EFFECTS OF ADDITIVES ON FORMATION RATES OF CO_2 HYDRATE FILMS

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1 INTRODUCTION

Naturally occurring clathrate hydrates are found in marine sediments and in permafrost. Because they contain a large amount of methane, they are thought to have potential as an unconventional energy resource. At the same time, however, clathrate hydrates are a serious problem for the gas and oil industries, because they form easily under suitable conditions at the sites of natural gas production, transportation, and processing. The inhibition and control of hydrates in pipelines adds tremendously to gas production costs.[1]

The usual technology for hydrate inhibition includes heating, pressure reduction and the addition of chemicals. The additives are classified into two types: the thermodynamic inhibitors and the kinetic inhibitors. The thermodynamic inhibitors, such as NaCl, methanol and glycol, shift the equilibrium conditions. These additives have been shown to inhibit the hydrate formation successfully, but typically they are required to work at relatively higher concentrations ranging from 15 to 50wt% of the free water phase.[1] On the other hand, certain types of polymers act as kinetic inhibitors that can delay the start of nucleation and thereby slow the hydrate growth rate at low concentration[2], such that hydrate masses will not grow sufficiently large to cause blockage during the residence time of the liquid phase in the pipeline.

These methods are often economically unsound or environmentally destructive. For example, it has been reported that methanol injection costs the oil and gas industry about $500 million per year.[3] Also, it would be advantageous to discover naturally occurring additives from an environmental perspective. Antifreeze proteins (AFPs) and antifreeze glycoproteins (AFGPs) are considered to be potential inhibitors, since they are thought to inhibit freezing in a non-colligative manner by binding to the surface of ice crystals and delaying ice crystal growth rates.[4,5] Whether AFPs might also inhibit the formation of clathrate hydrates has been questioned by the proposed mechanism of the inhibition of ice growth by AFPs.

A number of recent experimental and simulation studies have shown that two different AFPs are capable of inhibiting the growth of clathrate hydrates. Zeng et al.[6-8] studied the effect of type I and an insect AFPs on the formation of tetrahydrofuran (THF) clathrate hydrate by observing changes in the crystal morphology of THF hydrate and by determining the induction time for nucleation. They found that AFPs were more effective than the kinetic inhibitor polyvinylpyrrolidone (PVP). Zeng et al.[9] performed a Monte

Carlo simulation of ice-crystal growth to study the mechanism of inhibition of AFPs on the surface of the THF hydrate and propane hydrate. They found that most of the octahedron surfaces of the THF hydrate were covered with AFP molecules, which could reduce the growth rate of the THF hydrate only allowing plate growth perpendicular to that surface. It is thus necessary to look for other experimental evidences to clarify the common features of AFPs on the inhibition of the clathrate hydrate formation.

Other potential inhibitors with less environmental impact might be selected from among the cryoprotecting materials naturally produced in animals. One such material is trehalose, which consists of fructose and glucose rings connected by a glycosidic bond, and is known to decrease the melting point of ice below the molar freezing-point depression.[10,11] This material is expected to act as a thermodynamic inhibitor for clathrate hydrates.

In the present study, we investigated the effect of two cryoprotectants, type-III AFP and trehalose, on the crystal growth rate of CO_2 hydrate, a type-I gas hydrate. This is the first investigation of the effect of type-III AFP on the inhibition of clathrate hydrate, which has been confirmed to be a cryoprotectant.[12] It is also the first examination of the effect of trehalose on the crystal growth of clathrate hydrates. On the other hand, type-I clathrate hydrates, such as the CO_2 hydrate used here, have a crystal structure just slightly different from that of type-II clathrate hydrates, such as THF hydrate and propane hydrate. Uchida et al.[13,14] have extensively investigated the growth mechanisms of CO_2-hydrate films formed on the interface between CO_2 phase and water. The use of an experimental technique that has been used previously would be advantageous for the comparison of results with other conditions, such as pure water or NaCl solutions, and to accumulate the useful knowledge on the hydrate inhibition mechanism to search for feasible materials with less environmental impact.

