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Hydrate formation and re-formation in nucleating THF/water mixtures show no evidence to support a “memory” effect

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ABSTRACT

There are many reports in the chemical engineering literature citing a ‘memory’ effect in association with nucleation of clathrate hydrates. Some researchers appeal to this memory effect in order to explain the apparent reduction in induction time for hydrates formed repetitively from supercooled solutions. It is suggested that for various species of clathrate in liquid–liquid or gas–liquid systems, such as THF/water, CO_2/water and hydrocarbon gas/water, the ‘memory’ effect results from water which is obtained from melted hydrates possessing a “modified” structure which allows easier hydrate re-formation. We provide here data from several series of measurements of the stochastic nature of THF–water hydrate formation using an automatic lag time apparatus. Our data supports the existing molecular understanding of nucleation and does not require any appeal to a memory effect.

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1. Introduction

Clathrate hydrates are equilibrium crystal structures that are formed when gas molecules become permanently encaged by water molecules. They are of interest for a number of different applications including as a potential source of energy from naturally occurring deposits, as a potential greenhouse gas storage medium, for gas transportation, desalination, refrigeration and for flow assurance in oil and gas pipelines where they may form solid plugs and lead to a loss of production. Most gas hydrates form at high pressure and low temperature so specialist equipment is generally needed to form and study them. However, at one atmosphere pressure and at temperatures below 278 K, tetrahydrofuran (THF) forms a structure II hydrate (the same structure formed by natural gas hydrates at elevated pressure) making THF a useful model hydrate system to study at ambient pressure. For a THF/water mixture at a concentration of 81 mass% water (a 17:1 mole ratio), the melting point of the solution is raised to approximately +4.4 °C.

A popular technique for quantifying hydrate nucleation is the measurement of the ‘induction time’ or ‘lag time’. This involves cooling hydrate-forming mixtures below their equilibrium hydrate formation temperature (i.e. supercooling), and observing the time taken for nucleation and subsequent growth to occur. A variety of equipment has been developed by a number of different research groups to evaluate hydrate induction time [1–4].

The proposed existence of a so-called memory effect (ME) in hydrate-forming mixtures during sequential freeze–thaw cycles is inferred from an apparent reduction in induction time during successive measurements, based on a number of repetitions. This ME phenomenon has been reported with CO_2 hydrates [5], hydrocarbon systems [6], THF systems [7] and in molecular dynamics simulations [8], some of which have shown evidence for clusters of ordered water following hydrate formation. As many of the reports on the ME relate to hydrophobic guests, notably methane or ethane, a study on a miscible guest such as THF is not necessarily the ideal model system to probe the ME. There are however, also reports of ME being seen in THF systems [9,10] and we report here that our THF hydrate formation protocols not only find no ME at all but also that we cannot induce it when we try. When we seek to produce a ME by careful control of the melting of solid hydrate between one cooling run and the next we can see no evidence for any such effect. We argue rather that it is the stochastic nature of nucleation which is responsible for any previously perceived ME.

There is still little agreement between proponents of the ME about its possible cause.

Zeng et al. [8,9] point out that any nucleation in their THF system is heterogeneous rather than homogeneous and argue that the ME they see is not inherently structural, but rather that initial hydrate formation alters the state of heterogeneous nucleation sites, amplifying their subsequent nucleating action. They have suggested that the act of hydrate formation could in fact change the surface structure of silicon or iron oxide particles and further, that in their study

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using antifreeze proteins (AFPs), these proteins adsorb to the nucleation sites and mask them from subsequent hydrate – so negating the apparent ME.

In a recent look at the ME in systems containing methane hydrate Buchanan et al. [10] used neutron diffraction and found no evidence that water retains memory of its structure. Their conclusion was that the system had not fully equilibrated during the melt cycle. However, a year later, the same group reported on further neutron diffraction studies [12] and describe evidence that the local water structure is in fact affected by the presence of hydrate crystallites. They interpreted their results as local water density becoming greater than the average water density owing to confinement in pores formed by the surrounding hydrate crystal. They argue that this may be the cause of any perceived ME.

The long-lived metastable structure hypothesised in methane hydrates has not been dealt with definitively by computer simulations. An enhanced level of ice- and clathrate-structure in liquid has been found but no evidence of significant clusters of the ordered water [13,14]. Conversely, other studies have shown cage-like water clusters which would favour nucleation [11,12].

