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Investigation of factors affecting crystallization of cyclopentane clathrate hydrate

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We report the results of systematic investigations of the influence of thermal history and other factors on crystallization of a model clathrate hydrate (cyclopentane hydrate) studied as water-in-oil and oil-in-water emulsions to remove the nucleation influence of substrates other than ice and hydrates. Hydrate and ice seem to form simultaneously under the conditions of these experiments, with ice forming preferentially. Thermal treatment, melting the ice, and leaving only the hydrate, promotes further hydrate formation. Not all the hydrate formed can be accounted for by the recrystallization of water freed by melting ice. © 2008 American Institute of Physics.

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I. INTRODUCTION

Clathrate hydrates are crystalline icelike compounds that consist of cages composed of hydrogen-bonded water molecules (the host lattice) stabilized by small molecules (guests) that reside in the cages. These materials are fascinating from the scientific and technological perspectives. Naturally occurring clathrate hydrates are of importance to the petroleum industry where gas hydrate (i.e., clathrate hydrate with gaseous guests) formation in off-shore pipelines has caused delays in productivity, and also has led to safety and environmental concerns. A common solution to pipeline blockages has been to depress the hydrate formation thermodynamically, for example, by flushing pipelines with methanol or glycols. The high concentrations of these hydrate inhibitors can cost oil and gas companies hundreds of millions of dollars per year¹ and can be detrimental to the environment. Recent efforts in hydrate prevention have included development of kinetic inhibitors that prevent hydrate formation.^{1,2} Furthermore, there is considerable interest in gas hydrates as potential fuel sources since massive natural gas deposits in the form of hydrates are found in arctic permafrost and along the continental margins.³ Several recent studies have explored the potential of using clathrate hydrates for CO₂ sequestration^{4,5} and H₂ gas storage.⁶

Clathrate hydrates can crystallize in several different structures depending on the guest molecules in the cages. Structures identified to date include cubic structures I and II (sI and sII, respectively)⁷ and a hexagonal structure (sH).⁸ All three are naturally occurring with sH most recently discovered in gas hydrate samples collected off the coast of Vancouver Island.⁹ Methane forms sI and sII hydrates while propane crystallizes as sII hydrate.⁷

Gas hydrates typically require high pressure to achieve stability, so clathrate hydrates such as tetrahydrofuran (THF) hydrate and cyclopentane (CP) hydrate, which are stable at

ambient pressure, are often used as analogs for laboratory studies. Both THF and CP form sII cubic hydrates.⁷ Their structure consists of 16 small cavities (called 5¹² to indicate 12 pentagonal faces) and 8 large cavities (called 5¹²6⁴ to indicate 12 pentagonal faces and 4 hexagonal faces) per unit cell containing 136 water molecules.⁷ The THF and CP molecules reside in the large 5¹²6⁴ cavities at an ideal stoichiometry of 1 guest:17 H₂O.¹⁰

Previously we have shown that the thermodynamic driving force for clathrate formation is enthalpy stabilization relative to the separated components, whereas entropic factors work against formation.¹¹ However, formation and growth of clathrate hydrates are a complicated mix of thermodynamic and kinetic factors. For example, in detailed molecular dynamic simulations, the rate of growth of methane hydrate has been found to be considerably higher than that of ice Ih in similar circumstances.¹² In recent experiments, ice was found to be a good nucleating agent in the formation of clathrate hydrate,¹³ whereas other experiments suggest instead that hydrates form first on freezing.¹⁴ With an aim to understand clathrate hydrate nucleation and stability, we present a systematic study of the influence of conditions and thermal history on hydrate formation. We have concentrated on the CP hydrate system, prepared as water-in-oil or oil-in-water emulsions to remove the nucleation influence of substrates other than ice and hydrates.

