Methane hydrate formation in dispersed polyvinyl alcohol cryogel

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Abstract. Kinetics of methane hydrate formation in frozen water solutions (FWS) and polyvinyl alcohol (PVA) cryogel stabilized with hydrophobic silica nanoparticles was first studied. PVA cryogel is a macroporous heterogeneous gel formed at the special conditions of the freezing and subsequent melting processes of the PVA water solution. Such parameters as a rate and a conversion of water to hydrate were investigated for dispersed FWS, PVA cryogel, and dispersed ice at the same thermodynamics conditions using the same equipment. It was found out that the transformation the main part of water contained in FWT and PVA cryogel into hydrate was more than ten times faster than that for dispersed ice. The resistance to hydrate formation/dissociation processes was studied for dispersions of PVA cryogel. Gas hydrate formation and dissociation were carried out at isochoric conditions using temperature cycling. It was shown that cryogels of PVA water solution stabilized with hydrophobic silica nanoparticles were resistant to gas hydrate formation/dissociation processes prompting suggestions that cryogels of PVA water solution might be reused for gas hydrate formation/dissociation multiple times without significantly decrease in the conversion water to hydrate.

1. Introduction

Several approaches of natural gas transportation have been considered worldwide. One of the most perspective alternatives to the well-known approaches of natural gas transport is storing and transporting natural gas in clathrate hydrate (gas hydrate technologies) [1,2]. According to the fact that the natural gas production and consumption in the Far North is growing, there is an ever-increasing need to develop technologies that might be effective in a cold climate. In works [3-5] it was presented that “dry water” could show a great promise as a great material for gas hydrate formation with the purpose of its using in the technologies of natural gas transportation, storage and utilization. “Dry water” is a free-flowing powder containing up to 98 wt % of water in droplet form and produced by rapidly mixing of water and hydrophobic silica nanoparticles in air [6]. However, insufficient resistance of water containing in “dry water” to phase transformations (freezing/thawing and gas hydrate formation/dissociation) limits its using for gas hydrate formation/dissociation and applying at conditions of seasonal temperature fluctuations near the ice melting point.

Dispersions of the gelling gum aqueous solution of polysaccharide stabilized with hydrophobic silica nanoparticles are more resistant to gas hydrate formation/dissociation [4] and remain stable even after gas hydrate formation/dissociation in it. Whereas, to produce the polysaccharide dispersions it is required a rather great amount of the gellan gum (more than 20 wt %). Moreover, in case of replacing water to the gellan gum solution it might be observed the significant decrease in storage capacity (30 %) [4]. A macroporous heterogeneous gel formed at the special conditions of the freezing and
subsequent melting processes such as PVA cryogel (further cryogel) might be formed at the less concentration than that for polysaccharide (for example, 5 wt %) [7]. In the previous work we showed that dispersed cryogel stabilized with hydrophobic silica nanoparticles could remain stable after freezing/thawing cycles [8]. Therefore, it is reasonable to suggest that the dispersed cryogels will be stable to gas hydrate formation/dissociation cycles as well.

However, gas hydrate formation in cryogels stabilized with hydrophobic silica nanoparticles and the influence the gas hydrate formation/dissociation cycles on stability of cryogel dispersions have not studied yet. Moreover, there is no information about gas hydrate formation in FWS of PVA at the temperature near the ice melting point (at the conditions at which cryogel forms).

In this paper the results of the kinetics of methane hydrate formation in the dispersions of PVA FWS stabilized and data on cryogel stability to the processes of methane hydrate formation/dissociation.