In previous work Haymet et al. [15,16] introduced a new instrument which we call an Automated Lag Time Apparatus (ALTA) for the statistical evaluation of ice nucleation. This instrument was subsequently used to study THF/water hydrates [17]. A description of the apparatus is given later, but the main purpose of the instrument is to cool a single liquid sample on a linear cooling ramp until it becomes solid. Since the cooling ramp is linear, either the time or temperature at which freezing occurs is a useful parameter to measure the induction time to nucleation.

Here we report on mixtures of THF/deionised water using the ALTA apparatus. The first set of data is simply historical data [17] which we have re-analysed, looking for a correlation between the first subcooling run on a sample and the second. If the second run on a given sample always (or even often) showed less ability to supercool then we may see a ME evident.

Our second set of data is from deliberately designed experiments where we have warmed the solid hydrate to systematically lower temperatures above the equilibrium melting point to try to induce a signature which others interpret as a ME.

From the first set of data we find that no correlation exists between hydrate nucleation temperature and hydrate nucleation history for systems warmed well beyond the equilibrium melting point and fully melted. From the second set of data we find that eventually the melting temperature is insufficient to fully melt the hydrate and the sample simply will not supercool on the next run. We do not find any sign that it makes the next run easier to nucleate or partially melts the sample or structures the water in any way.

2. Experimental methods

Stoichiometric mixtures of THF/water are made using Anal R grade THF from a freshly opened bottle. The water is sourced from deionised house supply water treated by ion exchange then activated carbon filtration (>18 MΩ cm). The ALTA is described in detail elsewhere [15–17]. It consists of a cooling block (approximately 5 cm × 5 cm × 1 cm) that holds a 300 μl liquid sample in a glass tube. Two Peltier devices are used to accurately control the heating and cooling rate of the block using a custom designed computer program. A white LED is used to shine light through a hole in the sample block and through the tube. A photodiode detector measures the intensity of light passing through the sample. When hydrates are formed the liquid in the tube becomes crystalline and opaque. By monitoring the change in intensity of the light received by the photodiode it is possible to detect the hydrate growth point and we take this to be the nucleation temperature. We have shown [15] that for these small volumes supercooled by more than say 10 °C the growth is so fast compared to the lag time that the nucleation temperature/time and the growth time are effectively the same.

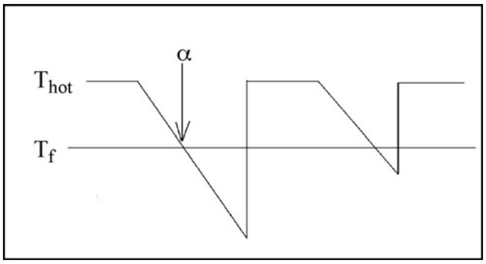

Fig. 1. The protocol for the ALTA measurements of nucleation temperature for the first data set. T_{hot} is the temperature used to melt the samples after freezing, T_f is the equilibrium melting point of that THF solution (+4.4 °C) and α is the cooling rate.

The entire system is automated and in both these sets of experiments the sample is cooled at a constant, (approximately) linear rate until hydrate formation is detected. For data set 1 that rate is ~1.0 °C min^{-1} and the temperature (and hence time) of formation is logged and the temperature then ramped back up to some predetermined melting temperature. The hydrate crystals are then melted and the light intensity received by the detector returns to its previous value. For data set 2 we use a cooling rate of ~8.0 °C min^{-1}. Following detection of freezing the system warms the tube at a predetermined rate and at some time/temperature the hydrate melts and the transmitted light level returns to its normal value. We then allow warming for a further 14 s and begin the cooling cycle again.

Clearly there exists a time lag of temperature caused by thermal resistance between the position of the temperature sensor and the liquid specimen. This has been measured for various cooling rates and has been taken into account in our data. Also, although the temperature of the sample is not strictly homogeneous the entire length of the tube containing sample is in a snug fitting hole in the aluminium block and is being cooled from the sides equally. We estimate any inhomogeneity in the temperature of the sample to be negligible. The sample solution experiences cooling first on the wall of the tube. Thus, one expects the initiation of phase transition to be on the tube wall, which is expected to be a heterogeneous one. Indeed, we have previously shown that THF hydrate nucleation does initiate on the tube wall [17].

2.1. *Protocol for data set 1*

In the first data set the sample is allowed to stand for 10 min at 20 °C following initial melting (as seen by the photodiode) to ensure that the contents of the sample cell have fully melted and reached equilibrium. The sample is then cooled a second time until hydrate formation is detected again, and the process repeated. This protocol is shown in Fig. 1. For THF/water mixtures a concentration of 81 mass% water is used in each case.

