

Differential Scanning Calorimetry Studies of Clathrate Hydrate Formation

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Differential scanning calorimetry was applied to investigate the formation of tetrahydrofuran (THF) and cyclopentane (CP) clathrate hydrates. An emulsion technique was developed to determine the hydration number and the enthalpy of CP hydrate dissociation to liquid water and liquid cyclopentane, which were found to be 16.8 ± 0.7 and 82.3 kJ/mol CP, respectively. The hydration number corresponds to the theoretical number of 17 if all of the large cavities in the structure II hydrate are occupied. Experiments with water-in-CP emulsions did not identify homogeneous nucleation for the hydrate since ice and hydrate always formed together on supercooling. With water-in-heptane emulsions, for which no hydrate forms, the homogeneous ice supercooling limit was -37.8 °C. With the CP emulsion, ice and hydrate formed close to this temperature. For bulk THF/H₂O solutions, even at the hydrate stoichiometric molar ratio of 1:17, ice and hydrate were found to form in the same crystallization event upon cooling, which impeded the identification of the homogeneous nucleation temperature of the hydrate. To overcome this, a method based on emulsification of stoichiometric THF/water solutions in an immiscible fluorocarbon fluid enabled determination of the homogeneous nucleation of THF hydrate without the formation of ice. The homogeneous THF hydrate nucleation temperature was -32 °C. We believe this is the first measurement of homogeneous nucleation of a clathrate hydrate. Our experimental results suggest that ice is a good nucleating agent for heterogeneous formation of clathrate hydrates, whereas the hydrates are not efficient nucleators for ice.

Introduction

Clathrate hydrates^{1–6} are nonstoichiometric icelike solids in which water molecules form a three-dimensional hydrogen-bonded network of cages (host) stabilized by the occupation of some or all cages by small molecules (guests). Three types of well-known structures can form⁴ depending on the size of the guest molecules: cubic structure I (sI), cubic structure II (sII), or hexagonal structure H (sH). Pipeline blockage by clathrate hydrates⁷ is a major problem in many oil and gas production fields. Strategies for maintaining flow continuity (termed in the industry “flow assurance”) include using thermodynamic or kinetic inhibitors^{3,8,9} or allowing the hydrates to form as flowable dispersions^{10,11} in either aqueous or oil/condensate phases. Hydrate formation is the initial step of a proposed method for transporting natural gas¹² and has also been investigated as an approach for purification of saline or contaminated waters.¹³ Recently, additional novel applications of hydrate formation include enzyme catalysis¹⁴ and the preparation of advanced materials such as nanocluster semiconductor colloids.¹⁵ Detailed knowledge of the mechanism of hydrate formation is important in all of the above examples. However, our understanding of this topic is rather limited at present.

In this study, we investigate hydrates formed from miscible and immiscible fluid phases: tetrahydrofuran/water (THF/H₂O)^{8,11,16–19} is a miscible single-phase precursor fluid, whereas cyclopentane/water (CP/H₂O) exhibits low mutual solubility. CP is a liquid from -97 to 49 °C at atmospheric pressure, covering the relevant temperatures for hydrate formation. CP forms an sII hydrate (which is the most common hydrate structure in oil fields) with a melting point of 7.8 °C at

atmospheric pressure.²⁰ Methane and other “helper” gases can be incorporated into the smaller cavities of the CP hydrate at modest pressures.²¹ Because of this, the cyclopentane hydrate is expected to be a good model system for the study of nucleation, surface and colloid properties, and the dispersion rheology of alkane hydrates, with the practical advantage of being able to work at atmospheric pressure.

Differential scanning calorimetry (DSC) was used to study the formation of CP and THF hydrates. Direct calorimetric measurement^{16,17,22} was found to be more accurate in some cases than the alternative method of determining the enthalpy of dissociation from the phase equilibrium line using the Clausius–Clapeyron equation, but good agreement has been found with several alkanes.³ We developed a new emulsion-based method to form cyclopentane hydrate to maximize mass transfer in this immiscible system and determined its composition and enthalpy of dissociation with DSC. Nucleation is the first step in hydrate formation and therefore is crucial toward a full understanding of the mechanism and kinetics of hydrate formation. A number of studies^{18,23–25} have been devoted to understanding hydrate nucleation phenomena, but no clear evidence of homogeneous nucleation of clathrate hydrates has been presented. We believe that we have successfully observed the homogeneous nucleation of THF hydrate in this study. Our experimental results for both the THF/H₂O and CP/H₂O systems show that hydrates are not efficient nucleators for ice, although ice nucleates hydrates readily.

