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Kinetics of hydrate dissociation at a pressure of 0.1 MPa

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ABSTRACT: Experimental data on the kinetics of propane hydrate dissociation at 0.1 MPa and different external temperatures were obtained. A two-stage mechanism of hydrate dissociation was observed visually. In the first stage hydrate dissociated into metastable water and gas. During the second stage the metastable water crystallized into ice. The release of metastable water during hydrate dissociation and its subsequent recrystallization exclude the possibility of achieving theoretical equilibrium temperatures during hydrate dissociation at 0.1 MPa (−14°C for propane hydrates), although temporary temperature decreases (to −1 to −2°C) and transient ice formation were observed.

1 INTRODUCTION

Hydrates of natural gases are unstable compounds at standard conditions, which is why they dissociate with absorption of heat. For example, at 0.1 MPa methane hydrate exists in equilibrium with ice and gas at −82°C. For ethane and propane hydrates the temperatures of the three-phase equilibrium at 0.1 MPa are −34°C and −14°C, respectively. This means that at atmospheric pressure hydrate of natural gases should dissociate into ice and gas with decrease of the sample temperature to its equilibrium value. Ice formation during dissociation of methane hydrates once pressure was reduced to atmospheric and at the positive initial temperature was observed by Yakushev (1989), Lysne (1995), Petters et al. (2000), Circone et al. (2000). But the sample temperature in these experiments never fell essentially lower than 0°C, irrespective of an external temperature. In most cases the sample temperature was buffered between 0°C and −2°C during hydrate dissociation. Different authors give different explanations for such a behaviour of the temperature. According to Yakushev (1989), an impermeable ice shell is being formed at the surface of hydrates during their dissociation. This shell prevents the release of gas from hydrates. The hydrate dissociation is stopped, and hydrates remain in a metastable state (the so-called self preservation effect (Yakushev, 1988)), until their temperature exceeds 0°C once again. Then ice begins melting and the hydrate dissociation continues. On the other hand, in the experiments by Lysne (1995), Petters et al. (2000), Circone et al. (2000) the hydrate dissociation was not stopped after depressurization, which was confirmed by permanent gas release from the reactor till the hydrates were completely dissociated. In this case the mechanism of hydrate dissociation and ice formation and also the causes of temperature stabilization near 0°C remain unclear, for the equilibrium temperature of methane hydrate dissociation into ice and gas at 0.1 MPa is −82°C.

The aim of this work was to try to answer questions on the mechanism of hydrate dissociation after rapid depressurization to atmospheric and the causes of anomalous temperature behaviour during hydrate dissociation. These questions are important to predict a temperature regime of hydrate-containing rocks after rapid depressurization, and also in deciding boundary conditions when modelling the processes of hydrate dissociation in pipelines.

This paper presents some experimental data on kinetics of propane hydrate dissociation at 0.1 MPa. In contrast to methane, which forms a structure I hydrate, propane forms a structure II hydrate. In addition, at 0.1 MPa the equilibrium temperature of propane hydrate dissociation is −14°C, which is essentially higher than the equilibrium temperature of methane hydrate dissociation at atmospheric pressure.

2 EXPERIMENTS

A schematic of the experimental apparatus is shown in Figure 1. Its main element is a high pressure reactor, within which the hydrates are formed and dissociated under controlled conditions. The reactor is made of organic glass in the form of cylindrical cup with the flanges of stainless steel. The reactor inner diameter is 55 mm and the effective volume is 285 cm^3. The reactor is placed within the air thermostat, which provides temperature regulation with an accuracy of ±0.2°C. Temperature within the reactor is measured with a differential copper-constantan thermocouple with zero junction placed into a Dewar vessel with melting ice. The accuracy of temperature measurements within the reactor is ±0.1°C. Pressure within the system is measured with MO 11202 manometers with an accuracy of ±4 kPa.

To form the hydrates we used 70 g of degassed distilled water and propane gas (CH_4 – 1.5%, C_2H_6 – 0.5%, C_3H_8 – 95%, C_4H_{10} – 3%). It is well known,

