FORMATION OF SUPERCOOLED WATER ON DISSOCIATION OF GAS HYDRATES FROM NUCLEAR MAGNETIC RESONANCE DATA

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Dissociation of CFC-12 (Freon-12) hydrate into gas and supercooled water at low temperatures has been discovered in a pulsed nuclear magnetic resonance (NMR) study of disperse ice. Supercooled water was investigated experimentally in terms of its quantity dynamics during dissociation. The dissociation rates in two gas hydrate samples were measured under different experimental conditions. Supercooled water was found out to crystallize on the surfaces and inside gas hydrate particles at different $P–T$ conditions of CFC-12 hydrate dissociation.

The present study continues earlier experimental research on the mechanism of gas hydrate dissociation into gas and supercooled water at subzero temperatures [*Melnikov et al., 2007, 2009, 2010*]. The objective of the first project stage was to expand the scope of gases forming hydrates that dissociate as 'gas hydrate → supercooled water + gas'. At the second stage, the dissociation process has been checked through direct experimental measurements using pulsed nuclear magnetic resonance (NMR) which is a reliable analytical tool applied lately to explore gas hydrate formation [*Aichele et al., 2009; Gao et al., 2009*]. There is reason to believe [*Watanabe and Wake, 2009*] that NMR can reveal the appearance of supercooled water in the beginning of gas hydrate dissociation and, moreover, can trace the dynamics of its content. This data has important implications for the dissociation mechanism, as well as for the role of supercooled water in the effect of gas hydrate self-preservation [*Istomin et al., 2006*].

The reported experiments were run with CFC-12 (CCl_2F_2 chlorofluorocarbon, or Freon-12) selected for its ability to form hydrates at low pressures. This facilitated the instrumental work performed on a Bruker *Minispec – mq* pulsed NMR relaxometer operating at the resonance frequency 19.65 MHz for hydrogen nuclei. Another advantage of CFC-12 is the lack of hydrogen nuclei which simplifies NMR analysis and allows recording signals from water molecules only (either free as liquid water or ice, or bound in hydrates).

The starting materials for preparing gas hydrate samples were distilled water and technological CFC-12. To promote hydrate formation, ice was used in ~400 μm grains and the samples were subjected to cyclic temperature changes [*Stern et al., 1996*] between −10 and +3 °C; the pressure of gaseous CFC-12 was maintained at 150 kPa. As a result, we obtained a system consisting of a great number of very small contiguous CFC-12 hydrate particles which enclosed cores of unreacted ice (or water, depending on the final temperature of the run). Note that as the number of runs increased from 1 to 8, the degree of ice-to-hydrate transformation P_h grew from 42 to 94 %, respectively.

The dynamics of liquid water content was studied by means of NMR relaxometry from free induction decay (FID) following a 90° pulse [*Chizhik, 1991*]. The technique was applied to estimate the T_2^* magnetic relaxation times separately for liquid water, ice, and gas hydrate in specially prepared CFC-12 hydrate samples, in order to isolate liquid water NMR signals. At temperatures between −10 and 0 °C, the characteristic FID times were T_{2i}^*, T_{2h}^* ~ 10 μs from ice and CFC-12 hydrate while liquid water relaxed at T_{2w}^* ~1.5 ms. With this knowledge, we estimated the FID amplitude A_m at the time t_s = 70 μs elapsed after the 90° pulse (Fig. 1). The signals from ice and gas hydrate being almost zero at that time, the measured FID amplitude corresponded uniquely to liquid water.

Before the NMR measurements in CFC-12 hydrate samples, the amplitude A_m was calibrated against the liquid water weight using standard samples with similar relaxation parameters ($CuSO_4$ aqueous solution). Furthermore, the experimental procedure was tested on CFC-12 hydrate dissociation at positive temperatures. In this temperature range, as we expected, the amount of liquid water released on decomposition of gas hydrate into water and gas obviously increased beyond the 'water–hydrate–gas' equilibrium line in all experiments. The dissociation process was also recognized from pressure increase in the box with the samples.

Additional water which may appear during gas hydrate dissociation at negative temperatures was revealed by NMR analysis using two samples with different initial degrees of ice-to-hydrate transformation: P_h = 68 % for sample 1 and P_h = 90 % for sample 2.
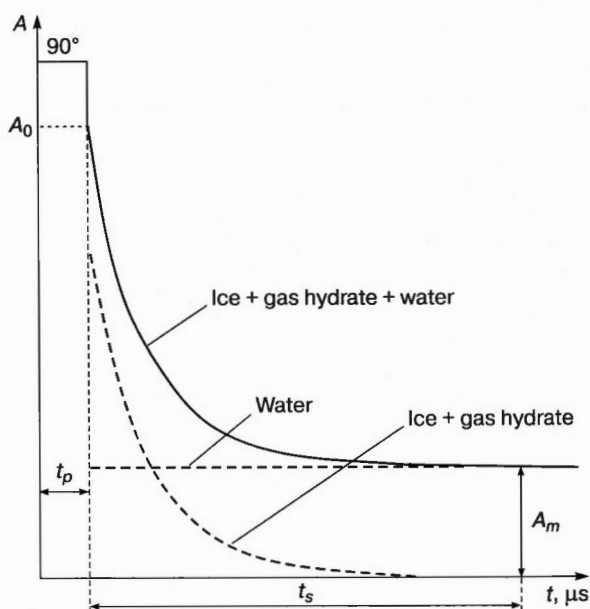
Fig. 1. Beginning of FID in the system ice + gas hydrate + water.