Experimental Section

Materials and Instruments. CP and THF of analytical grade were purchased from Sigma-Aldrich. Halocarbon oil 0.8, a low-molecular-weight polymer of chlorotrifluoroethylene (PCTFE), was obtained from Halocarbon Inc., River Edge, NJ. Sorbitan

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tristearate (STS), Tween 85, and lanolin were purchased from Sigma-Aldrich. Deionized (DI) water was filtered through a 0.22 micron pore filter before use. A Pyris 1 differential scanning calorimeter from Perkin-Elmer was used in the experiments. Emulsions were prepared with an Aquasonic 150D (VWR) ultrasonic generator. The sizes of the emulsion droplets were measured with an optical microscope (Nikon Inverted Microscope Eclipse TE200).

Methods. Preparation of CP in Water Emulsion. Tween 85 (4%) was dissolved in 10 mL of filtered DI water. Cyclopentane was then added to the aqueous solution at different volume ratios (1:10, 1:5) and was shaken, followed by 10 min of ultrasonication with the Aquasonic 150D (VWR) at a power level of 8 to generate the emulsion droplets.

Preparation of Water in Oil (CP or Heptane) Emulsions. A method similar to that used for the preparation of the CP-in-water emulsion was used; that is, the required weight (4%) of surfactant (Span 65, sorbitan tristearate) was first dissolved in cyclopentane or heptane and then mixed with filtered DI water followed by ultrasonication to prepare the emulsion. The size of the emulsion droplets, as measured by optical microscopy, was around 3 microns. No phase separation was observed for the emulsions over a 3 h period.

Preparation of THF/H₂O in THF/Oil Emulsion. We used lanolin and Halocarbon oil to prepare an aqueous-phase-in-oil-phase dispersion following an approach by Koop et al.^{26,27} for studying homogeneous water nucleation. THF is soluble in the Halocarbon oil continuous phase. To maintain the THF/H₂O composition inside droplets, the Halocarbon oil was equilibrated against excess THF/H₂O at the desired composition. The emulsion was prepared as follows: (1) THF/H₂O solution at a composition of 1:17 (molar ratio of THF to water) was prepared, hereafter called THF/H₂O. (2) About 1 volume of Halocarbon oil was mixed with 3 volumes of THF/H₂O by vigorous shaking. (3) After equilibration, the top layer (aqueous THF phase) was decanted and discarded. (4) Steps 2 and 3 were repeated on the Halocarbon phase two more times. (5) Weighed lanolin²⁷ (about 20 wt %) was dissolved in the equilibrated Halocarbon fluid phase. (6) Drops of THF/H₂O were added to the equilibrated oil + lanolin mixture and mixed by vigorous shaking and ultrasonication (VWR Aquasonic 150D, 10 min at power level 8) to make a dispersed aqueous-phase-in-oil emulsion. After three equilibration cycles, no change in the volume of the THF/H₂O phase was observed; therefore, the Halocarbon oil and the THF/H₂O phases were in equilibrium at the desired THF/H₂O stoichiometry. We expect the composition of THF/H₂O inside the emulsion droplets to be 1:17, on the assumption that forming an emulsion does not affect the partition of THF between the oil and water phases.

Calibration of DSC. Temperature and heat calibration were based on the melting point and fusion enthalpy of indium. This procedure was further checked with the melting temperature and heat of fusion of ice, corresponding more closely with the experimental temperature range. The temperature accuracy is estimated to be ± 0.1 °C.