2. Experimental section

Dispersed PVA frozen water solutions were produced by grinding the frozen and storing at the temperature of 258 K no less than ten hours PVA solutions or distilled water. Mechanical grinding of frozen PVA solutions and ice were carried out in the thermostatic camera Teledor for 30 s using the household blender Braun VX2050 with the speed of 18700 rotations per minute. To prepare the dispersed PVA frozen water solution the hydrophobic silica nanoparticles (HDK® H17 (Wacker Chemical AG, German), further H17) were added to the solutions in amount of from 5 till 8 wt % before the process of mechanical grinding. To form cryogel, gas hydrates, and studying the gas hydrate growth kinetics the fraction of 80–140 micrometers or less than 140 micrometers of the ground ice particles that were separated with sifting the ground PVA frozen water solutions with nanoparticles through a sieve. The sifting process was carried out with the electrodynamic vibration stand PE-6700 with a frequency of the desktop oscillation of 20 Hz at an ambient temperature of 253 K. For forming dispersed cryogel the separated fractions were stored at the room temperature up to full melting. Then, the free-flowing powder contained cryogel particles and about 95 wt % of water was observed.

“Dry water” was prepared according to the [9]. For preparing “dry water” H17 was used in amount of 5 wt %.

As a hydrate-forming gas methane was used (99.9 mol %). Gas hydrates were carried out in an isothermal reactor with a volume of 60 sm³ made of stainless steel. The experimental apparatus for gas hydrate formation and studying of kinetics of the gas hydrate growth and dissociation presented in [10]. To prepare gas hydrate the studied sample in amount of 7 g was loaded into the reactor. The sample was placed into the reactor in the thermostatically controlled chamber Teledor at the temperature of 253 K. “Dry water” and dispersed cryogel were loaded into the reactor at the room temperature. Then, the reactor with the sample was placed into the cryostat at a given temperature (further, the temperature of gas hydrate formation). After that the reactor with the sample was stored at the constant temperature up to the moment when the sample temperature was equal to the desired temperature. Then the reactor was evacuated and charged with methane up to the pressure of 4.9 MPa. The gas charging led to a slight heating of the reactor contents (not more than 0.7 degrees). In the absence of hydrate formation, the temperature of the gas after the reactor charging restored to the initially set temperature. The pressure in the reactor changed slightly in the absence of hydrate formation.

In all cases gas hydrate formation was carried out at isochoric conditions without any mixing of the contents of the reactor. Gas hydrate formation was prolonged for 1000 or 2000 min depending on the hydrate formation rate.

The quantity of mole gas transformed to hydrates (n) was determined from the pressure changing in the reactor at the temperature using the equation of Peng-Robinson for a gas phase [11].
Assuming that the composition of methane hydrates is determined by the stoichiometric ratio \( \text{CH}_4 \cdot 6.0\text{H}_2\text{O} \) [12], we calculated the degree of transition of water to hydrate using the following equation:

\[
\alpha = \frac{(6.0 \cdot M_w \cdot n)}{m_w},
\]

where \( M_w \) – a water mole weight; \( m_w \) – an initial water mass in the investigation sample.

Several cycles of gas hydrate formation/dissociation were conducted under the cycling temperature changing at isochoric conditions for dispersed cryogels (5 wt % of PVA and 8 wt % of H17; 7 wt % of PVA and 5 wt % of H17) to analyze their resistance to gas hydrate formation/dissociation processes. For comparing the results there were carried out several gas hydrate formation/dissociation cycles in “dry water” under the cycling temperature changing at isochoric conditions.

In figure 1 there was shown a typical view of temperature changing curves and pressure in the reactor after charging the reactor. According to the presented data the significant pressure decrease was obtained for all studied samples indicated that gas hydrates were being formed in the reactor. The delay of gas hydrate formation named the induction time for “dry water” samples changed stochastically was no more than 15 min. For frozen dispersion systems and cryogels were obtained the significant pressure decrease and insufficient temperature increase in the reactor after charging the reactor (figure 1), indicating that there was no any gas hydrate formation induction time. For dispersions of PVA frozen water solutions the pressure quickly decreased for about 300 min and then it was stabilized. For ground ice the pressure decreased fluently during the period of observation (figure 1).