2 MATERIAL AND METHODS

We used type-III AFP (RD3-N1; retrieved from Antarctic eel pout) and trehalose (research-grade; Hayashibara Biochemical Laboratories, Inc.) as the inhibitors. The characteristics of this AFP are described in detail in Miura et al.[12] We added a small amount of AFP (from 0.01 to 1 mg ml^{-1} water) to distilled and deionized water (approximately 18 MΩ in resistivity) for the experiments. Trehalose was added at concentrations ranging from 1 to 50 wt%. CO_2 was delivered from Hokkaido Air Water, Inc., and its purity was approximately 99%.

The experimental procedures were almost the same as in the previous studies.[13,14] In brief, a pressure vessel (approximately 10 cm^3 in volume) equipped with two optical windows was filled with liquid CO_2 at pressures ranging from 4 to 6 MPa at room temperature. Then a small amount of solution (prepared to the experimental concentrations of additives in advance) was added to form a water droplet in the vessel. The temperature was controlled within $\pm$ 0.2 K by the cooling jacket that covered the vessel. After setting the system temperature to the experimental condition, the formation and growth process of CO_2 hydrate film on the water droplet were observed by a microscope and CCD camera system, and recorded using an S-VHS time-lapse video. During the temperature change, the rates of temperature change did not controlled. Several sequences of the hydrate formation were tested to measure the induction period τ and the supercooling $\Delta T = T_f - T_e$, where T_f is the temperature in the vessel at the time the hydrate started to grow and T_e is

the equilibrium temperature of CO_2 hydrate at the experimental pressure, and to observe the lateral growth process of CO_2 hydrate film.

3 RESULTS AND DISCUSSIONS

3.1 Effects of type-III AFP on the formation process of the CO_2-hydrate film

Figure 1 shows a typical snapshot of the CO_2-hydrate film formed at the boundary between the AFP-solution droplet and the surrounding CO_2.

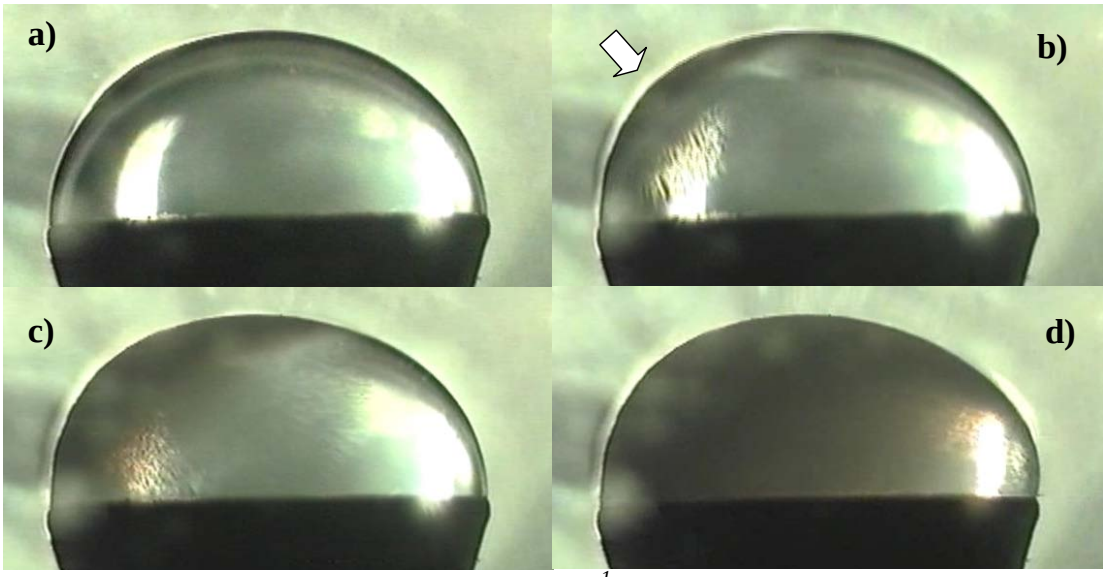

Figure 1 *CO_2-hydrate film on an 0.01 mg ml^{-1} AFP-solution droplet at P = 5.5 MPa and T = 264.2 K. The droplet is on a stainless-steel stand (approximately 5mm in diameter). a) The initial droplet shape. b) The hydrate film begins to form at the left-top of the droplet (shown by an arrow). (c)-(d): CO_2 hydrate film grows laterally along the droplet surface from left to right. Each image is about 0.4 s apart.*