DSC Method To Determine the Composition and Enthalpy of Dissociation for CP Hydrate. About 20 mg of the cyclopentane-in-water (O/W) emulsion with excess water was sealed in a stainless steel pan with an O-ring. The cyclopentane in the O/W emulsion was converted completely into hydrates using thermal cycling: (step 1) cool the sample to a low temperature T_{low} , which was usually -40 °C; (step 2) heat the sample to a temperature T_{hold} , which is between the melting point of ice

and the dissociation point of the hydrate; (step 3) keep the sample at T_{hold} for different time periods (t_{hold}); (step 4) cool the sample to T_{low} again to make the excess liquid water freeze; (step 5) heat the sample to let ice and hydrate melt. The DSC scan rate (cooling or heating) in the above steps was 1 °C/min. Nitrogen purge gas was used at a flow rate of 30 mL/min. The amount of excess water ($n_{\text{w,i}}$) in the DSC sample can be determined from the melting peak of ice from the DSC thermograph in step 5:

$$n_{\text{w,i}} = \frac{Q_{\text{IP}}}{\Delta H_{\text{f,i}}} \quad (1)$$

where Q_{IP} is the heat associated with the ice melting and $\Delta H_{\text{f,i}}$ is the heat of fusion for ice at atmospheric pressure. Before the final heating step, all the water that does not form hydrate is converted into ice by cooling to T_{low} . So water exists in the form of either ice or hydrate. Based on the mass balance of water, the hydration number, n , and thus the hydrate composition can be obtained from

$$n = \frac{n_{\text{w,t}} - n_{\text{w,i}}}{n_{\text{CP}}} \quad (2)$$

where $n_{\text{w,t}}$ is the total number of water molecules in the sample and n_{CP} is the number of CP molecules in the sample. The enthalpy for CP hydrate dissociation to liquid water and liquid cyclopentane at one atmosphere ΔH (based on a mole of CP) is then

$$\Delta H = \frac{Q_{\text{HP}}}{n_{\text{CP}}} \quad (3)$$

where Q_{HP} is the heat determined from the CP hydrate dissociation peak.

Results and Discussion

Hydration Number and Enthalpy of Dissociation for Cyclopentane Hydrate. A typical DSC thermograph of a CP-in-water (O/W) emulsion with water in excess is given in Figure 1. When the sample is first cooled, there is only one exothermic peak which begins at about -14 °C. Once all the cyclopentane is converted to hydrate, the final heating produces two peaks: the ice peak at 0 °C and the hydrate peak at about 8 °C. In a control experiment, the enthalpy of melting for ice from the surfactant solution was found to be indistinguishable from that for pure water. Hence, from the mass and composition of the sample loaded into the DSC and the peak areas of the two endothermic peaks, the hydration number and heat of dissociation of CP hydrate are determined with eqs 1–3. Experiments were carried out with different T_{hold} (1 – 5 °C) and t_{hold} (0 – 20 h). The calculated hydrate number from eqs 1 and 2 is insensitive within the experimental error with respect to T_{hold} and t_{hold} when t_{hold} is longer than 2 h. This indicates that the cyclopentane is completely converted into hydrate under the experimental conditions. The average hydration number thus determined is 16.8 with a standard deviation of 0.7, which is consistent with the fact that the theoretical occupation number for an sII clathrate hydrate is 17 if all the large cavities are occupied.

From the hydrate peak at full conversion in the emulsified system, ΔH is estimated as 82.3 kJ/mol. Adding the enthalpy of vaporization of CP (28.7 kJ/mol) gives the heat of dissociation to liquid water and CP vapor as 106 ± 4 kJ/mol. Another