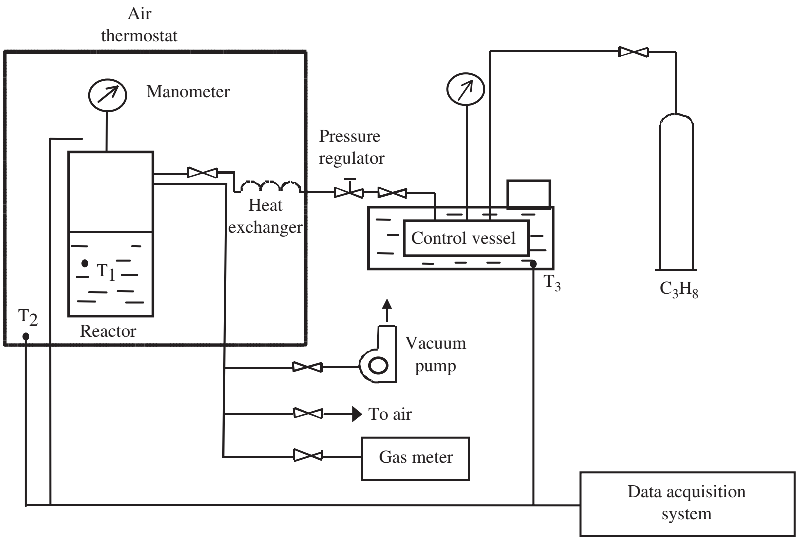

Figure 1. Schematic diagram of experimental apparatus.

that hydrates are usually formed at the water-gas interface. Therefore a permanent renovation of this interface is necessary for hydrate growth. This renovation is usually provided by mixing the reactor contents.

As we have shown earlier (Kutergin et al., 1992), the application of additives containing anionic surfactants make it possible to increase the rate of propane hydrate formation by several orders and to achieve the complete transformation of water into hydrate without any agitation or mixing. Similar data for ethane are presented in paper by Zhong & Rogers (2000). This method for hydrate formation was used in this work. The surfactant additive (sodium dodecyl sulfate, SDS) amounted to 10–20 ppm. Hydrates were formed at constant pressure within the reactor, and the additional amount of gas was supplied to reactor from the control vessel. The amount of gas consumed during hydrate formation was calculated from the drop of pressure in the control vessel. The degree of water conversation into hydrate was calculated supposing that the forming hydrate had a $C_3H_8 \cdot 17H_2O$ composition. The process of hydrate formation was considered to have finished with the transition of the whole amount of water (70 g) into hydrate, when the control vessel pressure stopped dropping. Notice that the amount of consumed gas calculated from pressure drop in the control vessel coincided within the 5% accuracy with the amount of gas necessary for conversation of all reactor water into the hydrate.

As a rule, hydrates were obtained at 1°C and 0.4 MPa. During the process of hydrate formation the temperature within the reactor increased by 1.0–1.5°C. But by the end point of hydrate formation it decreased to the value of thermostat temperature. In some cases we lowered temperature within the reactor below 0°C in order to reduce the induction time. Immediately after beginning of ice formation the reactor temperature was again increased to 1°C. Ice nucleation accelerated the process of hydrate formation. In the presence of surfactants hydrates grew mainly at the reactor walls and the thermocouple pocket. The front of hydrate formation moved up alongside the reactor walls and the thermocouple pocket surface toward the gas phase, and water migrated from the body of the liquid to the front of hydrate formation. Usually complete conversation of water into hydrate took 20–22 hours.

After all water have conversed into hydrate, the thermostat temperature was increased or decreased depending on the chosen external temperature of hydrate dissociation. If the specified temperature of hydrate dissociation exceeded the temperature of propane hydrate quadruple point ($T_q = 5.5$°C), the reactor with hydrates was stored in a domestic refrigerator at 1–3°C until the thermostat temperature reached the specified value. Then the reactor was placed into the thermostat once again to study the hydrate dissociation. To dissociate hydrates the pressure within the reactor was abruptly lowered to the atmospheric level. Two parameters were registered during the hydrate decomposition – the temperature of hydrates within the reactor and the amount of evolved gas. The amount of gas evolved during hydrate dissociation was measured with a gas meter, model RG 7000. The amount of gas measured after complete hydrate dissociation coincided to 10% accuracy with the amount of gas consumed in the process of hydrate formation. The small difference between the consumed and evolved amounts of gas is explained by the fact that we could not measure and take into account some portion of gas evolved due to hydrate dissociation at the instant a pressure was released.

As the reactor was made of transparent plexi-glass, it was also possible to control the processes within the reactor visually.

3 RESULTS AND DISCUSSION

Data on kinetics of propane hydrate dissociation at 0.1 MPa and thermostat temperatures −1°C, 4°C and 22°C are presented in Figure 2. The zero time corresponds to the moment of the reactor depressurization to 0.1 MPa. The degree of hydrate decomposition is defined as $(V_e/V_c) \cdot 100\%$, where V_e is the measured amount of gas evolved during hydrate decomposition; V_c is the amount of consumed gas necessary for the conversion of 70 g of water into the propane hydrate $C_3H_8 \cdot 17H_2O$. Data presented in Figure 2 have the same character as data on the methane hydrate decomposition (Circone et al., 2000, Petters et al., 2000).

