Statistical Study of Clathrate-Hydrate Nucleation in a Water/Hydrochlorofluorocarbon System: Search for the Nature of the "Memory Effect"

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This paper describes an experimental study on the statistical nature of clathrate-hydrate nucleation in a quiescent hydrochlorofluorocarbon-in-water system in which a hydrate was once formed and then dissociated. The primary objective of the study is to investigate how hydrate nucleation in the system depends on its thermal history (i.e., the time evolution of system temperature), through which the preceding hydrate dissociation was carried out, and thereby better characterize the nature of the "memory effect" for hydrate formation. Isolated drops of HCFC-141b (CH_3CCl_2F) immersed in water were employed as test samples for use in detecting hydrate formation on the drop surfaces by video-monitoring. The thermal history of these samples was characterized by the temperature at which the hydrate covering the drops dissociated and also by the length of time for which the samples were held at that temperature before they were cooled again to a prescribed level to induce hydrate nucleation. Thirty to fifty samples were used in each thermal history program, to collect a sufficient amount of induction-time data for statistical data processing. The processed data indicated that hydrate nucleation in a system with a "memory" of prior hydrate formation/dissociation is an intrinsically stochastic event and that the rate of nucleation strongly depends on the thermal history of the system. A qualitative discrepancy is found between these data and predictions based on assumptions that the rate of nucleation is essentially the same for all samples subjected to the same thermal-history program and that the rate is held constant with time under constant hydrate-formable thermodynamic conditions. A hypothetical explanation is provided for this point, assuming that the "memory" of prior hydrate formation/dissociation that remains in individual samples could differ despite the samples having the same thermal history.

Introduction

Nucleation of clathrate hydrates, solid compounds made up of hydrogen-bonded water molecules that form cages that enclose guest molecules, has long been of scientific interest.[1−22] An enigmatic concept emerged in studies on the nucleation of hydrates in the form of the memory effect. This concept originated from empirical observations that the induction time for hydrate nucleation (i.e., the duration for which a hydrate-forming system endures in the metastable hydrate-free state) strongly depends on the thermal history of the system. A hydrate is formed after a much shorter induction time, if the system is cooled and/or pressurized to form a hydrate, then heated and/or depressurized to completely dissociate it (in a macroscopic sense), then re-cooled and/or pressurized to the same initial temperature/pressure conditions. This phenomenon is called the memory effect. Vysniauskas and Bishnoi[2] presented experimental data of the induction time for hydrate nucleation in a methane/water system, which demonstrated a substantial reduction in induction time as a result of prior hydrate formation in the system. The memory effect may also result from prior ice formation/melting of the water used in a hydrate forming system; this possibility was revealed in the methane/water and CO_2/

water systems by Parent and Bishnoi[12] and Takeya et al.[14] The memory effect thus empirically recognized has gained researchers' interest, and its mechanism has been considered and discussed from various aspects. A hypothesis was presented that asserts that the memory effect originates from residual clusters of water molecules after hydrate dissociation. Several experimental studies have been performed to detect any sign of such water clustering by measuring some physical properties (viscosity, interfacial tension, refractive index, etc.) of hydrate-forming systems just after hydrate dissociation.[15−18] Some of these studies demonstrated results that support the residual water-clustering hypothesis[15,16] and some exhibited negative results.[17,18] Molecular-dynamics simulation studies[19−22] have also been performed to examine the validity of the hypothesis and to reveal the mechanism of the memory effect. One of these studies reported a dominant distribution of ice-like water-molecular structures, instead of hydrate-cage-like structures, in liquid water generated by hydrate dissociation, and thereby led to a negative view of the above hypothesis.[20] However, more detailed analyses of simulation data may be necessary to derive a conclusive physical image of the memory effect.

The aim of the present study is not to directly discuss the mechanism of hydrate nucleation or of the memory effect but to clarify the statistical characteristics of hydrate nucleation and, thereby, to derive a better understanding of the nature of the memory effect. We outline the background of the present study more specifically below.