Figure 2 shows the temperature change of typical experimental run with various concentrations of AFP solution. Arrows in this figure indicate the formation times of CO_2 hydrate film on the solution droplet. The origin of the time axis (t=0) was defined as the time when the temperature reached T_e at the experimental pressure. Because the concentration of AFP was very small, the value of T_e for this experiment was taken as the same as that for pure CO_2 hydrate. From Figure 2, we estimated both τ and ΔT.

Table 1 summarizes the results obtained for CO_2-hydrate film formation in AFP-solution experiments. In each column, the upper value is that obtained in the first run, while the lower number in brackets is the average for all subsequent runs with its variation. For AFP-0.01 mg ml-1 samples, we showed the values in brackets are <average +/- standard deviation> for 8 times repeating experiments. Table 1 shows that τ was estimated as ranging between 60 and 100 min, which is much longer than the periods observed on the pure water droplet.[13] It is concluded that CO_2 hydrate formation was clearly inhibited by the presence of AFP molecules, even though the concentration was as small as 10^{-3} ppm.

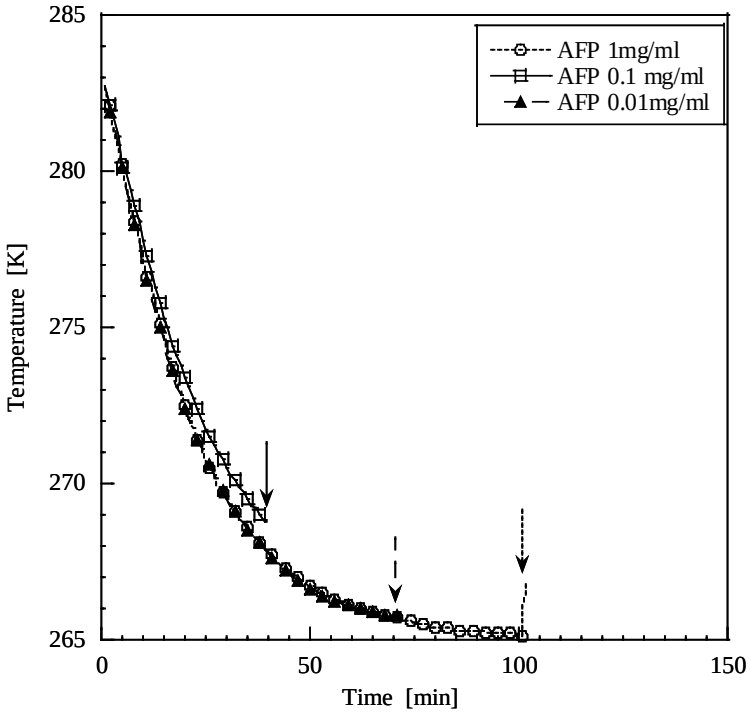

Figure 2 *Temperature profiles of the CO_2-AFP solution system at various AFP concentrations during the induction period. Each arrow indicates a formation point of CO_2 hydrate film on the droplet.*

When we compare τ and ΔT of the first run with those of the subsequent average ones, we find that the memory effect is small, or even be recovered, in the solutions with a small AFP concentration. The recovering of memory effect tended to larger in higher AFP concentrations. This is a very interesting phenomenon, and has been reported to be unique for AFPs,[8] although this effect should be confirmed by statistical analysis in future studies.

Zeng et al.[7,8] reported the formation ratio of THF hydrate and propane hydrate in type-I AFP solution within 24 hours. The supercooling for THF hydrate formation was approximately 4.4 K and that for propane hydrate was 7.4 K. These small supercooling conditions would make the induction period longer than that in the present study. Although a direct comparison between their results and the present ones is difficult, the effectiveness of both types of AFP on the hydrate inhibition seems to be higher than that of other kinetic inhibitors. Since the AFP concentration is low enough not to change the physical properties of the dominant part of water, such as the melting point or the surface tension, the effective mechanism of the growth inhibition would consist of disturbing the nucleation process.