![Figure 1](image_url)

**Figure 1.** Pressure changing (1-5) and temperature of methane (6-10) in the reactor at isochoric conditions immediately after the reactor charging. “Dry water” (5 wt % of H17) (1 and 6); ground ice (2 and 7); frozen water solution (5 wt % of PVA and 5 wt % of H17) (3 and 8); cryogel (5 wt % of PVA and 8 wt % of H17) (4 and 9); cryogel (5 wt % of PVA) (5 and 10).
3. Results and discussion

In figure 2 it was demonstrated the typical character of changing of the water to hydrate conversion in the investigated frozen water solution dispersions of PVA, cryogel and ground ice systems immediately after the moment the reactor had been charged. From the presented data it might be assumed that the replacing ground ice by frozen water solution dispersions of PVA or cryogel dispersions let significantly decrease the conversion time of the main part water to hydrate. Based on the experimental kinetic curves of the water to hydrate transition the value of $t_{0.8}$ and $\alpha_f$ were calculated for the frozen water solutions of PVA, cryogel. To compare the results the parameters $t_{0.8}$ and $\alpha_f$ were also calculated for ground ice. The obtained results were presented in table 1. The time $t_{0.8}$ for the ground ice correlated with a transition 0.8 of mass fraction of initial water to hydrate was more than 1000 min, and the water to hydrate conversion $\alpha_f$ was only 0.35 after 1000 min of the gas hydrate formation. At the same conditions the time $t_{0.8}$ for frozen water solutions of PVA and cryogel (with the content of 7 wt % of PVA and 5 wt % of H17) was no more than 200 min, and the final conversion $\alpha_f$ was almost 0.95.

![Figure 2](image-url)  
*Figure 2. Changing of water to hydrate conversion during the process of gas hydrate formation for samples of “dry water” (1), ground ice (2), dispersions of PVA frozen water solution (5 wt % of PVA and 5 wt % of H17) (3), cryogel (5 wt % of PVA and 8 wt % of H17) (4), cryogel (7 wt % of PVA and 5 wt % H17) (5) at isochoric conditions. The desired temperature for gas hydrate formation in the samples of ground ice, dispersions of PVA frozen water solution was 272.2 K, for the samples of cryogel and “dry water” the temperature of gas hydrate formation was 273.2 K. The initial pressure was 4.9 MPa.*
**Table 1.** Values of a parameter $t_{0.8}$ and the final water to hydrate conversion $\alpha_f$ in methane hydrates at isochoric conditions. The initial pressure was 4.9 MPa.

| Sample      | PVA concentration (wt %) | H17 concentration (wt %) | Temperature of gas hydrate formation (K) | $t_{0.8}$ (min) | $\alpha_f$ (in 1000 min) |
|-------------|--------------------------|--------------------------|-----------------------------------------|-----------------|--------------------------|
| PVA FWS     | 5                        | 5                        | 272.2                                   | 170             | 0.93                     |
| Ground ice  | 0                        | 0                        | -/-                                     | > 2000          | 0.35                     |
| Cryogel     | 5                        | 8                        | 273.2                                   | 1100            | 0.79                     |
| "Dry water"| 0                        | 5                        | -/-                                     | 200             | 0.96                     |
| Ground ice  | 0                        | 0                        | -/-                                     | 460             | 0.87                     |

From the given results the transition water to hydrate rate $\frac{d\alpha}{dt}$ was calculated for studied samples of the PVA frozen water solutions and ground ice. In figure 3 the results on changing the transition water to hydrate rate and the temperature gauge readings in the samples of the PVA frozen water solutions and ground ice (at the given temperature of gas hydrate formation of 272.2 K).

**Figure 3.** Changing of the water to methane hydrate conversion rate (1-2) and temperature (3-4) during the process of gas hydrate formation in the samples of ground ice (1 and 3), frozen water solutions (5 wt % of PVA and 5 wt % of H17) (2 and 4) at isochoric conditions. The initial pressure was 4.9 MPa.