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When we discuss hydrate nucleation in relation to the memory effect, its stochastic nature needs to be considered. The induction time that precedes hydrate nucleation should be a stochastic quantity if hydrate nucleation is stochastic by nature, such as spontaneous nucleation causing a phase change in a one-component system that has been kept under metastable thermodynamic conditions (e.g., nucleation of ice from supercooled liquid water). We may fail to perceive this stochastic nature of hydrate nucleation if insufficient induction-time data is obtained under each experimental condition. The number of data items should typically be several tens or larger to enable application of any statistical data processing procedure that can reveal the stochastic nature. Lingelem et al.[10] were the first to examine the stochastic nature of hydrate nucleation. They used a CFC-12/water system, to obtain about 20 induction-time data items under each experimental condition and demonstrated how the probability of survival of hydrate-free samples decayed with time over $10-25$ h. The induction-time data that Parent and Bishnoi[12] obtained in the methane/water system also indicated the stochastic nature of hydrate nucleation. A study by Takeya et al.[14] is the only one that investigated the stochastic nature of hydrate nucleation to characterize the memory effect. However, the memory that they investigated was given by prior ice formation/melting of water samples before their use in subsequent hydrate-formation experiments. We are aware of no study yet reported that investigates the stochastic nature of hydrate nucleation in a system with prior hydrate formation/dissociation.

We performed induction-time measurements in this study in an isobaric HCFC-141b/water system that had been cooled to form hydrate, then held at a higher temperature for a prescribed time to dissociate the hydrate, and then cooled again to a temperature at which the hydrate would re-form. We monitored the system temperature in, and the duration of, the intermediate hydrate-dissociating period as experimental parameters to characterize the thermal history of the system, on which the retained memory in the subsequent hydrate-forming period may depend. We obtained a sufficient amount of induction-time data in each set of experiments with a fixed thermal history to manifest the stochastic nature of hydrate nucleation and document how it varies with the thermal history of a given system.

Experimental Section

(a) Materials. Hydrochlorofluorocarbon HCFC-141b (CH_3-CCl_2F), which is known to form a structure-II hydrate at temperatures below 281.6 K ($\equiv T_{tri}$, the triple liquid-water/hydrate/liquid-HCFC-141b equilibrium temperature) under atmospheric pressure (or any other pressures higher than 0.042 MPa),[23-25] was selected as the hydrate former. Commercial HCFC-141b of 99.9 wt % certified purity was used as received from the supplier (Daikin Kogyo Co., Osaka, Japan). The water used with the HCFC-141b sample had been deionized and distilled.

(b) Apparatus. A schematic illustration of the experimental apparatus is given in Figure 1. Pyrex test tubes of 6 mm i.d. were used as test cells, each holding a 2-cm^3 liquid water pool and an HCFC-141b drop ($\sim$3.5 mm dia.). The HCFC drop lying on the round-bottom of each test tube was almost completely surrounded by water because of the high wettability of Pyrex with water and thereby retained a nearly spherical form. Eleven test tubes (10 test cells plus one dummy cell) were aligned and immersed in a temperature-controlled rectangular water bath made of transparent poly(methyl methacrylate) (PMMA) plates. The bath was integrated with a PMMA-made water jacket and was covered with a rectangular PMMA-made water channel. Two independent water circulation loops were prepared, one
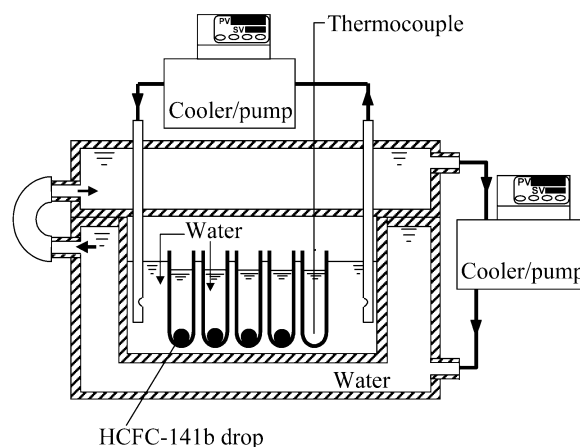