Table 1 *Summary of CO_2-hydrate formation on the droplet of AFP solutions*

AFP concentration	τ [min]	ΔT [K]
1 mg ml^{-1}	101 (50 ± 33)	17.9 (17.0 ± 2.1)
0.1 mg ml^{-1}	63 (31 ± 8)	16.8 (12.5 ± 1.3)
0.01 mg ml^{-1}	71 <73 ± 33>	17.0 <18.2 ± 0.7>
pure water[13]	~ 20	< 10

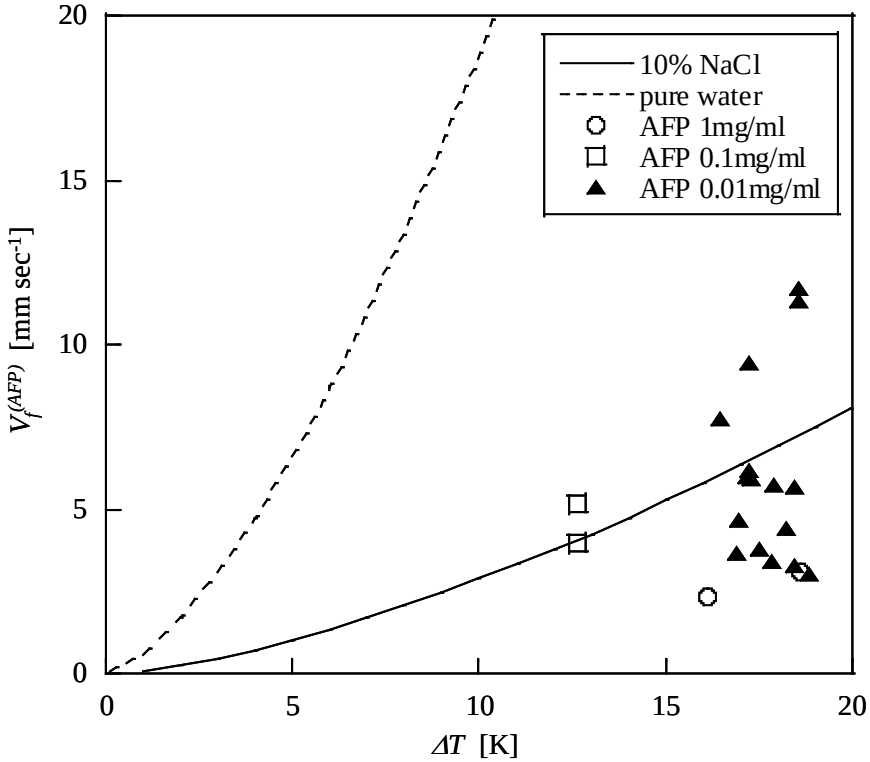

Figure 3 *Lateral growth rate of CO_2 hydrate film $v_f^{(AFP)}$ as a function of supercooling ΔT and for various AFP concentrations. The dotted line and solid line indicate the previous data on pure water and 10 wt% NaCl solution, respectively.*[14]

Using the time sequence of images in Figure 1, we measured the lateral growth rate of CO_2 hydrate by observing the position of the front edge of the hydrate film on the droplet surface. Figure 3 shows the lateral growth rate $v_f^{(AFP)}$ at each AFP concentration as a function of ΔT. In this figure, data from previous studies[13,14] are also shown (dotted and solid lines for pure and 10wt% NaCl solution, respectively). This figure indicates that the lateral growth rates obtained in the present study varied from 2 to 10 mm sec^{-1} as ΔT varied from 12 to 18 K. The lateral growth rates of CO_2-hydrate film on AFP solutions were much smaller than those on pure water, and were of the same order as those on the NaCl solution with approximately 10 wt%.[14] The dependence of $v_f^{(AFP)}$ on ΔT in each concentration is not clear. The inhibition effects of AFP also seem to have weak dependence on AFP concentrations.