II. EXPERIMENTAL SECTION

The type of emulsion formed in the CP/water system depends on the type of surfactant used for stabilization. Surfactants can be characterized by the hydrophilic/lipophilic balance (HLB) value, where a higher number indicates a greater hydrophilic portion for that surfactant and greater water solubility. As in the studies of Zhang *et al.*,¹³ we used Span 65 (sorbitane tristearate), which has a low HLB value (2.1) to stabilize water-in-oil emulsions. To stabilize oil-in-water emulsions, Tween 65 (polyoxyethylenesorbitan tristearate), which has an HLB value of 10.5, was used. Span

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65 was obtained from Sigma-Aldrich and Tween 65 was obtained from Fluka. CP at 95% purity was obtained from Sigma-Aldrich. De-ionized water was obtained from a nanopure filtration system and had a resistivity of ca. 18 M Ω cm. The emulsions were prepared as per Zhang *et al.*¹³ Span 65 or Tween 65 was dissolved in the continuous phase at 4% w/w. The dispersed phase was added and the resultant emulsion was hand shaken for 30 s. The emulsion was placed in an ice bath (to ensure that CP did not evaporate) and was homogenized for 10 min using a 4710 ultrasonic homogenizer from Cole Palmer. The output power was ca. 8 W. The average diameter of the droplets determined by optical microscopy was 3 ± 1 μm , with typical diameters ranging from 2–7 μm . Water-in-oil emulsions with water:CP v/v ratios of 1:5, 1:10, and 1:20 (i.e., CP rich compared to 3.3:1 v/v for the stoichiometric hydrate) were investigated in this study. Oil-in-water emulsions with water:CP v/v ratios of 5:1 also were studied.

Clathrates are known to be poor thermal conductors, so special care must be taken to ensure good heat flow for reproducible results. We melted small samples (5–10 mg of emulsion) in Perkin–Elmer volatile aluminum pans. The reproducibility of our results at different scan rates (0.25 to 1 K min⁻¹) indicates efficient heat flow. Differential scanning calorimetry (DSC) was carried out using a Q200 instrument from TA Instruments with a helium gas atmosphere in the sample chamber (flow rate=25 mL min⁻¹). The DSC was calibrated using the melting point of standard indium ($T_{\text{onset}}=156.61$ °C and $\Delta_{\text{trs}}H=28.71$ J g⁻¹) and the melting point of de-ionized water ($T_{\text{onset}}=0$ °C). In general, the samples were cooled and heated (as described below) to observe the thermal events. Unless noted otherwise, the scan rates for heating and cooling was 1 K min⁻¹. All enthalpies given are in J/g of emulsion. By knowledge of the specific enthalpy changes for various events (e.g., melting of ice), we can ascertain the proportions of each phase in the emulsion (*vide infra*).

III. RESULTS AND DISCUSSION

A. Water-in-oil emulsions

1. Varying water:oil ratio

DSC studies were carried out for 1:5, 1:10, and 1:20 water:oil (v:v) water-in-oil emulsions. The thermal treatment consisted of three cooling and heating stages of the same sample. The temperature range in stage 1 was from 20 to -50 °C and then immediately back to 20 °C. In stage 2, the sample was scanned from 20 to -50 °C then up to 3 °C where ice would have melted, but the CP clathrate hydrate would not have (CP hydrate has a reported melting point of 7.7 °C).¹⁰ In stage 3, the sample was cooled from 3 to -50 °C and then heated to 20 °C to allow both ice and hydrate to melt. In this study, we found an onset of the melting temperature of CP hydrate at ca. 7 °C. (All temperatures given here are onset temperatures.)

The DSC results were similar for each of the three water ratios tested although the values of $\Delta_{\text{trs}}H$ varied. Figure 1 gives an example of the thermographs obtained for the emulsions and includes the obtained values of T_{onset} and $\Delta_{\text{trs}}H$.