Figure 1. Schematic illustration of the major portion of the apparatus. Eleven test tubes (10 test cells plus one dummy cell for temperature measurement) were aligned in the water bath, although only five test tubes are shown here.

to circulate water through the jacket, the covering channel, and an external cooler/pump unit, and the other to circulate water through the bath and another cooler/pump unit. Only the former cooler/pump unit was operated to circulate temperature-controlled water through the jacket and the covering channel to maintain a constant temperature inside the test tubes, leaving the water inside the bath stagnant. The latter cooler/pump unit was operated, in addition to the former one, exclusively to quickly change the temperature in the test tubes with the aid of forced convection of water crossing the aligned test tubes inside the bath. Both water circulation loops were open to the atmosphere at the cooler/pump unit incorporated into the loop. Hence, the liquids in the test tubes are considered to have been under atmospheric pressure.

One of the eleven test tubes contained only water in the amount of $\sim$2 cm^3. No HCFC drop was held in this tube so that no hydrate could form in this tube. This dummy cell was prepared only for temperature measurement with the aid of a type-T thermocouple inserted into the water pool contained in the cell. No thermocouple was inserted into the other test tubes in order to avoid any effect of the thermocouple surface on hydrate nucleation. The temperatures in those tubes (i.e., the test cells) were assumed to be the same as that measured in the dummy cell.

(c) Procedure. The thermal history of each HCFC-in-water sample inside each test tube during the experiment is illustrated schematically in Figure 2. The sample was first cooled to a hydrate-formable temperature, 277.2 ± 0.2 K. The formation of hydrate crystals at the HCFC drop surface was artificially triggered by sprinkling a trace amount of hydrate particles formed in an external crystallizer into the test tube. The hydrate crystals grew into the form of a film enclosing the HCFC drop in several tens of seconds. The temperature was held constant at 277.2 ± 0.2 K for 15 min after the drop was completely enclosed by the hydrate film. The temperature was then raised to a prescribed level, T_{pri}, above T_{tri} (=281.6 K) to make the hydrate crystals dissociate. This temperature rise was accomplished within 2 min. Dissociation of the hydrate crystals commenced just after the temperature exceeded T_{tri} and was completed within about 10 min. [Dissociation completed simultaneously (within an uncertainty of ±30 s) in all of the tested samples subjected to the same temperature-rise operation, indicating that the temperature histories of the individual samples were nearly the same, although their temperatures were not
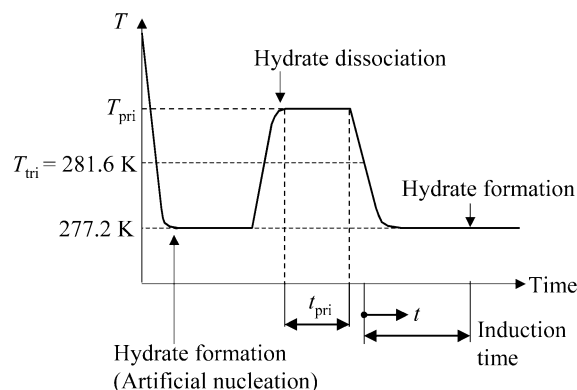
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Figure 2. Thermal history of each hydrate-forming sample. The sample was first cooled to 277.2 ± 0.2 K to form a hydrate, then heated to T_{pri} (282.1 ± 0.1 K, 282.6 ± 0.1 K, or 283.1 ± 0.1 K) and held at that temperature for a period of t_{pri} (40 or 720 min) to completely dissociated the hydrate, and re-cooled again to 277.2 ± 0.2 K. The sample temperature was maintained at that temperature thereafter to measure the induction time until hydrate formation occurred again in the sample. Here, the induction time is defined as the time of hydrate re-formation measured from the time when the sample temperature passed T_{tri} (=281.6 K), the three-phase (water/HCFC-141b/hydrate) equilibrium temperature.
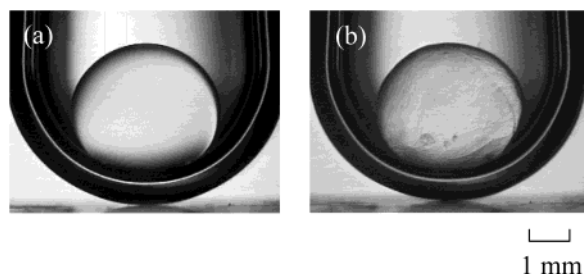