Rapid lowering of the sample temperatures to −1–2°C right after the depressurization is related to propane hydrate dissociation into water and gas. The enthalpy of propane hydrate dissociation into water and gas is $\Delta H_h = -380$ J/g (Handa, 1986). The minus sign means that dissociation of hydrates goes on with absorption of heat. The subsequent temperature jump and its increase practically up to 0°C is related to water-ice transformation of water produced during hydrate dissociation. When 1 g of propane hydrate dissociates, 0.87 g of water is being produced. When water turns into ice, the amount of released heat is $\Delta H_i = 333$ J/g. Thus the resulting heat balance $\Delta H = \Delta H_h + \Delta H_i$ is negative, which explains the negative temperature of the samples.

From the data presented, ice formation is not an obstacle for the further dissociation of hydrates. But it is no longer accompanied with the lowering of the sample temperature. However temperature stabilization is observed near values minus 0.2–0.3°C (Fig. 2a,b). This can be understood assuming that even after formation of ice the hydrates continue to dissociate into metastable water and gas with a subsequent conversion of water into ice. Such a two-stage mechanism is consistent with the Ostwald step rule. According to this rule, formation of an intermediate metastable phase is possible during phase transitions, which is related to the fact that this metastable phase is kinetically more preferable than the formation of a thermodynamically stable phase.

Small negative temperatures (over −3°C) are also not obstacles for propane hydrate dissociation (Fig. 2c). However, in this case an abrupt deceleration of hydrate dissociation is observed, as compared to the dissociation of hydrates at positive temperatures. The reasons of the abrupt deceleration of hydrate dissociation at negative external temperatures are not clear and being studied.

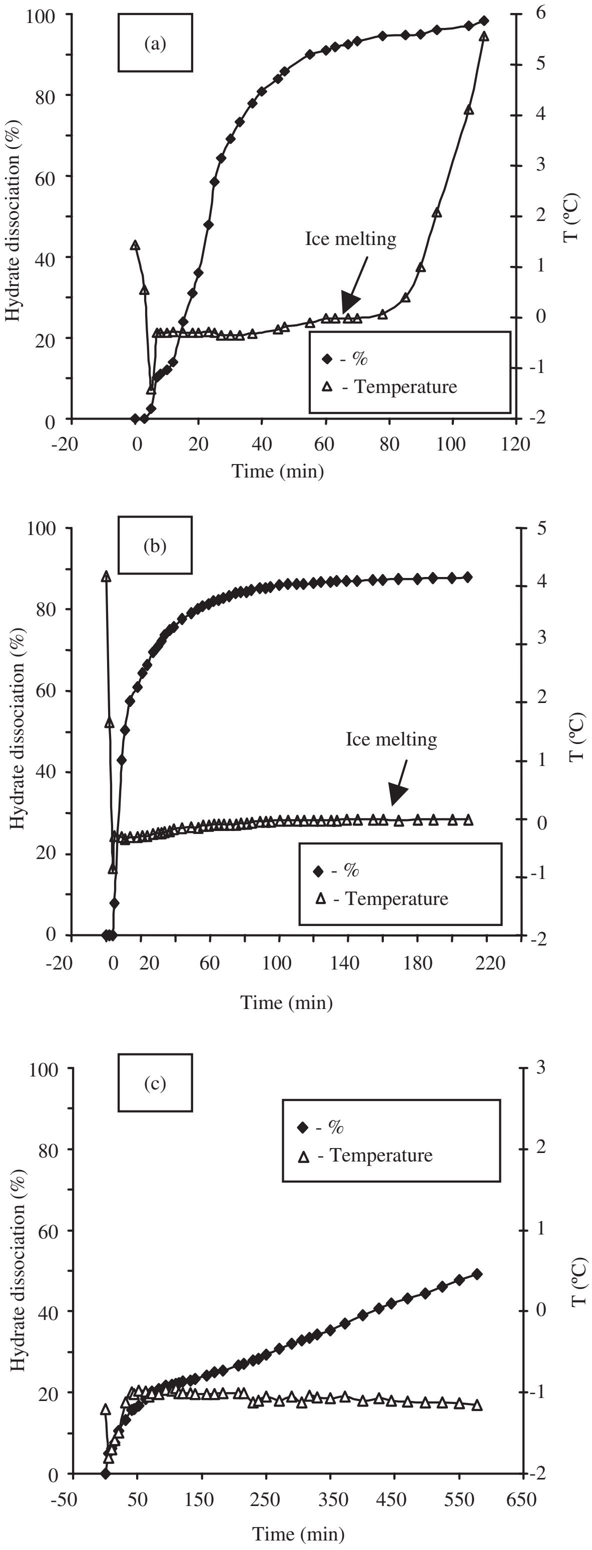

Figure 2. Kinetics of propane hydrate dissociation at 0.1 MPa and different external temperatures T_{ex}: (a) $T_{ex} = 22$°C, (b) $T_{ex} = 4$°C, (c) $T_{ex} = -1$°C.