2.2. *Protocol for data set 2*

In the second data set we have set up a temperature protocol for the sample as shown in Fig. 2. Although the cooling is not exactly linear it is the same for each run and set at ~8 °C min^{-1}. What we deliberately change is the slope of the warming part of the curve and so the tube is heating at a different rate than previous runs and when the melting takes place the light level is restored at a different time and this changes the actual highest temperature which the sample reaches.

As with all heterogeneous nucleation measurements the actual nucleation temperatures of the supercooled solution are different for each run (i.e. the bottoms of each of the sawteeth in Fig. 2 are

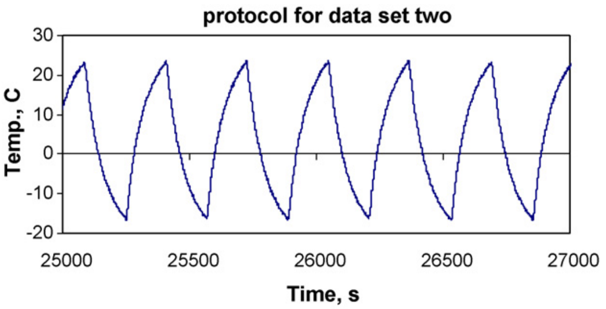

Fig. 2. Protocol for heating and cooling a given sample under the second data set regime. This is a short section of actual data from a set of 400 runs on the same sample.

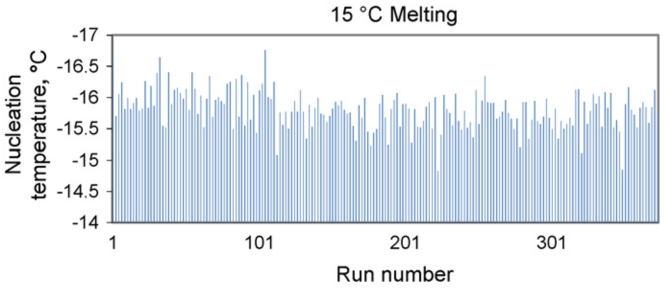

Fig. 3. Manhattan showing the various nucleation temperatures for 400 runs on the same sample of THF/water where the sample is warmed to 15 °C above the equilibrium melting point. The average nucleation temperature is about 16 °C below the equilibrium melting point of the solution.

actually different). When only the bottom points for each of the hundreds of runs on the same sample are plotted we produce a graph such as that shown in Fig. 3. We have called these graphs "Manhattans" [15–17] and they illustrate well the inherent stochasticity of liquid to solid nucleation. In all the data which follows we report the level of supercooling below the equilibrium melting point (+4.4 °C, in this case) and not just the actual temperature in °C.

3. Results

3.1. Data set 1

The results of 14 different sets of runs in 5 different glass tubes are presented in Fig. 4. In each case the solution is 19 wt.% THF/distilled water. Each set of runs is in fact made up of ∼200 freeze/thaw cycles but only runs 1 and 2 of each experiment are considered here. The percent difference between the degree of supercooling reached in runs 1 and 2 are plotted and they show clearly that no correlation exists between runs 1 and 2 in 14 separate solutions.

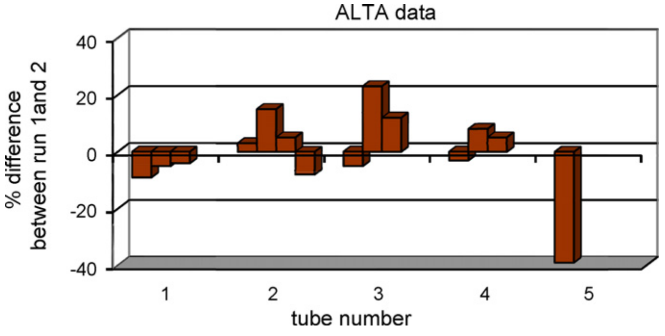

Fig. 4. Data set 1 shows the percent difference in nucleation temperatures between runs 1 and 2 for 14 solutions in 5 different tubes using the ALTA. If the T_{nuc} in run 1 is warmer the result is taken as positive.

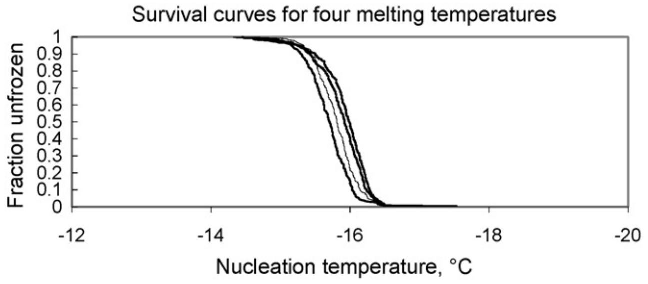

Fig. 5. Four survival curves for the same THF/water sample where it was heated to four different melting temperatures (from right to left 15, 11, 8 and 6.5 °C) above the equilibrium melting point. The slope of each curve between the 10 and 90% limits is the same.