Figure 3. Videographs of an HCFC-141b drop in water (a) before hydrate formation and (b) after hydrate-film growth on the drop surface.

directly measured.] The temperature was held constant at T_{pri} for a prescribed time lapse, t_{pri}. The temperature was then again decreased to 277.2 ± 0.2 K. The induction time measurement for a given sample commenced when its temperature was lowered to T_{tri}, and the measurement continued for 7 h or less. It must be noted that the sample cooling from T_{pri} to 277.2 K was completed within 90 s in every experimental run, whereas the measured induction times extended from several minutes to several hours. Thus, the initial transient-temperature portion of each test accounted for only a minor proportion of each induction-time data.

The test samples held in the 10 test tubes laterally aligned in the water bath were continuously monitored, using a micrographic zoom lens connected to a video camera. The hydrate formation in any sample could be readily recognized by the appearance of crystalline morphology on the HCFC-drop surface, as shown in Figure 3. We could safely determine the time of hydrate nucleation with an uncertainty less than 1 min even if we could not detect the hydrate formation until a hydrate film had already covered a substantial proportion of the drop surface; this is because the lateral growth rate of the hydrate film on the drop surface was observed to be 2−3 mm/min at 277.2 ± 0.2 K.

We performed six sets of experiments, with each set comprised of induction-time measurements for 30−50 samples with the same thermal history that could be specified in terms of T_{pri} and t_{pri}, as illustrated in Figure 2. Three different levels of T_{pri}−282.1 ± 0.1 K, 282.6 ± 0.1 K and 283.1 ± 0.1 K−and
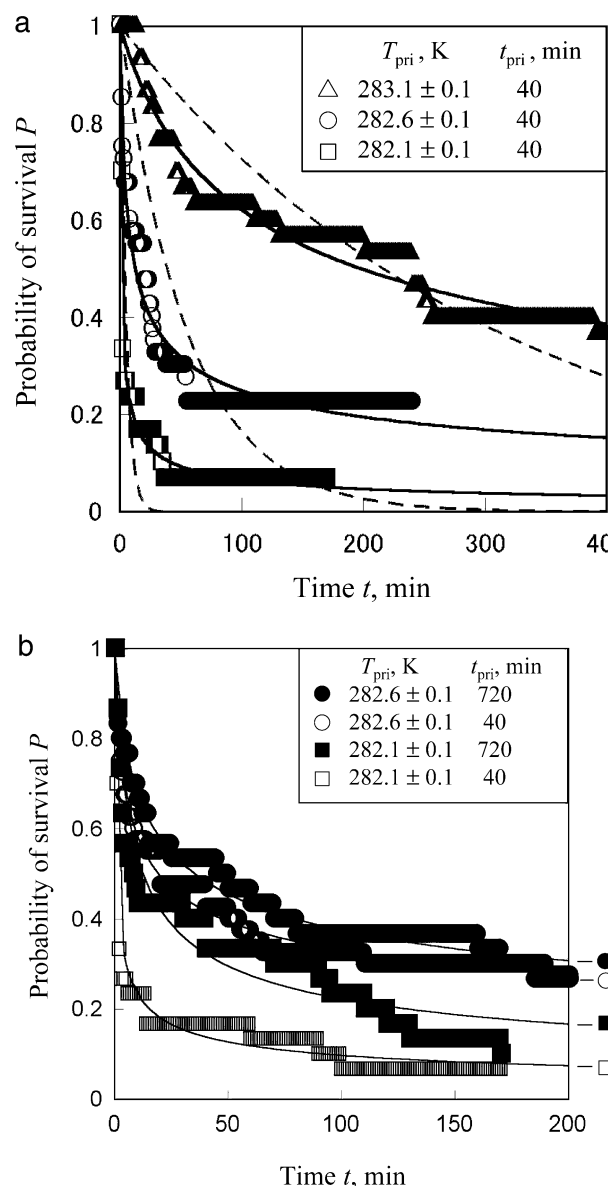