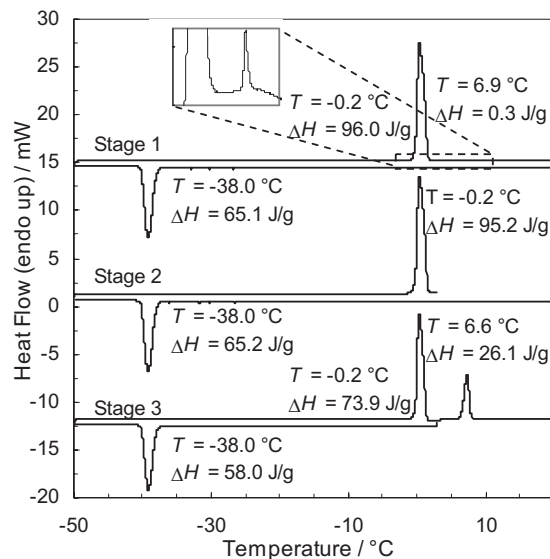


FIG. 1. DSC thermograph of 1:5 water-in-CP emulsion stabilized with 4% Span 65. Cooling curves are below heating curves. Thermographs for a duplicate trial of 1:5 and of 1:10 and 1:20 were qualitatively similar (same onset temperatures of features, but different $\Delta_{\text{trs}}H$). Values of $\Delta_{\text{trs}}H$ are J/(g of emulsion) and temperatures are T_{onset} .

The $\Delta_{\text{trs}}H$ values are reported in the figures in units of J/(g of emulsion) and their experimental uncertainties are $\pm 10\%$, although the reproducibility of small thermal events can be less (*vide infra*). During stage 1, each sample underwent an exothermic phase transition on cooling at approximately -38 °C. The small number and low intensity of spikes on cooling in the results reported here, together with the appearance of a broad peak at -38 °C, confirm predominantly homogeneous nucleation. On heating, there was a large endotherm at approximately 0 °C and a very small endotherm at about 7 °C, corresponding to the melting of ice and of hydrate, respectively. Stage 2 showed an exotherm at -38 °C on cooling, and an endotherm on heating corresponding to ice melting. Stage 3 exhibited an exotherm on cooling, but it was smaller in magnitude than in the other stages, for example 58.0 versus 65.2 J g⁻¹ for 1:5 water-in-CP as in Fig. 1. On heating, there was a smaller endotherm at 0 °C (73.9 versus 95.2 J g⁻¹ for 1:5 water-in-CP) and an endotherm at ca. 7 °C. There was also a very small exotherm between the 0 °C and the 7 °C events. This could be due to the formation of additional clathrate hydrate as the ice melts. The magnitude of this exotherm was $\leq 15\%$ of the magnitude of CP hydrate dissociation at 7 °C for the emulsions stabilized by Span 65. Decreasing the scan rate of the heating cycle from 1 to 0.25 K min⁻¹ did not appreciably increase the enthalpy of the exotherm: it was ca. 20% of the magnitude of CP hydrate dissociation at 7 °C in the lower scan rate.

The total enthalpy changes on cooling are less than the changes on warming, indicating some gradual processes that would be missed in a scanning experiment. Nevertheless, the decrease in $\Delta_{\text{trs}}H$ for the exotherm at -38 °C and the endotherm at 0 °C for stage 3 compared to stage 1 can be understood by comparing the enthalpy of fusion of water with the enthalpy of dissociation of the CP hydrate into aqueous CP solution. Water has a specific enthalpy of fusion of

TABLE I. T_{onset} of the endothermic peaks in the stage 3 heating scans of water-in-oil CP hydrates stabilized by Span 65. The scanning rate was 1 K min^{-1} for heating and cooling. The lower temperature onset is melting of ice, and the higher one is melting of hydrate. The ice:hydrate mass ratios were calculated from the measured $\Delta_{\text{trs}}H$ (in J/g emulsion) and the values of specific enthalpy of fusion of water and hydrate.

Water:CP(v:v)	$T_{\text{onset}}/^\circ\text{C}$	$T_{\text{onset}}/^\circ\text{C}$	Ice:hydrate mass ratio
1:5	-0.2	6.6	1.9 ± 0.1
1:10	-0.3	6.6	2.3 ± 0.2
1:20	-0.4	6.7	11 ± 1

334 J g^{-1} ,¹⁵ while the enthalpy of dissociation of CP hydrate determined by Zhang *et al.*¹³ was 82.3 kJ mol^{-1} , which corresponds to 219 J g^{-1} . Since water has a greater specific $\Delta_{\text{trs}}H$ than hydrate, forming more hydrate leads to a reduction in $\Delta_{\text{trs}}H$ of the exotherm at -38°C . This finding, along with the results of Fig. 1 and further results presented below, indicates that the endotherm at -38°C is due to virtually coincident formation of hydrate and ice.

