NUCLEATION OF CLATHRATES FROM SUPERCOOLED THF/WATER MIXTURES SHOWS THAT NO MEMORY EFFECT EXISTS.

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ABSTRACT

The liquid-to-crystal nucleation temperature is measured for clathrate-forming mixtures of tetrahydrofuran and water using both an automatic lag time apparatus (ALTA) and a ball screening apparatus. Our results are conclusive evidence that no so-called "memory effect" exists. Either the solid form melts fully or it does not. If it does not, then no supercooling is possible on the next cooling down of that sample, and if it does then the second cooling run and freezing on a sample is just as likely to have a colder nucleation temperature as a hotter one.

Keywords: memory effect, ALTA, tetrahydrofuran, supercooling

INTRODUCTION

For many years researchers have described studies in which they measured the induction times for hydrate formation and claim to find markedly shorter induction times for systems that have previously formed hydrates (see for example, [1,2,3]). Most workers have suggested that water that has been structured, by belonging to a solid hydrate, is then able to regain that structure more easily during subsequent cooling, even after dissociation of the hydrate during melting. The structure has been attributed to partial hydrate cages. This phenomenon has been reported with CO_2 hydrates (eg. [4]), hydrocarbon systems (eg. [5]) and tetrahydrofuran systems (eg. [6]). An overview has recently been published by Buchanan et al. [5]. The consensus seems to have been that if a hydrate solution is heated sufficiently then the memory effect can be destroyed. Similarly if the solution is held for long enough at a temperature above the equilibrium melting point the effect can be destroyed. This implies immediately to us that in all previously reported cases the system simply was not at equilibrium before the cooling process had begun again.

METHODS

We use a stoichiometric mixture of THF and water to examine both the induction time and the actual nucleation temperature required to form hydrates and show that previous hydrate formation does not affect subsequent formation ability in a system warmed beyond the equilibrium melting point and fully melted.

1. Screening Apparatus Experiments - induction time at constant supercooling

A screening apparatus was built, similar to that described by Sloan [8]. The apparatus has a motor to rotate test tubes in iced water. Prior to hydrate formation Teflon bars are able to move inside the tubes as they are inverted. The time at which the bars were no longer able to move freely along the length of the test tubes was taken as the time for hydrate formation. The tubes contain samples from the same stock solution and are held at a constant supercooling until they freeze (taken as

the induction time, for each tube.) Once all tubes have frozen they are melted and the process repeated. The protocol is shown in Figure 1.
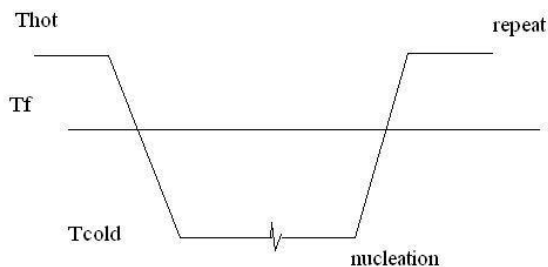

Figure 1. The protocol for the ball screening apparatus measurements of induction times. T_{hot} is the temperature used to melt the samples after freezing, T_{cold} is the level of supercooling used and T_f is the melting point of that THF solution.

Results for the induction time measurements are represented schematically in Figure 2. Clearly there is no trend for run 2 to be shorter than run 1.
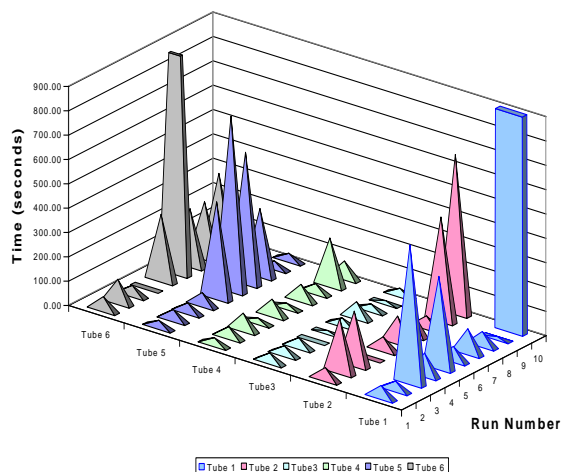

Figure 2. Hydrate Induction Time vs Run Number (19% THF/deionised Water – Teflon coated stirrer bars)

2. Automatic Lag Time Apparatus (ALTA) Experiments – nucleation temperature at constant ramping

The automatic lag time apparatus has been described in detail elsewhere [9,10,11]. The 200 μl sample is linearly cooled until nucleation and freezing occurs and then warmed up to 25 °C, as shown in Figure 3. The process is repeated many hundreds of times.
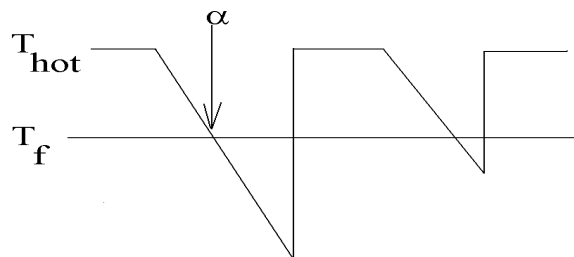

Figure 3. The protocol for the ALT- apparatus measurements of nucleation temperature. T_{hot} is the temperature used to melt the samples after freezing, T_f is the melting point of that THF solution and α is the cooling rate.

Results for the ALTA experiments are represented schematically in Figure 4 and again they show clearly that no correlation exists between runs 1 and 2 in 14 separate solutions.
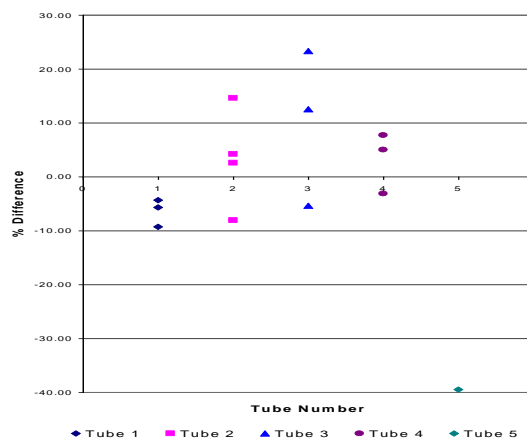

Figure 4. Difference in nucleation temperatures between Run 1 and Run 2 for 14 samples using the ALTA (19% THF/deionised Water).

CONCLUSION

The data presented in Figures 2 and 4 are consistent with the hypothesis that hydrate nucleation is a stochastic process. Nothing is changed between each run, yet there is no apparent pattern to the nucleation induction times. Several short induction times may be followed with an exceptionally long one or vice versa.

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