}{T_Q} \right) \right] \quad (2)$$

Here ΔH_{hwg} is 54.2 kJ/mol (Handa, 1986). We calculated a value of 0.926 for z at T_Q and P_Q using the Peng–Robinson equation of state (Peng and Robinson, 1976). It is suggested additionally that z does not change along the three-phase water–hydrate–methane gas boundary extended into the metastable region of supercooled water.

We compared both of these calculation methods to extend the equilibrium curve into the metastable region and found that they provided data which were in a good agreement with one another.

The measured values of P_d in the temperature range of 253.2 K– T_Q can be expressed in a form of a regression equation as follows:

$$\ln(P/\text{MPa}) = 24.763 - 6509.1/T, \quad r^2 = 0.9988 \quad (3)$$

where r^2 is the regression coefficient.

Using Eqs. (1) and (3), we obtain the molar enthalpy of dissociation for the small hydrate particles below T_Q

$$\Delta H \text{ (J/mol)} = 6509.1zR \quad (4)$$

Averaged the temperature and pressure dependence of the z along the three-phase water–hydrate–methane gas boundary extended into the metastable region of supercooled water

$$z = [z(T_Q, P_Q) + z(T, P_d)]/2 \quad (5)$$

we calculated an average value of 51.7 kJ/mol for the molar enthalpy of dissociation for the small methane hydrate particles at the temperature range of 253.2 K– T_Q . This value agrees with the molar enthalpy of hydrate dissociation into water and gas for bulk methane hydrate $\Delta H_{hwg} = 54.2$ kJ/mol (Handa, 1986). Therefore, the liquid phase detected visually in our experiments below T_Q during dissociation of the hydrate samples is nothing more nor less than the supercooled water.

Fig. 5 shows successive shots of changes observed at 268.2 K during dissociation of methane hydrates formed from water droplets. The initial instant of time (Fig. 5(a)) immediately preceded the appearance of the first signs of changes in the image. By this time the pressure in the reactor was decreased to 1.61 MPa and it then remained constant (evacuation of the gas from the reactor was terminated). Only the hydrate phase is observed in Fig. 5(a). The droplets of liquid with gas bubbles appeared during the hydrate dissociation (Fig. 5(c)). Although we did not study in detail the effect of the hydrate dissociation temperature on the induction time of crystallization of the supercooled water forming during dissociation of methane hydrates, our findings show that the induction time decreases with a decrease in the temperature. In particular, at 268 K and higher, water droplets forming during dissociation of hydrates did not freeze even in 24 h (more prolonged observations were not made), whereas at 253 K, we observed that the liquid phase formed during hydrate dissociation existed in the metastable state no longer than a few seconds and then transformed into the solid. Crystallization of the supercooled water was observed during methane hydrate dissociation below 268 K (Fig. 6). When a pressure in the reactor was decreased, one of the hydrate particles (the big particle at the left of the picture) changed its color (Fig. 6(b)) as soon as the curve of pressure in the reactor intersected the extension of the three-phase water–hydrate–methane gas boundary into the metastable region of supercooled water. We suppose that the dark solid particle in Fig. 6(b) is the ice. The reasons of such behavior of this particle are unknown yet, because the rest hydrate particles dissociated into supercooled water and gas (Fig. 6(c)). The induction times of crystallization for the supercooled water droplets were 18 min for the second big droplet (Fig. 6(d)) and more than 5 h for the small droplets (Fig. 6(f)). The dependence of the induction time of crystallization of the supercooled water on the size of water droplets may be responsible for absence of the self-preservation effect for the small hydrate samples in our experiments (the large induction time), whereas this effect is observed for bulk methane hydrates (the short induction time). The formation of metastable (supercooled) water during dissociation of methane hydrates was reliably observed in the temperature range of 253 K– T_Q . At any temperature of this range, the transformations observed in the reactor were analogous to those shown in Figs. 5 and 6, and the measured hydrate dissociation pressures P_d in all cases fell on the extension of