The 1:5 water-in-oil emulsion was run in duplicate with similar results. The 1:10 and 1:20 thermographs were all qualitatively identical although the magnitude of $\Delta_{\text{trs}}H$ for the transitions varied, as did the amount of hydrate formed relative to the ice peak in stage 3, even for the two 1:5 concentrations. Table I gives the T_{onset} of the phase transitions in stage 3 of each experiment. The relative amounts of ice and hydrate formed in the emulsions were calculated from the measured $\Delta_{\text{trs}}H$ and the values of the specific enthalpy of fusion of water and hydrate as given above.

The maximum temperature for the stage 2 heating scan was 3°C , which allows only hydrate (no ice is present) to act as a nucleation site for further hydrate formation in the subsequent cooling scan. In the study by Zhang *et al.*,¹³ both CP hydrates and THF hydrates were studied. They concluded that ice readily nucleates and promotes hydrate formation, but that hydrate does not nucleate ice. In this study, we extended their methodology and found that when no ice is present, but small amounts of hydrate are, more hydrate is formed on subsequent cycles. For all samples of varying ratios of water:CP, heating to 3°C and then cooling increased the amount of hydrate on subsequent warming. Although some hydrate can be expected to form from the water freed from melting ice, the magnitude of the corresponding exotherm between 0 and 7°C shows that this is not the major origin of hydrate.

2. Varying heat treatment

To test whether or not the increase in hydrate described above was simply a function of multiple cooling and heating cycles, a sample was heated and cooled twice from 20 to -50°C . The $\Delta_{\text{trs}}H$ values for hydrate melting in stages 1 and 2 of Fig. 2 are of the same order of magnitude, much different from the 10-fold increase between stages 1 and 3 of Fig. 1, indicating that performing two cooling and heating stages to the full melt does not in itself induce substantially more clathrate hydrate.

To determine whether leaving ice in the sample at a relatively high temperature would cause an increase in hydrate,

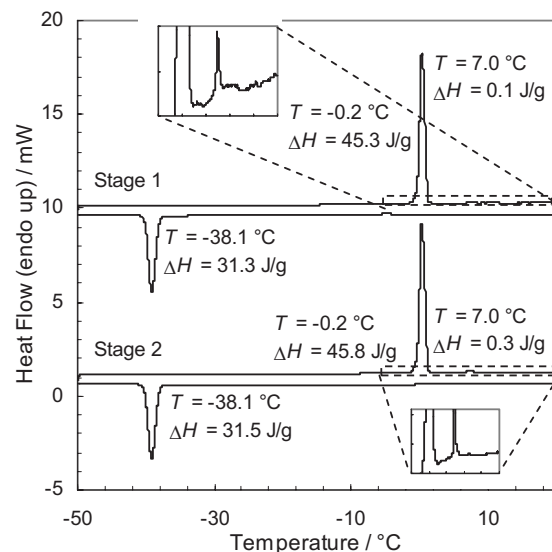


FIG. 2. DSC thermograph of 1:10 water-in-CP emulsion stabilized by 4% Span 65, cycled twice from 20 to -50°C . Cooling curves are below heating curves. Values of $\Delta_{\text{trs}}H$ are $\text{J}/(\text{g}$ of emulsion) and temperatures are T_{onset} .

the stage 2 heating cycle was taken up to -3°C so that ice would be present in the sample for stage 3. We found that there was not much increase in $\Delta_{\text{trs}}H$ of the small endothermic peak associated with hydrate dissociation (Fig. 3). We repeated the process with stage 2 heating to -30°C and found qualitatively similar results.