Figure 4. Probability of survival of hydrate-free samples plotted versus the time of their preservation under hydrate-formable conditions. (a) The data obtained with three different levels of T_{pri} and the same length of t_{pri}. (b) The data obtained with two different settings of t_{pri} for each of two levels of T_{pri}. Dashed and solid lines indicate the curves of $P = \exp(-\lambda t)$ and $P = (1 + t/a)^b$, each of which is best-fitted to the experimental data.

two different lengths of t_{pri}−40 and 720 min−were combined to arrange six different T_{pri}−t_{pri} pairs, each corresponding to one of the six sets of experiments.

Results and Discussion

(a) Probability of Survival of Hydrate-Free Samples. The induction-time data obtained in each set of experiments were processed into the form of an evolution of the probability of survival of the hydrate-free samples, $P \equiv n/n_0$, with a lapse of time t after the samples were placed under hydrate-formable conditions, $T \leq T_{tri}$ (see Figure 2), where n is the number of hydrate-free samples in which hydrate nucleation had not occurred until a given instant, and n_0 is the number of samples used in this set of experiments. The obtained P−t relations are depicted in two diagrams, a and b, in Figure 4. Every P−t relation relevant to a particular T_{pri}−t_{pri} pair exhibits a nearly

exponential decay of P with time t extending to several hours or even longer. This fact is in itself conclusive evidence of the nondeterministic nature of hydrate nucleation in a system with prior hydrate-formation/dissociation experience. The nucleation must be stochastic or random in nature.

Figure 4a contains the $P-t$ data obtained with three different settings of T_{pri} but with the same setting of t_{pri}. Here we note that only a slight increase ($\sim$0.5 K) in T_{pri} causes a substantial decrease in the rate of decay in P, i.e., a significant decrease in the hydrate nucleation rate. Thus, it appears that the fading of the memory of prior hydrate formation/dissociation in a given system is very sensitive to the temperature at which the system has been held in advance of the subsequent hydrate formation.

Figure 4b compares the $P-t$ data sets obtained with two different settings of t_{pri} for each of the two levels of T_{pri}. A slower decay in P is observed with the longer t_{pri} as long as T_{pri} is the same. This fact indicates that memory of prior hydrate formation/dissociation fades with a time lapse while the system is held at a temperature exceeding T_{tri}.

(b) Comparison between Experimental Data and Nucleation Theory. The following $P-t$ relation should hold if all of the samples with the same thermal history (i.e., the samples to which the same $T_{pri}-t_{pri}$ pair has been applied) have the same, time-independent nucleation rate λ

$$P = e^{-\lambda t} \tag{1}$$

The dashed lines superposed on the data points in Figure 4a represent the exponential $P-t$ relations best-fitted to the relevant $P-t$ data sets. The hydrate nucleation in our experimental system can be considered to be a simple stochastic phenomenon if the experimental data are well reproduced by eq 1. However, the observed $P-t$ relations deviate significantly from the exponential curves based on eq 1. This indicates the possibility that the nucleation rate is not uniquely determined for all samples but differ from sample to sample. Therefore, the state of memory preservation may differ from sample to sample despite the same thermal history apparently having been commonly experienced by all of the samples. We present below a hypothetical interpretation of the experimental observations based on this concept.