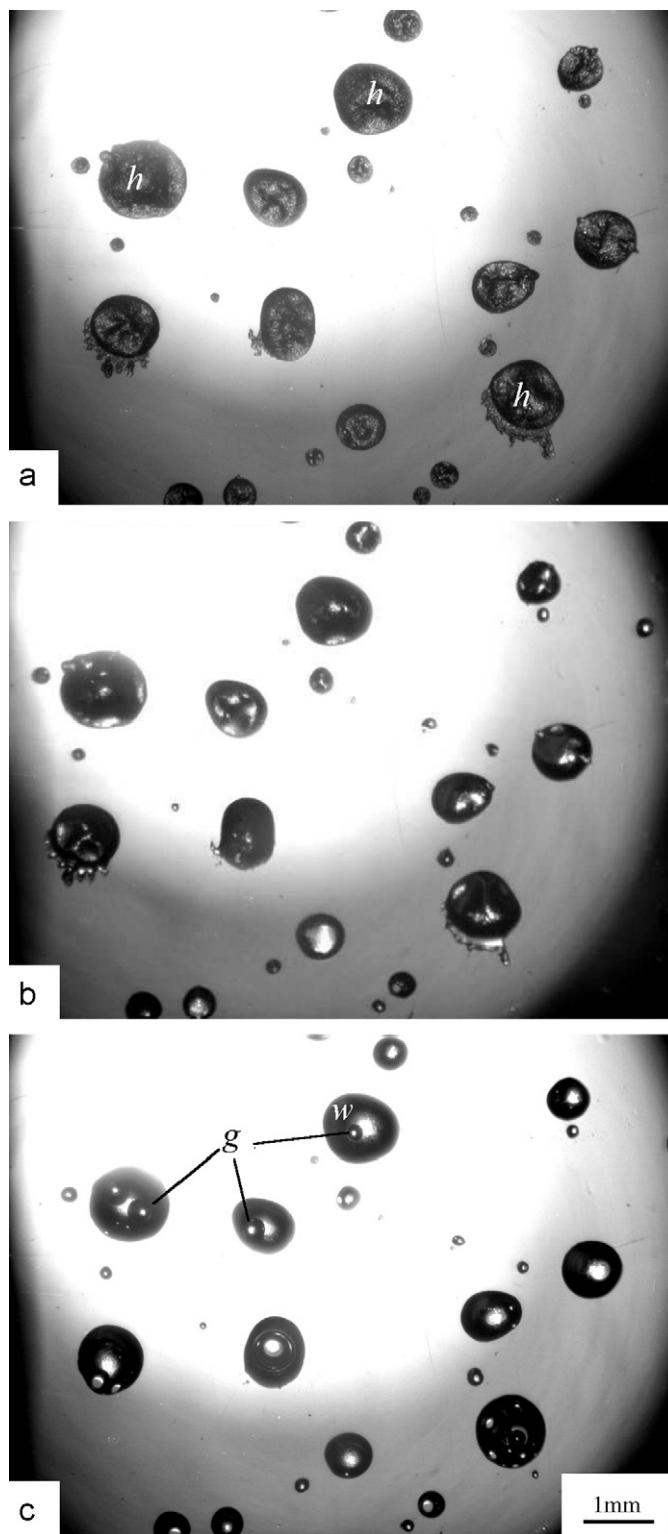


Fig. 5. Dissociation of methane hydrates at 1.61 MPa and 268.2 K. (a) Time = 0; (b) time = 2 min; (c) time = 6 min. w is water, g is gas.

the water(liquid)–hydrate–gas equilibrium curve into the metastable region of existence of a supercooled water at temperatures below T_Q .