As an additional check, a water-in-CP emulsion was tested with two extra stages to establish whether the lack of substantial hydrate in stage 3 of Fig. 3 was due to the thermal history or some other factor. For this sample, the first three stages were similar to the processes shown in Fig. 3 (except the sample was cooled to -42°C and heated to 15°C ; the slightly shorter range was required to complete the five stages without running out of cryogenics). In stage 4, the

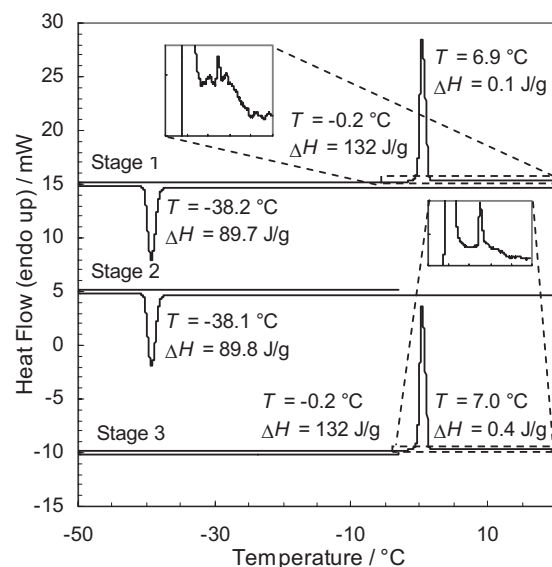


FIG. 3. DSC thermograph of 1:5 water-in-CP emulsion stabilized by 4% Span 65. The maximum temperature in the Stage 2 heating was -3°C . Cooling curves are below heating curves. Values of $\Delta_{\text{trs}}H$ are $\text{J}/(\text{g}$ of emulsion) and temperatures are T_{onset} .

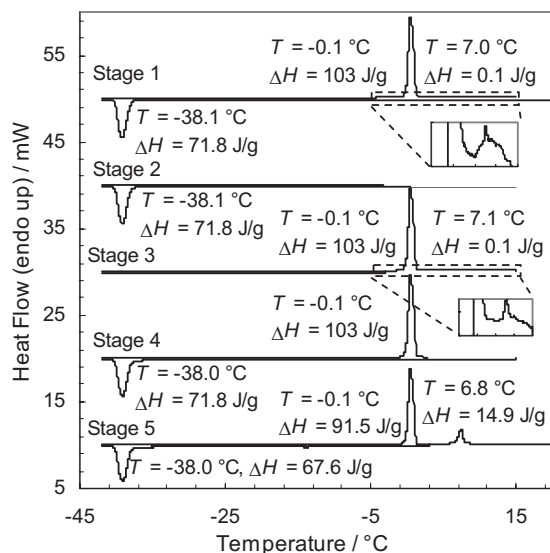


FIG. 4. DSC thermograph of 1:5 water-in-CP emulsion stabilized by 4% Span 65. The maximum temperature in stage 2 heating was -3°C , while the maximum temperature in stage 4 heating was 3°C . Cooling curves are below heating curves. Values of $\Delta_{\text{tr}}H$ are J/(g of emulsion) and temperatures are T_{onset} .

sample was cooled to -42°C and heated to $+3^{\circ}\text{C}$ and in stage 5 the sample was cooled to -42°C and heated to 20°C . The results are shown in Fig. 4. The stage 3 heating cycle still shows only a slight amount of hydrate formation, but stage 5 shows appreciable hydrate formation. The present results collectively indicate clearly that the presence of ice does not promote growth of CP hydrate. When the ice is melted, either the presence of hydrate promotes further hydrate crystallization, or the freed water allows additional hydrate formation. We showed above that the latter effect is not the major contributor to hydrate formation.

In another heat treatment experiment, a 1:5 water-in-CP sample was held at -35°C to determine if significant crystallization is occurring before the major exothermic event at -38°C . For the usual stage 1 of the heat treatment, very little hydrate was formed. However, during stage 2 of this experiment, after the sample was held at -35°C for 1 h, there was an increase in both ice and hydrate formations: $\Delta_{\text{tr}}H$ increased from 6.0 to 13.4 J g^{-1} for ice, and 0.1 to 3.1 J g^{-1} for hydrate. The results indicate that only little ice is formed by cooling to -35°C for an hour, but most of the hydrate is formed by this treatment.