We assume here that a given set of hydrate-forming samples with a common thermal history has a particular spectrum of the nucleation rate λ, instead of a single value. We can express the overall probability of survival for all samples, P, as follows if we denote the probability density of samples relevant to the variable λ by $\phi(\lambda)$:

$$P(t) = \int_0^\infty \phi(\lambda) \exp(-\lambda t)\, d\lambda \tag{2}$$

Mathematically, $P(t)$ in eq 2 is nothing but the Laplace transform of $\phi(\lambda)$. Thus, we can determine $\phi(\lambda)$ as $L^{-1}\{P(t)\}$, the inverse Laplace transform of $P(t)$, as long as we know $P(t)$. The experimentally obtained $P-t$ data should ideally be well approximated by a closed-form function before calculating $L^{-1}\{P(t)\}$. We have found through trial and error that the experimental data are well represented by a simple functional form, $P = (1 + t/a)^b$, where a and b are arbitrary constants. The solid curves drawn in the two diagrams in Figure 4 are due to functions of the above form best-fitted to the relevant experimental data. We determined the probability density function $\phi(\lambda)$ relevant to each thermal history by calculating the inverse Laplace transforms of these functions, as illustrated in Figure 5. Here we find that the λ spectrum of the hydrate-
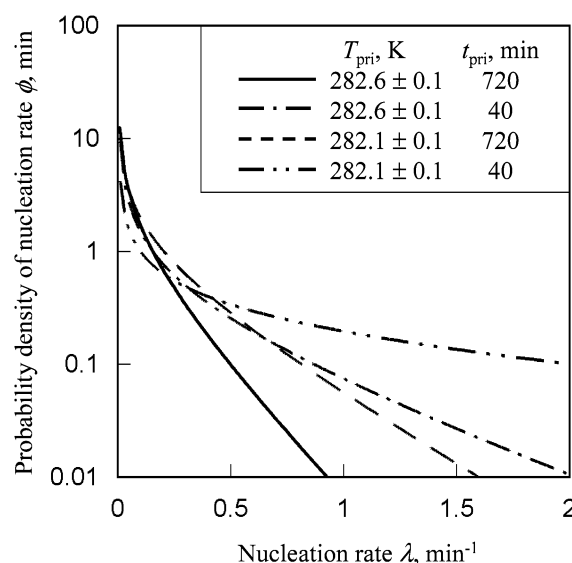

Figure 5. Probability density of the hydrate nucleation rate. Each $\phi(\lambda)$ curve is deduced from a closed form function for the probability of survival, $P = (1 + t/a)^b$, best fitted to the corresponding $P-t$ relation shown in Figure 4.

forming samples reduces and shifts into a lower range with an increase in T_{pri} and/or t_{pri}.

Conclusions

The statistical characteristics of hydrate nucleation in an HCFC-141b/water system with prior hydrate-formation/dissociation experience were examined by collecting induction-time data under atmospheric pressure. The induction-time data obtained with several tens of experimental HCFC-in-water samples with the same thermal history were widely scattered, demonstrating the stochastic nature of the nucleation. The induction time tended to lengthen with an increase in the highest temperature at which the samples were held in advance and also with an increase in the duration of the highest-temperature period. This indicates fading of the memory of prior hydrate formation in those samples by their preheating above the three-phase equilibrium temperature. A statistical analysis of the induction-time data suggested that the nucleation rate cannot be the same even for the samples subjected to the same thermal history before the induction-time measurements. The data were well interpreted, assuming that the samples had different states of memory preservation and therefore widely different nucleation rates. The distribution of nucleation rates thus estimated for each sample set with the same thermal history is presented in the form of a probability density function of the nucleation rate as a continuous variable.

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