3.2. Data set 2

Fig. 3 represents one of four Manhattans from four ALTA experiments which use heating temperatures of 15, 11, 8 and 6.5 °C above the hydrate melting point. The other three are very similar to Fig. 3 and are not reproduced here. Rather than try to gain insight from the Manhattans we instead plot the fraction of runs a sample is unfrozen at a given temperature [15–17]. These "survival" curves are more useful and demonstrate ideally the spread of nucleation temperatures for a given sample. Fig. 5 shows the survival curves for the four Manhattans discussed above. The offset seen in these curves is due to thermal lag between the aluminium sample holder block and the actual liquid sample. The thermocouple is in the aluminium beside the outside of the glass sample holder tube, not inside the liquid. Thus when the aluminium is heated at a faster rate the sample reaches a higher temperature before the cooling run is started and so there exists a bigger lag between the sample temperature and the block temperature in the supercooled region. Even though the nucleation is happening at the same average temperature there is time lag between sample and block, which can be seen in Fig. 5. For samples melted at 15 °C this lag time was approximately 25 s, i.e. the time difference between the sample reaching say −4 °C after being heated to 15 °C compared to that after heating to 6.5 °C.

However, when we use a heating rate which results in a maximum sample temperature of ∼3 °C above T_{m} we get either the usual nucleation temperature or no supercooling at all. The Manhattan for 3 °C heating is shown in Fig. 6. The arrows indicate where the heating rate was manually changed, and so the highest melting temperature was altered by as little as 0.2 °C.

The less cold nucleation temperatures seen in Fig. 6 are due to the sample not having melted fully and not supercooling at all on the next run. Rather, the sample simply freezes again as soon as the liquid is cooled below its equilibrium melting point. The apparent nucleation temperature seen in Fig. 6 of say 4 °C below the m.p. is simply an artefact due to the heat capacity of the sample. The block is getting colder approximately linearly with time and even though the sample in these cases contains solid hydrate and starts freezing immediately the block reaches temperatures below 4.4 °C the photodiode is not triggered until the solid hydrate has blocked the beam sufficiently. This takes a few seconds; meanwhile the thermocouple is inside the block that is continually getting colder.

The sawtooth representing part of the data in Fig. 6 (the second pair of arrows) is shown in Fig. 7 and we see that very small changes in the peak melting temperature (as little as 0.2 °C) can drive the resulting nucleation temperature between the two states.

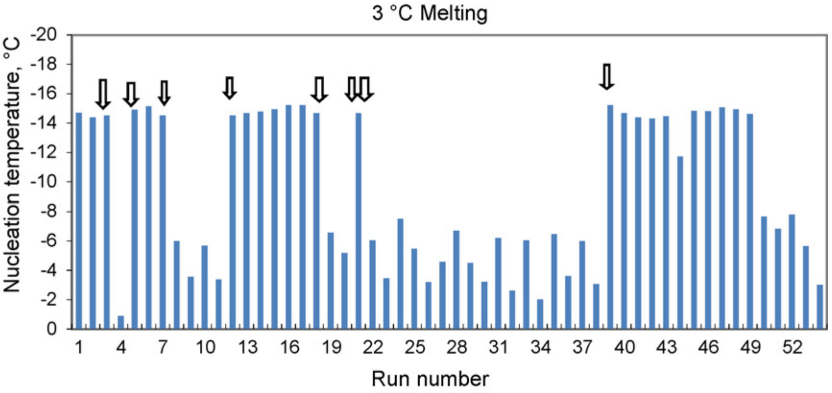

Fig. 6. Manhattan for the 3 °C heating protocol shows that there are two states of the sample, normal nucleation at about −15 °C or nucleation at a block temperature of a few °C. The arrows indicate where the heating rate was manually changed.

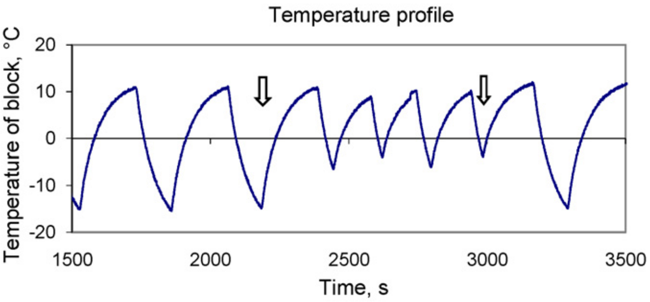

Fig. 7. Temperature profile of the tube forming part of the data in represented in Fig. 6. The arrows indicate where the rate of heating the sample was manually changed, resulting in slightly lower and higher melting temperature peaks, respectively. Very small changes in the heating rate, and so peak melting temperature, can drive the resulting nucleation temperature between the two states.