Dashed line is modeling results. A_0 is initial FID amplitude; A_m is FID amplitude at time t_s elapsed after 90° pulse; t_p is pulse duration.

Fig. 2. Time-dependent variations in contents of supercooled water while pressure was reduced above the sample.

1: Sample 1, temperature −1 °C, stepwise lowered pressure (at 5 to 10 kPa); *2*: Sample 2, temperature −3 °C, pressure lowered at 3 kPa/min. Arrows point to contents across the equilibrium lines of ice–hydrate–gas (*a*) and supercooled water–hydrate–gas (*b*).

In the beginning of the experiment, the prepared samples stayed at the temperature +3 °C and the pressure of hydrate-forming gas 150 kPa for at least an hour, in order to ensure complete melting of unreacted ice in the cores of gas hydrate particles, which was confirmed by stable measured A_m. At the following step, samples 1 and 2 were cooled to −1 °C and −3 °C, respectively, at a rate of 0.5 K/min, at ~150 kPa pressure of CFC-12 over the samples. The subsequent transition to the domain of hydrate thermodynamic instability was at constant temperatures and the pressures lowered stepwise (stepsize varied from 5 to 10 kPa) for sample 1 or continuously at a mean rate of 3 kPa/min for sample 2.

The content of liquid water (Fig. 2) changed in the same way in the two samples irrespective of both their temperature and mode of pressure reduction. Note that additional supercooled water released on dissociation of CFC-12 hydrate in sample 2 appeared near the 'supercooled water–hydrate–gas' equilibrium line we obtained through extrapolation of experimental data from [*Byk, 1980*] onto the subzero temperature domain. In sample 1 of more supercooled water, however, it occured at 15 kPa below this line for the difficulty to precisely constrain the dissociation pressure reduced in the stepwise mode.

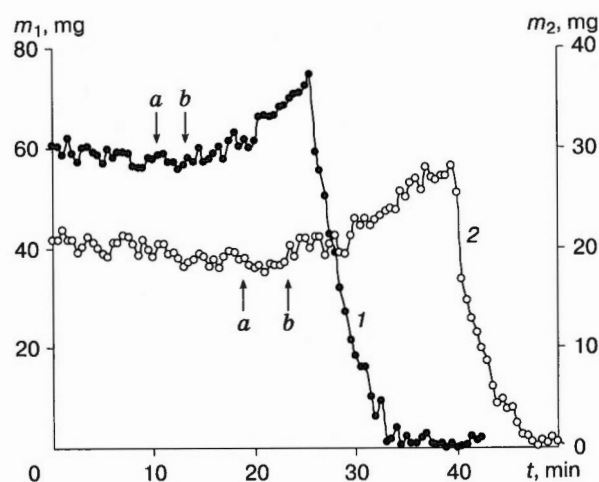The dynamic growth of supercooled water recorded in Fig. 2 corresponds to a constant rate of CFC-12 hydrate dissociation, which we estimated at ~1 mg/min for the given samples and experimental conditions. Furthermore, we also calculated the maximum thicknesses of water films on the surfaces of gas hydrate particles, with regard to the total content of the formed liquid water, which were no larger than 4.2 and 3.6 μm for samples 1 and 2, respectively.

At some point after its peak, the content of liquid water began to decrease as a result of crystallization, at a rate more than an order of magnitude faster than the dissociation rate (Fig. 2). Note two pieces of the curves that record the crystallization of bulk water into ice at rates times different from each other. The early segment corresponds to crystallization of additional water released on dissociation on the surfaces of hydrate particles while the late one is crystallization of water that existed originally inside the particles. This is quite reasonable as, being an endothermic process, dissociation cools down the surface water and increases the probability for ice nucleation in it. On the other hand, crystallization beginning from the surface triggers the water-to-ice phase change in the liquid cores of gas hydrate particles.

Thus, the NMR analysis has provided solid evidence for dissociation of CFC-12 hydrate into gas and supercooled water at subzero temperatures, which may be a starting point for further estimating the magnetic-relaxation parameters of this water.

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