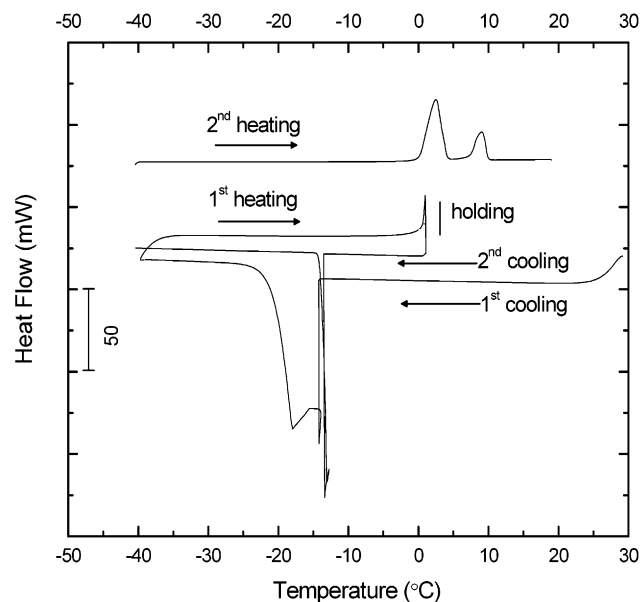


Figure 1. Thermograph of cyclopentane dispersed in water with Tween 85 (4%). The sample was first cooled to -40 °C (labeled as 1st cooling) and then heated to 2 °C (1st heating) at which temperature it was held for an hour (holding); after that it was cooled again to -40 °C (2nd cooling) and heated to 20 °C (2nd heating). The scan rate in all steps is 1 °C/min. The heating curve in the last step was shifted upward for clarity.

estimate of the dissociation heat may be obtained from the measurements of Fan et al.²⁸ on the hydrate–liquid water–vapor ($H-L_w-G$) three-phase equilibrium for CP hydrate. Several previous studies with alkanes have given good agreement between estimates of the enthalpies of hydrate formation from calorimetry and the Clausius–Clapeyron equation applied to the temperature variation of the gas pressure along the phase boundaries of gaseous alkane hydrates.³ In all these examples, the water vapor pressure makes a negligible contribution to the total pressure. In the case of the CP L_w-H –vapor equilibrium, the partial vapor pressure for water is smaller than the CP vapor pressure but not negligible. Following Sloan,³ we write

$$\frac{d(\ln P)}{d(1/T)} = -\frac{\Delta H}{R} \quad (4)$$

where P is the total pressure, R is the universal gas constant, and T is the temperature. ΔH is the enthalpy of dissociation of CP hydrate to liquid water and CP vapor. The data are shown in Figure 2, giving $\Delta H = 98.3$ kJ/mol. This is in fair agreement with the value from our DSC measurements with the emulsified CP system (106 kJ/mol). The discrepancy may indicate small thermal contributions from the surfactant in the melting of the dispersed solid hydrate or subtleties involved in the application of the Clausius–Clapeyron equation for multiple phases in equilibrium. Corrections to the calorimetric heat for evaporation into the free space of the calorimeter cell over the temperature range of integration for the endothermic hydrate peak area are negligible. ΔH for CP hydrate is lower than the related heats for a number of noncyclic alkane sII hydrates. For example, ΔH for the isobutane hydrate is 133.2 kJ/mol from calorimetry and 130.4 kJ/mol from the Clausius–Clapeyron method.³

Nucleation Study of the CP/Water System. Figure 3 shows the DSC thermographs obtained when CP/water without surfactant is cooled to two different temperatures T_{low} and then heated. It is observed that hydrate and ice form in the same exothermic peak around -15 °C. This corresponds to the typical

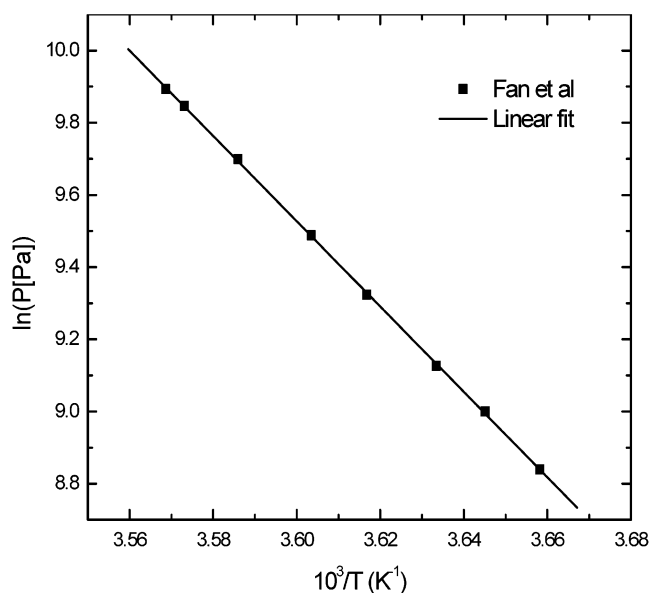


Figure 2. Arrhenius plot of the equilibrium pressure for the CP– H_2O system along the hydrate–liquid water–vapor three-phase equilibrium line. The data are taken from Fan et al. (ref 28). The line represents the best linear fit of the experimental data with a correlation coefficient of 0.9999.