The arrows indicate where the rate of heating the sample was manually changed, resulting in slightly lower and higher melting temperature peaks, respectively.

The survival curve for the 3 °C heating regime is shown in Fig. 8. The destruction of the normal s-shape survival curve is due to the two states shown in Fig. 6. There is, however, no obvious step function in the warm end curve because the process of freezing in the tube is different each time and the time (or percent of solid in the tube) is different for each freeze event. The light detector is connected to an electronic comparator and triggers at some predetermined light level. This level is a function of the ice crystal size, number and orientation. So, when the tube is being cooled on any given run and some small crystal has remained in the tube (due to lack of sufficient melting temperature) the crystal begins to grow as the temperature passes below the melting point, but the growth rate and details are different for each run.

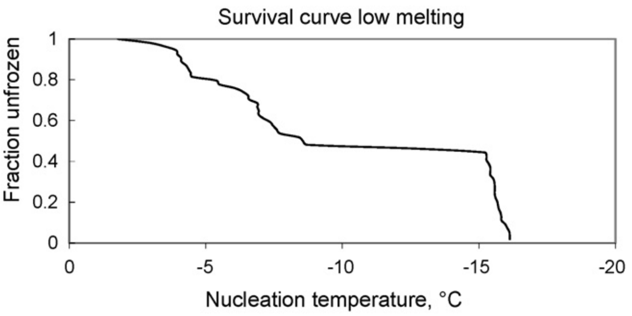

Fig. 8. Survival curve for the data shown in Fig. 6.

We also argue that the solid formed will be hydrate rather than just water-ice, based on evidence found by us in an earlier study looking at the optically birefringent properties of the initial solid [18]. Zeng et al. [2] do report that ice and THF hydrate can form together at these concentrations and it is possible that ice forms in the tubes. However, in many previous studies by our group with pure ice or aqueous solutions in these tubes, at these cooling rates, we have never seen ice nucleation above about −10 °C [15–18].

4. Conclusion

Both the data sets presented here are consistent with hydrate nucleation being a stochastic process, and they do not support the hypothesis of a 'memory' effect. In data set 1, nothing is changed between the first and second runs and there is no correlation between the nucleation temperatures. As always with heterogeneous nucleation, several short induction times may be followed with an exceptionally long one, or vice versa. Because nucleation is stochastic, a sample repeatedly supercooled will, by definition, have a shorter lag time on run two half of the time (or possibly more if sufficiently few runs are carried out, rather like dealing a deck of cards and getting four black cards in a row). In data set 2, changing the melting temperature does not alter the nucleation temperature of the sample at all until there is insufficient heat to fully melt the sample, and thereafter the sample simply does not supercool.

Thus, in the case of THF hydrates, all the statistically significant evidence we know supports the standard theory of equilibrium liquids and no memory effect. It seems likely that the issue can be finally resolved unequivocally for the case of methane/ethane by using a high pressure ALTA and making several runs on each of various samples with a range of melting/holding temperatures to determine if run "$n+1$" is consistently shorter than run "n" for each new sample.

It could be argued that our cooling rates of either 1 or 8 °C/min are too fast and the sample is too far out of equilibrium for comparison with other hydrate data. However, our experiences with water–ice show no problems in cooling fast in order to generate data similar to that of other groups who cool more slowly. Slow cooling simply provides more time for the supercooled solution to nucleate and generally allows for nucleation at warmer temperatures. It does not however, in our experience, change the inherent stochastic nature of nucleation or the slope of the survival curves, for instance [15–17].

We conclude that previously reported instances of the memory effect are likely due to the inherent stochastic nature of heterogeneous nucleation and to the protocols having too few runs on the same sample for meaningful statistics to become evident. It has also been reported that with gas hydrates the memory effect is lost if the samples are heated to more than 4 °C above the equilibrium melting temperature [4]. We would suggest that the observed step function seen in those experiments agrees with our data and that with insufficient melting the sample simply does not supercool, rather than the water having a memory. The solubility of methane and ethane into water is clearly very temperature- and time-dependent and it would seem plays a bigger part in the repeated thermal cycling of a sample than is currently understood.

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