At temperatures between 240 and 253 K, the formation of liquid water in our hydrate dissociation experiments was not observed

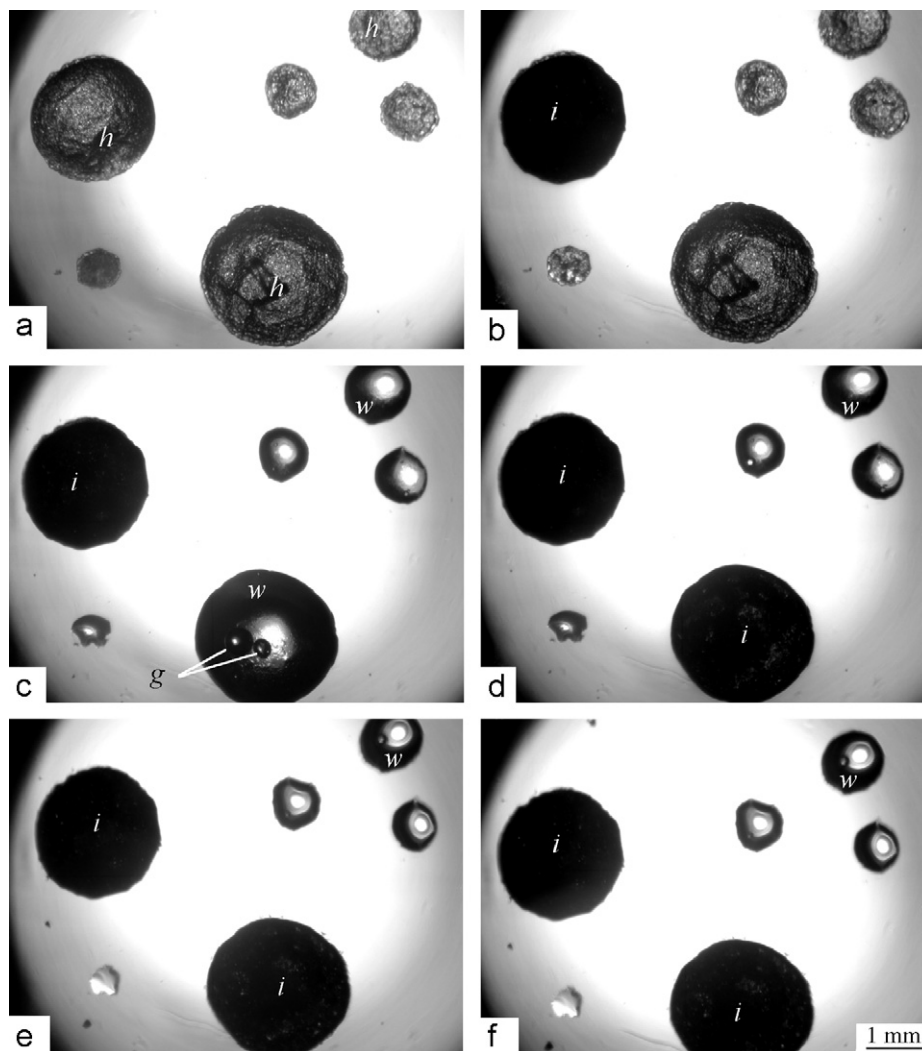


Fig. 6. Dissociation of methane hydrates at 263.2 K. (a) At the beginning of experiment, $P = 5$ MPa; (b) onset of hydrate dissociation, $P = 1.0$ MPa, time = 0; (c) $P = 1.0$ MPa, time = 16 min; (d) $P = 1.0$ MPa, time = 18 min; (e) $P = 1.0$ MPa, time = 115 min; (f) $P = 1.0$ MPa, time = 325 min.

visually, but the solid phase changed its color. The pressure at which the color began to change was higher than it followed from Eq. (3), but lower than the equilibrium pressure of the hydrate dissociation into ice and gas at a given temperature. The changes visually observed during the methane hydrate dissociation at 243.2 K are shown in Fig. 7. When the pressure in the reactor decreased to 0.57 MPa (the equilibrium pressure for the methane hydrate dissociation at 243.2 K is 0.89 MPa, CSMGem Sloan and Koh, 2007), the first signs of the color change of the sample appeared that was taken as an indication of a beginning of the hydrate dissociation. During the next 6 min the samples changed their color, then no changes were observed in the reactor. Because the dark solid droplets formed during the methane hydrate dissociation melted to liquid at 273 K, we have suggested that they were composed of water ice.