Interesting data are presented in Figure 3. They are related to the stochastic character of the crystallization processes and correspond to that rare case when water produced during hydrate dissociation exist in an supercooled state at −2.5°C for a long time without crystallization. Production of water within the reactor was observed visually. The exclusiveness of data presented is that the presence of decomposing hydrates didn't initiate the heterogeneous crystallization of

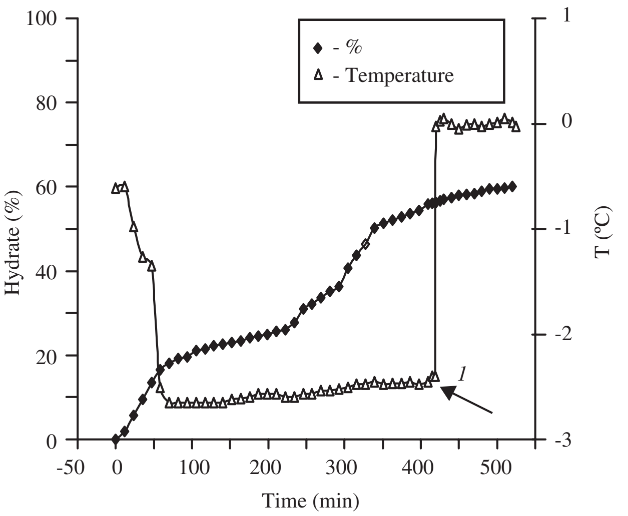

Figure 3. Kinetics of propane hydrate dissociation at 0.1 MPa and $T_{ex} = -2.5°C$. *Point 1:* A few ice crystals were added into the reactor.

water. At the same time after a few ice crystals were added into the reactor a rapid crystallization of ice was observed in the whole volume of the supercooled water.

Stabilization of the reactor temperature at −2.5°C (Fig. 3) was due to the establishment of a dynamic equilibrium between the heat absorbed during hydrate dissociation and the heat supplied from the surroundings. This temperature depends on the rate of hydrate dissociation and the thermostat temperature. In its turn, the rate of hydrate dissociation is proportional to the driving force of the dissociation ΔT, which is defined as a difference between the equilibrium temperature T_{eq} of hydrate dissociation at given pressure and the reactor temperature T_r, $\Delta T = |T_{eq} - T_r|$. For propane hydrates at 0.1 MPa the equilibrium temperature is −14°C, and for methane hydrates $T_{eq} = -82°C$. This means that the driving force of dissociation for propane hydrates at atmospheric pressure will be smaller than the driving force of dissociation for methane hydrates. The use of propane for modelling hydrate dissociation made it possible for us to observe visually the two stages of the hydrate dissociation process at 0.1 MPa: (1) hydrate dissociation into water and gas at the first stage; (2) metastable water crystallization at the second stage. In the case of methane hydrate dissociation the induction time of ice formation is significantly shorter (dissociation driving force ΔT is greater). Therefore the probability of visual observation of metastable water production stage during methane hydrate dissociation is extremely low.

4 CONCLUSION

This paper presents experimental data on kinetics of propane hydrate dissociation at 0.1 MPa. Results coincide with the data obtained earlier for the dissociation of methane hydrates (Circone et al., 2000, Petters et al., 2000). A two-stage mechanism of hydrate dissociation is suggested. During the first stage hydrates dissociate into metastable water and gas. The formation of metastable water is kinetically more preferable than the formation of stable at given conditions ice phase. During the second stage the metastable water transforms into ice. The production of supercooled (up to −2.5°C) water was observed visually during propane hydrate dissociation. Metastable water formation and its crystallization exclude the possibility of accessing the equilibrium temperatures during hydrate dissociation (for example, −82°C for methane hydrate or −14°C for propane hydrates), though temporary lowering of temperature to −1–2°C makes ice formation possible. This circumstance should be taken into account when predicting the temperature regime of hydrate-containing rocks during hydrate dissociation and also when choosing the boundary conditions for modelling hydrate dissociation within pipelines.

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