B. Oil-in-water emulsions

DSC studies were carried out for 1:5 (v:v) oil-in-water emulsions stabilized with Tween 65. The thermal treatments were similar to those used for the emulsions stabilized with Span 65, consisting of several cooling and heating stages at 1 K min^{-1} . For the oil-in-water emulsions, there was more hydrate formation than for the water-in-oil emulsions. Taking into account the different specific enthalpies of dissociation, Fig. 5 shows that by mass, hydrate formation was favored over ice by a factor of about 2.

The additional exotherm between the 0 and 7°C endotherms was more apparent in the oil-in-water emulsions. A

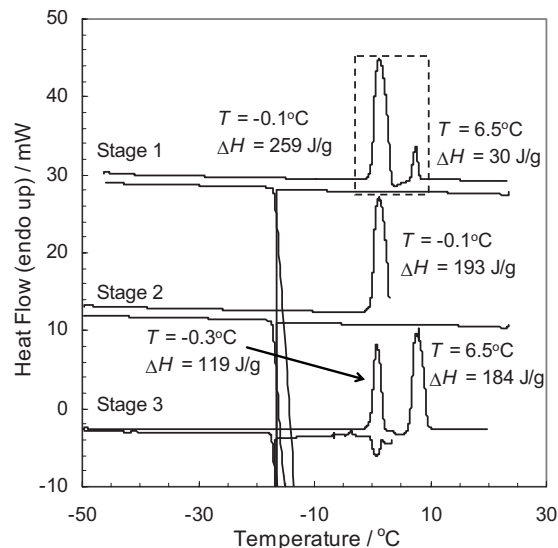


FIG. 5. DSC thermograph of 1:5 CP-in-water emulsion stabilized by 4% Tween 65. Cooling curves are below heating curves and, on cooling, the large exotherm at ca. -20°C leads to momentary warming. The maximum temperature in stage 2 heating was 3°C . The dotted box is shown enlarged in Fig. 6. $\Delta_{\text{tr}}H$ values are J/(g of emulsion) and temperatures are T_{onset} .

close-up of the event is given in Fig. 6. However, the enthalpy of the highlighted exotherm is still small, less than 50% of the enthalpy change due to melting of the hydrate, indicating that hydrate formation does not solely (or even predominantly) occur upon melting of the ice.

An important consideration is the possible influence of surfactant on hydrate formation. Because there is more hydrate for the oil-in-water emulsion than for the water-in-oil, the surfactant presumably influences the hydrate-to-water ratio. However, the most important observation is the common trend for both cases that does not depend on the surfactant

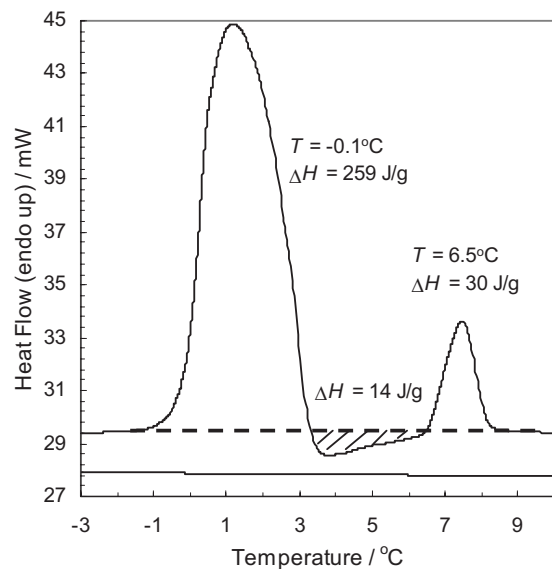


FIG. 6. DSC thermograph of 1:5 CP-in-water emulsion stabilized by 4% Tween 65. The exothermic event could be due to water from melted ice being used to form more hydrate. However, the enthalpy change of the exotherm is much smaller than the enthalpy change due to hydrate melting, so it is unlikely that all (or even most) of the hydrate is being formed during this event. Values of $\Delta_{\text{tr}}H$ are J/(g of emulsion) and temperatures are T_{onset} .

used: existing hydrate promotes more hydrate. Thus, the type of surfactant does not seem to be of critical importance to CP clathrate growth in emulsions.