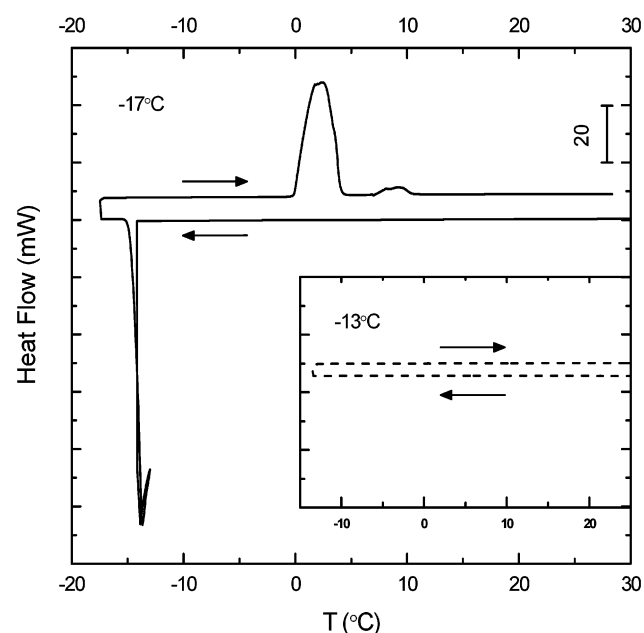


Figure 3. DSC thermograph of CP/water without surfactant at a scan rate of 1 °C/min. Samples are cooled to low temperatures (solid line, -17 °C; dashed line, -13 °C) and then heated.

water freezing temperature found under this experimental condition, most probably due to heterogeneous nucleation. However, since hydrate also forms, which is indicated by the endothermic peak around 8 °C, it is not clear which solid forms first. There are several possibilities: (1) ice forms first and subsequently serves as nucleation sites for hydrate; (2) both ice and hydrate form due to heterogeneous nucleation in the presence of dust particles; (3) hydrate forms, which then serves to nucleate ice crystallization. The possibility of ice forming by homogeneous nucleation is ruled out because homogeneous nucleation of ice occurs below -37 °C.^{27,29} To avoid the heterogeneous nucleation that might be involved, we investigated the nucleation phenomena with a water-in-cyclopentane emulsion.

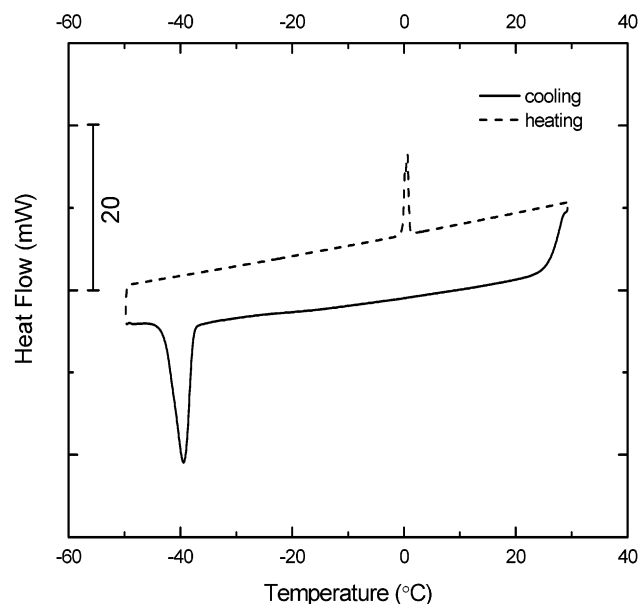


Figure 4. Thermograph of a water-in-heptane emulsion with sorbitan tristearate (4% STS in heptane) prepared by sonication. The water-to-oil ratio is 1:5 (volume). Scan rate: 10 °C/min (cooling), 1 °C/min (heating). The crystallization temperature (onset of the exothermic peak) is -37.8 °C.