Zeng et al.[7] estimated the effectiveness of the growth inhibition of the type-I AFP on the type-II propane hydrate. It is also difficult to compare these data directly with those obtained in the present study. However, type-III AFP can work as an inhibitor at a concentration 10^{-2} times smaller than type-I AFP. It is thus clear that the effectiveness of the growth inhibition of the type-III AFP on the type-I CO_2 hydrate is much larger than that of the classic inhibitors. This allows us to hypothesize that type-III AFP may have various functional sites fitting on the hydrate (and ice) crystal because its shape is spherical. Since the growth inhibition effect of AFPs on clathrate hydrates was observed even though their concentrations were too low to affect the equilibrium condition shift, we consider that the inhibition process is mainly due to the disturbance of growth kinetics. More

experimental efforts, especially the direct observations of molecular scale, and theoretical approaches are necessary to reveal the detailed mechanism of the inhibition.

3.2 Effects of trehalose on the formation process of the CO_2-hydrate film

The formation process of CO_2-hydrate film on the trehalose-solution droplet was almost the same as shown in Figure 1: CO_2 hydrate nucleated somewhere on the droplet, and thethin film of CO_2 hydrate laterally grew at the interface between CO_2 and solution. At higher trehalose-concentration, the nucleation was observed to occur near the top of the droplet for several times as observed on the NaCl solutions.[14]

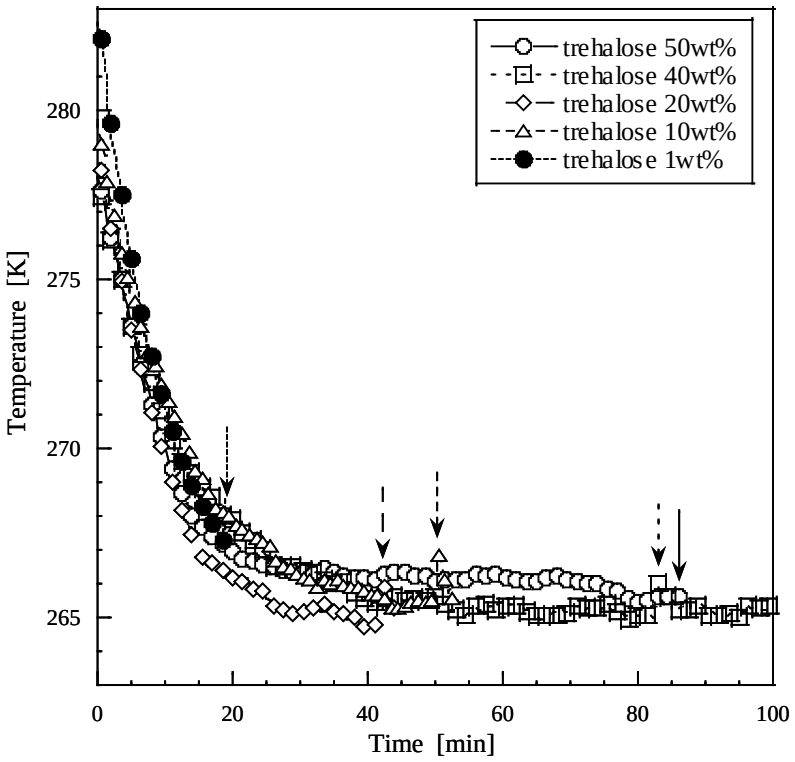

Figure 4 *Temperature profiles of CO_2-trehalose solution system at various trehalose concentrations during induction period. Each arrow indicates the formation point of CO_2 hydrate film on the droplet.*

Figure 4 shows a *T-t* diagram of some experimental runs with different trehalose concentrations. The origin of the time axis and arrows are the same as in Figure 2. This picture indicates that τ varies from approximately 20 minutes to more than 80 minutes at temperatures even at supercooling conditions. This is the same tendency as seen for other hydrate inhibitors, so trehalose is considered to be an effective inhibitor.