IV. PREVIOUS HYDRATE NUCLEATION AND FORMATION STUDIES USING THERMAL TECHNIQUES

Many features of our results look similar to those of Zhang *et al.*,¹³ e.g., both ice and hydrate nucleate on cooling. Although our compositions and heat treatments are virtually identical, and our emulsion methods and sizes are as similar as possible (average droplet size 3 μm), the results of Zhang *et al.*¹³ show more hydrate formation on stage 1 cooling than we see. Furthermore, in our extensive studies, we saw only minor sharp spikes at ca. -25°C (see Fig. 1) not major spikes as Zhang *et al.*¹³ reported for Span 65 stabilized water-in-CP emulsions and attributed to hydrate formation. These relatively minor discrepancies likely are indications of the stochastic component of the nucleation process. As discussed above, we found that the peak on cooling at ca. -38°C (water-in-oil emulsions) seems to be due to crystallization of *both* ice and hydrate, although there appear to be gradual processes at higher temperatures that also crystallize ice and/or hydrate. We show for this system that the presence of hydrate promotes hydrate more than the presence of ice promotes hydrate. Although we cannot rule out mass transport issues, if a protective hydrate shell formed during initial freezing, then our results (growth of hydrate after melting the ice, e.g., Fig. 1) indicate that the shell was significantly disrupted when the ice melted.

Tombari *et al.*¹⁴ recently described a detailed calorimetric study of THF clathrate hydrates. One advantage of their method is the increased sensitivity; in this case, the authors discerned crystallization events for both ice and hydrate. The time period used to make clathrate hydrates also plays an important role and their method allows slower scanning rates (e.g., 0.1 K min^{-1}). Also, pure THF water solutions can be used in this method instead of an emulsion, allowing larger sample sizes, more precise concentrations, and homogeneous mixtures. Furthermore, THF and water are miscible, so there are no mass transport issues. They concluded from their studies that THF clathrate hydrates form preferentially over ice. They also found that THF clathrate hydrate formed first on cooling and only residual water in the sample crystallized to ice. This is in contrast with the conclusions of Zhang *et al.*¹³ who found that ice nucleates preferentially. Here we find that ice and hydrate form concurrently on cooling. (We note that the hydrate and ice crystallization phenomena seen by Tombari *et al.*¹⁴ are very close in temperature, albeit at a different stoichiometry from that used here.) It is possible that the more rapid cooling rates used both here and in the prior study¹³ did not allow sufficient time for clathrate hydrate to equilibrate. We do not find a significant difference between scanning at 1 and 0.25 K min^{-1} , but it has been suggested that samples be conditioned for several hours below 275 K to achieve complete hydrate formation,¹⁶ as we have done for previous heat capacity determinations of THF clathrate

hydrate.¹⁷ The matter of heating and cooling rates and its influence on crystallization has yet to be explored thoroughly.

Another recent study looked at CCl_3F hydrate formation and dissociation in NaCl-containing water oil emulsions using DSC and x-ray diffraction (XRD).¹⁸ Their DSC results were similar to the present results and those obtained by Zhang *et al.*,¹³ i.e., a single crystallization peak was present at approximately -40°C on cooling and two endotherms were present on heating. On the basis of temperature-dependent XRD studies, they found that on cooling no hydrate was formed, only ice. On the heating scan, XRD showed hydrate formation as the sample was warmed, with hydrate forming only as water from ice becomes available. However, we see evidence that both ice and hydrate form on crystallization. A more complete comparison between our work and the study of Fouconnier *et al.*¹⁸ is prevented by the presence of NaCl in their experiment; the low-melting point of the resultant saline solution plays an important role.

V. CONCLUSIONS

The nucleation and stability of CP hydrates as water-in-CP and CP-in-water emulsions were studied using DSC. We found that hydrate and ice seem to form simultaneously under the conditions of these experiments, with ice forming preferentially in water-in-CP emulsions and hydrates forming preferentially in CP-in-water emulsions. Our systematic studies of the water:oil ratio and thermal history showed that thermal treatment leaving only hydrate promotes further hydrate formation, more than the promotion of hydrate in the presence of ice. By quantification of the thermal events, we see that only a minor amount of hydrate is formed by crystallization from water freed by the melting of the ice.

ACKNOWLEDGMENTS

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