The minimal temperature 253.2 K at which we observed the formation of supercooled water during dissociation of the methane hydrates is a distinctly higher than the water's homogeneous nucleation limit, about 233 K (Angell, 1983; Debenedetti, 2003). But it should be remembered that the homogeneous nucleation temperatures reached its limit in the experiments with small water droplets of size 1–10 μm . We are going to continue an investigation of disso-

ciation of small hydrate samples, using water-in-oil emulsion with droplet size of 1–10 μm and NMR relaxometry for a monitoring of the liquid phase.

4. Conclusion

Visual observations of methane hydrate formed from water droplets and their dissociation at temperatures below 273 K were carried out. Direct optical evidences of the formation of metastable (supercooled) water during methane hydrate dissociation between 253 and 270 K were obtained for the first time. The induction time for recrystallization (freezing) of this supercooled water ranged from tens of hours at 270 K to a few seconds at 253 K and additionally depended on a size of water droplets. The dissociation pressures P_d of methane hydrates formed from water droplets were measured. At temperatures below T_Q and up to 253 K, the values of P_d fall on the extension of the water-hydrate-gas equilibrium curve into the metastable region where supercooled water can exist. Molar enthalpy for the dissociation of methane hydrates formed from water droplets was calculated using Clausius–Clapeyron equation. In the range of 253–273 K, the calculated molar enthalpy is in good

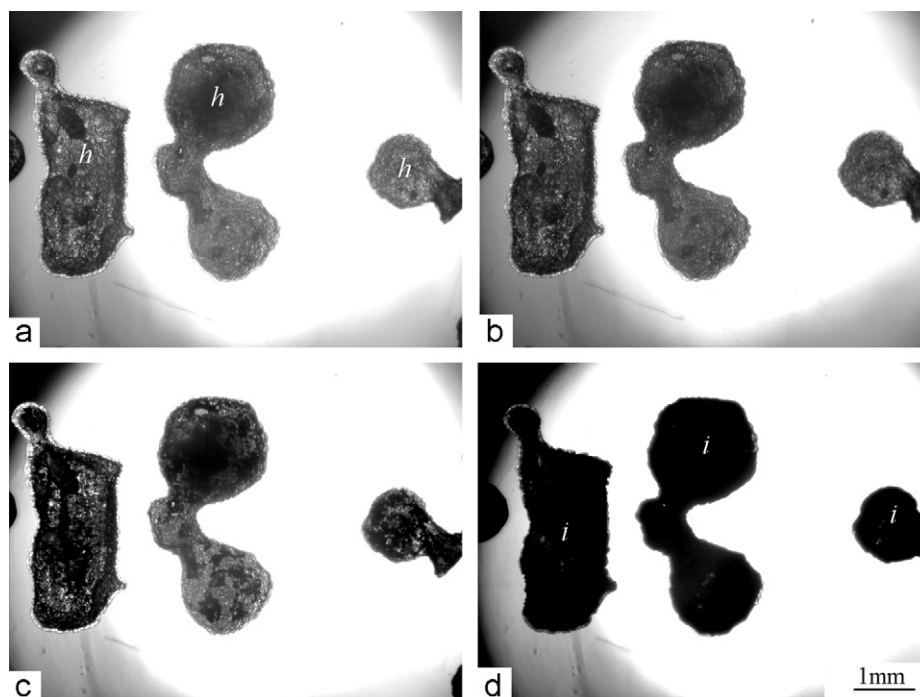


Fig. 7. Methane hydrate dissociation experiment at 243.2 K. The equilibrium pressure of methane hydrate dissociation at the given temperature is 0.89 MPa. The pressure in the reactor decreased with a rate of 0.02 MPa/min from the equilibrium pressure to that when the first signs of the color change of the samples appeared. (a) $P = 5.0$ MPa, at the beginning of the experiment; (b) $P = 0.64$ MPa. No changes are observed in the reactor; (c) $P = 0.57$ MPa, onset of the change of the hydrate samples color (hydrate dissociation); (d) $P = 0.57$ MPa, 6 min after the onset of hydrate dissociation.

agreement with the enthalpy of dissociation of bulk methane hydrates into water and gas at $T > 273$ K. The data obtained supplement our knowledge about the mechanism of the gas hydrates dissociation below the ice melting point and self-preservation effect.

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