Table 2 summarizes the results of CO_2 hydrate film formation obtained in trehalose-solution experiments. For both τ and ΔT columns, the upper value is that obtained in the first run, while the lower number in brackets is the average for all subsequent runs with its variation. For trehalose-50 wt% samples, we showed the values in brackets are <average +/- standard deviation> for 8 times repeating experiments. The equilibrium temperature shift of CO_2 hydrate in each trehalose solution $\Delta T_e = T_e - T_e^0$, where T_e^0 is the dissociation temperature of CO_2 hydrate at the same pressure in pure water system[1], is also

roughly estimate by the dissociation process observations of CO_2-hydrate film during the heating process. The increasing rates were more than 1 K min^{-1}, which were not controlled. So the accuracy of the estimation would be approximately +/- 0.9 K. Compared to the effect of NaCl on the equilibrium conditions, ΔT_e measured in the present study is found to be of almost the same order. Therefore, trehalose may function as a thermodynamic inhibitor.

Table 2: *Summary of CO_2-hydrate formation on the droplet of trehalose solutions*

trehalose concentration	τ [min]	ΔT [K]	ΔT_e [K] ($\pm$ 0.9 K)
50 wt%	84 <42 $\pm$ 39>	5.8 <7.7 $\pm$ 3.2>	3.1
40 wt%	83 (139 $\pm$ 149)	12.9 (11.6 $\pm$ 2.6)	2.3
20 wt%	42 (101 $\pm$ 58)	14.0 (13.8 $\pm$ 0.2)	0.5
10 wt%	50 (51 $\pm$ 10)	13.8 (16.2 $\pm$ 2.5)	0.7
1 wt%	19	14.9	0
pure water[13]	~ 20	< 10	-

This table shows that τ becomes remarkably longer at trehalose concentrations higher than 10 wt%, and that ΔT is within an almost similar range at different concentrations. Therefore it is suggested that the inhibition effect of trehalose on the CO_2 hydrate nucleation is larger at a trehalose concentration higher than 20 wt% in the solution.

It is noted that τ in the same concentration scattered vary widely, and the difference of τ between the first run and those of all subsequent runs is included in the variation. The memory effect in the trehalose solutions was, therefore, not clearly observed in the present study. This may indicate that the nucleation process of CO_2 hydrate crystals in the trehalose solution is slightly complicated. Further systematic studies are required to clarify this problem.

Then the growth rate of CO_2 hydrate films on the trehalose-solution droplet $v_f^{(treha)}$ was examined in the same manner as in the previous section. Figure 5 shows $v_f^{(treha)}$ in each trehalose solution as a function of ΔT. Data from previous studies[13,14] are also included in the figure for purpose of comparison (dotted and solid lines for pure and 10 wt% NaCl solution, respectively). It can be seen that the $v_f^{(treha)}$ values were on the order of 10^{-0} mm sec^{-1} as ΔT varied from 4 to 18 K. $v_f^{(treha)}$ was found to be smaller than those on pure water and similar to those of the NaCl solution with similar concentration (approximately 10 wt%).[14] Therefore it was concluded that trehalose is one of the effective inhibitors of clathrate hydrates. At a similar ΔT condition of approximately 13 K, $v_f^{(treha)}$ tends to have been smaller at the higher trehalose-concentration solutions. This concentration dependence may suggest that trehalose works as a kinetic inhibitor. The large distributions of $v_f^{(treha)}$ at the same concentration observed at large ΔT conditions may have resulted from the variety of nucleation conditions. This kind of variation was also found in the experiments of pure water.[13]

However, the value of $v_f^{(treha)}$ at a trehalose concentration of 50 wt% is almost independent of ΔT. This is not the case for thermodynamic inhibitors such as NaCl,[14] but as shown in the present study, it is the case for kinetic inhibitors such as type-III AFP.

The result obtained by the transmission electron microscope observations of the freeze-fracture replica on trehalose solutions[15] suggested that the ice-crystal nucleation is enhanced in the solution with higher trehalose concentration. Based on these experimental results and assuming a similar nucleation process between ice and clathrate hydrates, we can speculate that trehalose, as a kinetic inhibitor, may not inhibit the nucleation but may work as an anti-agglomerant, keeping small hydrate particles dispersed as they form.