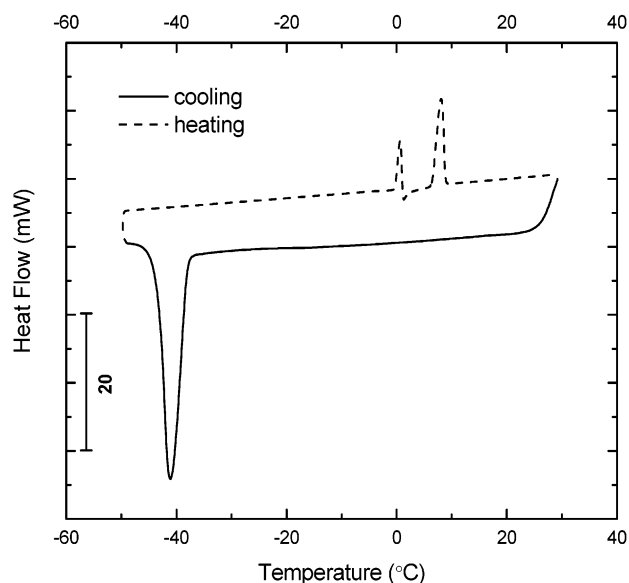


Figure 5. Thermograph of a water-in-cyclopentane emulsion, stabilized with STS surfactant prepared by sonication. The water-to-oil ratio is 1:5 (volume). The scan rate is 10 °C/min for cooling and 1 °C/min for heating. The onset crystallization temperature during the cooling stage is -37.8 °C.

As a control, an emulsion that will not form hydrates was studied first. The nucleation of a water-in-heptane emulsion with Span 65 as the surfactant is shown in Figure 4. The homogeneous nucleation of water is clearly demonstrated by the exothermic peak near -38 °C, which agrees well with values in the literature.^{27,29} The mean value of the onset temperature was -37.7 °C with a standard deviation of 0.2 °C from five experiments. For the thermograph obtained with a water-in-cyclopentane emulsion (see Figure 5), the large crystallization peak occurs at almost the same temperature as that of the water-in-heptane emulsion. But when the frozen sample is heated to 30 °C, two endothermic peaks are observed, one around 0 °C and the other around 8 °C. These two peaks correspond to ice melting and hydrate dissociating, respectively. This shows that

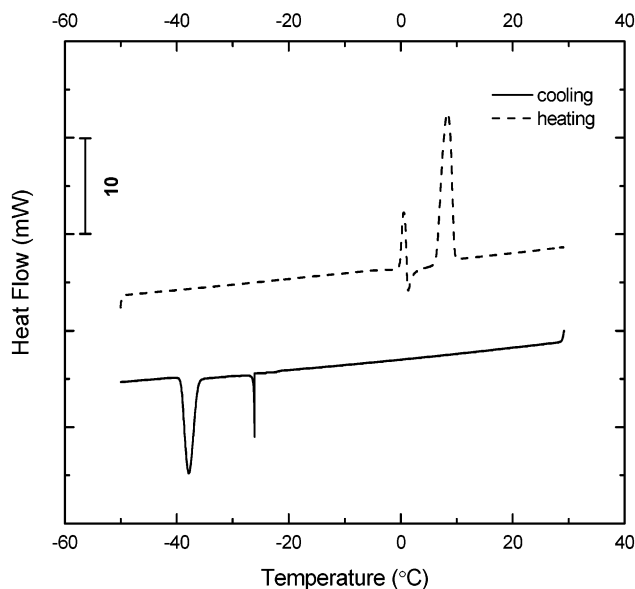


Figure 6. Thermograph of a water-in-cyclopentane emulsion, stabilized with STS prepared by sonication. The water-to-oil ratio is 1:5 (volume). The scan rate is 1 °C/min for cooling and 1 °C/min for heating.

both hydrate and ice form during cooling. From the area of the melting peaks, it is noted that the hydrate dissociation peak is larger than that of ice melting, which indicates comparable amounts of hydrate and ice form in the experiment. These observations suggest that in this experiment ice formed first through homogeneous nucleation around -38 °C and subsequently serves as a nucleating agent for hydrate formation. Since the size of the emulsion droplets is small (about 3 microns as measured with the microscope), the mass transfer of CP to the hydrate is enhanced greatly compared with the case of CP/water without surfactant. It is also possible that fast cooling under this experimental condition masks the homogeneous nucleation of CP hydrate until the homogeneous nucleation of ice sets in. When the cooling rate is reduced, some small crystallization peaks are observed at higher temperature (Figure 6), but most of the hydrate still forms in the crystallization peak around -38 °C. Some heterogeneous nucleation occurs in some small fraction of the emulsion droplets, but the bulk of the material nucleates homogeneously.