According to the data, the gas hydrate formation rate of PVA frozen water solutions after no less than 200 min period of time was several times higher than that for ground ice. Moreover, the temperatures of the samples were not higher than the temperature of ice melting (272.7 K taking into account the pressure in the reactor) for all period of gas hydrate formation. It seems reasonable to say that the presence of micro-inclusions of a concentrated solution of polymer in the PVA frozen water solutions inhibited the aggregation of hydrate crystals and this made the formation of the hydrate crust impervious to gas.
In figure 4 the typical curves of pressure and temperature changing in the reactor during the gas hydrate formation/dissociation cycles were presented for cryogel dispersions. According to the data, the cooling of the reactor from 293.2 to 273.2 K was followed with the pressure decrease in it. Near the temperature of 291.2 K there was observed the significant increase of the falling pressure rate that was due to the gas hydrate formation. For the period of time approximately 1000 min the temperature in the reactor was maintained up to the 273.2 K.

![Methane pressure changing in the reactor using the cycling temperature changing at isochoric conditions for cryogel dispersions (7 wt % of PVA and 5 wt % of H17).](image)

**Figure 4.** Methane pressure changing in the reactor using the cycling temperature changing at isochoric conditions for cryogel dispersions (7 wt % of PVA and 5 wt % of H17).

The pressure declining in the reactor during that time attested that the process of gas hydrate formation was continued. Heating of the reactor from 273.2 K to 293.2 K led to the pressure increase. When the temperature of the reactor was close to 275.2 K there was observed a marked rate increase of the pressure growth that was evidence of gas hydrate dissociation. For approximately 300 min the temperature in the reactor was hold equal to 293.2 K. Then, the cycle of pressure changing in the reactor was repeated. The same cycle of gas hydrate formation/dissociation was carried out for “dry water”. In table 2 there were presented the data on the reduction (in percent) of the final water to hydrate conversion after gas hydrate formation/dissociation cycles. It is known that the processes of gas hydrate formation/dissociation in “dry water” lead to the loss in stability (splitting into layers of a phase of bulk water and dispersed water stabilized with hydrophobic nanoparticles of silica dioxide) [4]. That was the reason for a considerable decline (about 20 %) of water to hydrate conversion that was obtained even after one gas hydrate formation/dissociation cycle. According to the data presented in table 2, the cryogel dispersions might be more stable to the processes of gas hydrate formation/dissociation as compared with “dry water” in the event that both systems had the comparable initial water to hydrate conversion. For “dry water” the water to hydrate conversion was down by 50 % after three cycles of gas hydrate formation/dissociation. Although, the water to hydrate conversion was down by 17 % in case of using cryogel.
Table 2. The value of reduction (in percent) of the final water to hydrate conversion after cycles of gas hydrate formation/dissociation. The initial water to hydrate conversion (before the dissociation cycle) was 0.91.

| Sample | PVA concentration (wt %) | H17 concentration (wt %) | Cycle numbers |
|--------|--------------------------|--------------------------|---------------|
| Cryogel | 5                        | 8                        | 5  | 22 | -  |
| "-/-" | 7                        | 5                        | 1  | 11 | 17 |
| “Dry water” | 0                        | 5                        | 24 | 43 | 53 |

4. Conclusion

1. It was established that the PVA inclusions into the frozen water solutions might ten times increase the gas hydrate formation rate and the water to hydrate conversion.

2. It was shown that the stability of PVA cryogel dispersions to the processes of gas hydrate formation/dissociation might be ten times higher than that for “dry water”.

Acknowledgements

The present work was supported by the Basic Research Program of RAS No. IX.135.2.3. 502 One of us, N S Molokitina, expresses her grateful thanks to the Council of Russian President grant for President's scholarship SP-3113.2018.1.

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