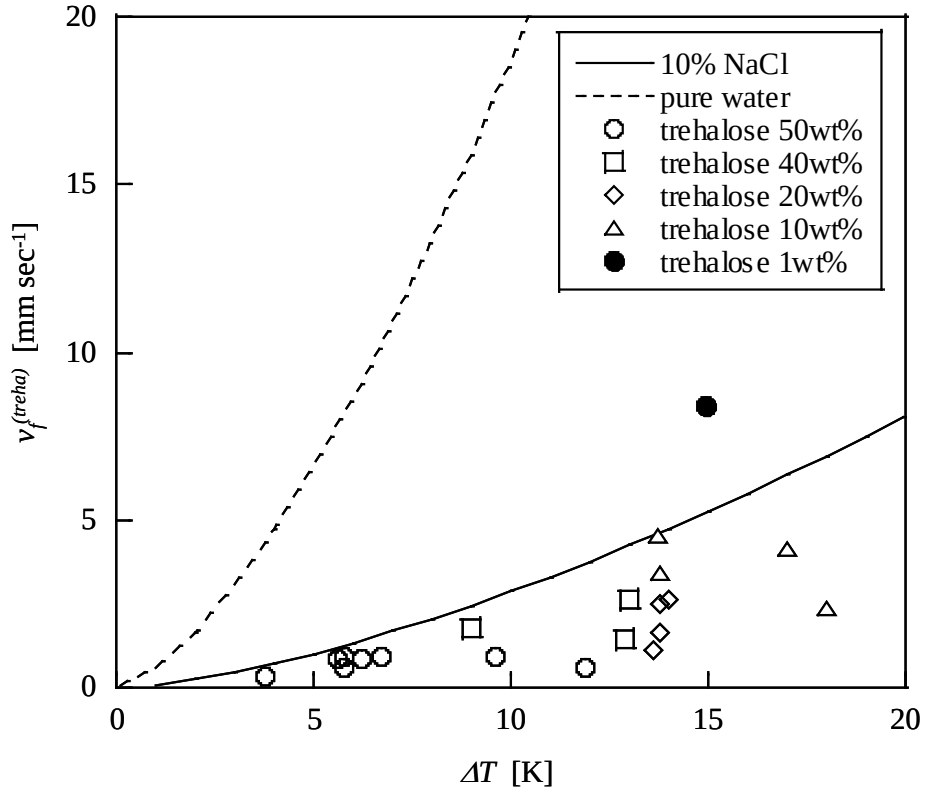

Figure 5 Lateral growth rate of CO_2 hydrate film $v_f^{(treha)}$ as a function of supercooling ΔT and for various trehalose concentrations. Dotted line and solid line indicate the previous data on pure water and 10 wt% NaCl solution, respectively. [14]

Another possible mechanism of trehalose molecules as a kinetic inhibitor is mentioned below. In the growth process of CO_2 hydrate, trehalose may work as the kinetic inhibitor that prevents the rate-determining process of the crystal formation at the reaction site which might have small dependence on ΔT. Trehalose has been observed to prevent ice-crystal growth with the reduction of the free-water providing because trehalose strongly hydrated in the solution.[11,15] This effect is found apparently when the trehalose concentration increases beyond the intrinsic hydration number of trehalose molecules. It is thus reasonable that the kinetic effect of trehalose on the inhibition of the hydrate formation would be resulted from the smaller supplement of free water from the solution of higher trehalose concentrations.

4 CONCLUSIONS

The inhibition effects of type-III AFP and trehalose, two cryoprotecting materials produced in animals, on type-I CO_2 clathrate-hydrates were examined. For comparison with the results of a previous study in which the lateral growth rates of CO_2-hydrate film were dependent on temperature, pressure and NaCl concentration, the solution droplet was observed in a high pressure vessel filled with CO_2. Type-III AFP was found to increase the induction period and to reduce the lateral growth rate of CO_2-hydrate films. It worked well at low concentrations, indicating that AFP works as a kinetic inhibitor. It was also indicated that AFP would weaken the memory effect of CO_2-hydrate formation. Trehalose had similar inhibition effects on both the induction period and the lateral growth rate, but it had little apparent concentration-dependence on them. Since trehalose also causes the equilibrium conditions of the CO_2 hydrate to shift to lower temperatures, it works not only as a thermodynamic inhibitor but also as a kinetic inhibitor, especially as an anti-agglomerant.

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