Nucleation Study of the THF/Water System. The thermograph corresponding to cooling and heating THF/H₂O with a composition of 1:17 molar ratio is shown in Figure 7. The phenomena observed are similar to the results for the immiscible CP/H₂O system: when the solution was cooled, only one exothermic peak is observed at about -18 °C. However, two melting peaks, that is, ice melting and hydrate dissociating, are evident when the frozen sample is heated. The result is surprising. Even at the stoichiometric molar ratio, the THF/H₂O solution did not form the hydrate alone. For the nucleation mechanism involved, there are again several possibilities. We believe it most likely to be heterogeneous nucleation, but it is not possible to determine from this experiment which solid phase forms first. To further investigate this question, we again employed an emulsion technique. The THF/H₂O was dispersed in the form of small droplets inside an immiscible oil phase to render the majority of drops free of heterogeneous nucleation sites. The DSC thermograph of water dispersed in Halocarbon oil with lanolin as the surfactant is shown in Figure 8. The homogeneous nucleation of water was again clearly demonstrated by the peak around -38 °C.

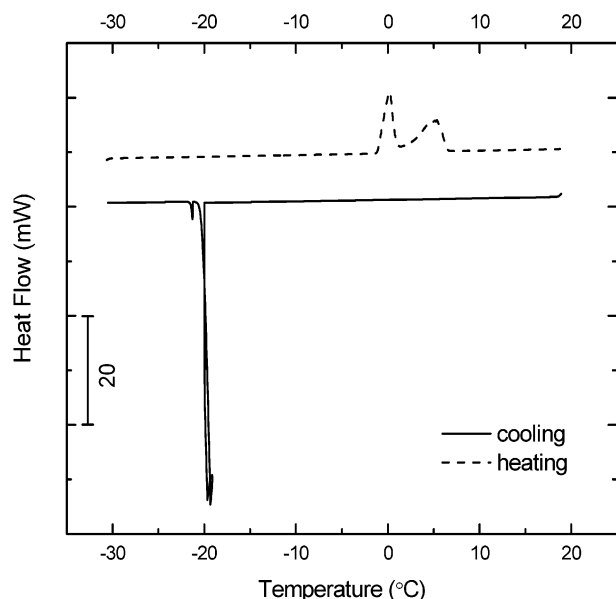


Figure 7. DSC thermograph of THF/H₂O at a molar ratio of 1:17. The scan rate is 1 °C/min.

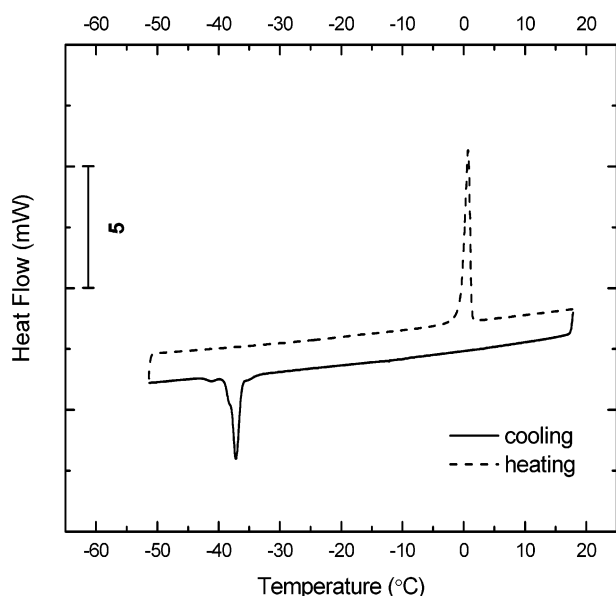


Figure 8. Thermograph of water dispersed in Halocarbon oil with lanolin. The sample was first cooled to -50 °C and then heated to 20 °C at a scan rate of 1 °C/min.

We developed a method for dispersing THF/H₂O (1:17 molar ratio) in Halocarbon oil which had been pre-equilibrated with the THF/H₂O solution (see Experimental Section, Methods). Ideally, when forming such a dispersion, no further partition of THF between the aqueous-THF phase and the oil phase would occur, so that the composition of the THF/H₂O solution phase remains at the stoichiometric molar ratio (1:17). The DSC thermograph of the equilibrated Halocarbon emulsion is shown in Figure 9. The striking observation is that no ice is found upon heating; the crystallization peak is only due to hydrate formation. The crystallization peaks in different DSC thermographs are of two different types, that is, minor “spikes” and a “broad peak” starting at about -32 °C, characteristic of homogeneous nucleation. The mean value of the onset is 32.0 °C with a standard deviation of 0.4 °C from five measurements. We believe this is the first report of the homogeneous nucleation temperature of THF hydrates. The spiked peaks are probably related to heterogeneous nucleation confined to a minority of

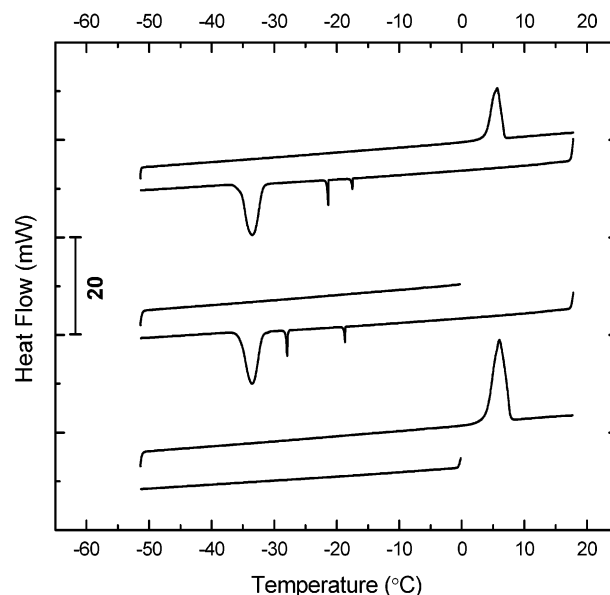


Figure 9. Thermograph of THF/H₂O (1:17) dispersed in Halocarbon oil/THF previously equilibrated with THF/H₂O (1:17). The surfactant used is lanolin. Curves, from top to bottom, correspond to the following sequence: cool from 20 to -50 °C, heat from -50 to 20 °C; cool from 20 to -50 °C, heat from -50 to 2 °C and hold for 12 h, cool from 2 to -50 °C, heat from -50 to 20 °C. (The heating curve is always the top curve in a cooling–heating cycle.)

the emulsion drops. The spike peaks occur at different temperatures, indicating they are random in nature. When hydrate forms at -32 °C, the hydrate does not nucleate ice from the highly supercooled solution.

These results, together with those obtained from the water-in-CP emulsion, nonemulsion THF/H₂O, and nonemulsion CP/H₂O, support the interesting conclusion that ice nucleates and promotes hydrate formation, while hydrates are not good nucleators for ice. From the THF hydrate dissociation peak (the endothermic peak in Figure 9), the enthalpy of THF hydrate dissociation can be determined from the mass of THF/H₂O in the sample. This enthalpy change was determined to be 106 ± 4 kJ/mol, which agrees well with the values in the literature.¹⁷ This again confirms that the solid formed in Figure 9 is THF clathrate hydrate.

Conclusion

We have used differential scanning calorimetry to study clathrate hydrate formation with either cyclopentane or tetrahydrofuran. Using an emulsion technique to maximize mass transfer, we have determined the hydration number in CP hydrate to be 16.8 ± 0.7 and the heat of dissociation of cyclopentane hydrate into liquid water + liquid CP to be 82.3 kJ/mol. Studies of nucleation phenomena with CP/H₂O, CP/Tween 85/H₂O, H₂O/Span 65/CP, THF/H₂O, and THF/H₂O/lanolin/Halocarbon oil systems show that ice nucleates hydrates readily, whereas hydrates are not good nucleators for ice. We have also successfully obtained homogeneous nucleation of THF hydrate at -32 °C.

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