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Nucleation from a Supercooled Binary Mixture Studied by Crossed Polarizers†

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Polarized light passing through a supercooled binary liquid mixture sample is analyzed during the moment of the nucleation of the crystal phase to determine whether the stable equilibrium crystal is nucleated, or whether a transient phase of different composition or broken-symmetry is formed. This experiment is performed for the particular case of heterogeneous nucleation of a supercooled clathrate-forming liquid mixture, tetrahydrofuran (THF)/water, compared with ice nucleating from pure supercooled water. The new experimental results are consistent with the hypothesis that the equilibrium clathrate hydrate crystal is nucleated directly, with no transient phase detected on the time scale of these experiments.

Background

Supercooled liquids eventually nucleate to form the stable equilibrium crystal phase, but much is still unknown about the factors which govern the rate at which this happens.[1] Even less is known about the path by which the disordered supercooled phase eventually becomes the symmetry-broken stable crystal. Are phases of yet different symmetry involved? We begin here a study which addressed that question.

The binary liquid mixture formed by tetrahydrofuran (THF; C_4H_8O) and water is known to form Structure II clathrates at one atmosphere, below a temperature which depends on concentration. This binary mixture is a favorite surrogate for studies of clathrate nucleation in undersea gas pipelines, which occurs only at elevated pressures. For a THF/water mixture at a concentration of 81 mass % water (a 17:1 mole ratio), the melting point of the clathrate is raised to approximately +4.5 °C at 1 atm. Because THF/water forms the same structure as most commercial gas hydrates, it is an ideal system to use to model industrial gas hydrates such as those found in subsea pipelines. It is also convenient for the current study of the nucleation pathway.

Recent work on the statistics of heterogeneous nucleation of THF/water mixtures has clarified the effects of a catalyst added to THF/water mixtures.[2] In that work we used our automatic lag time apparatus (ALTA)[3] to repeatedly supercool, freeze, and rewarm a 300-μL sample to gather reproducible statistical data about the exact nucleation temperature from many hundreds of runs on the same sample. In that work, we assumed that when the THF solution was supercooled by as much as 14 °C, the freezing event was very fast compared with the time spent supercooled. Prior to this paper we had no evidence of what exactly happened at the nucleation event. For example, is the first solid phase an embryo of water-ice or is it the clathrate itself?

Many workers have studied THF clathrate growth and melting.[4−6] In most cases, it appears that they also assume that after some degree of supercooling of the mixture, the initial solid-phase nucleated was in fact the clathrate. Devarakonda et al.[7] looked at the density, viscosity, turbidity, and conductivity of THF mixtures just prior to, and at time of, clathrate formation. However, their results do not unambiguously show that it was clathrate and not water-ice in the first moments following nucleation. Carstensen et al.[6] used Raman spectroscopy to look at the effects of various inhibitors on the growth of THF hydrates. However, it was the structure of the hydrates formed which was studied in this way, not the seconds following nucleation. In fact, the structure of THF clathrates is very well documented, but the actual path to clathrate formation seems not to have been studied in detail. Many studies have simply assumed that at any temperature below the melting point, if the solution is seeded, then the clathrate forms and it can be subsequently examined.[8] Kashchiev and Firoozabad[9] looked at the nucleation rate theoretically from a classical nucleation theory point of view, and they also assumed that the heterogeneous nucleation would be wholly of the clathrate—that is, not from a small embryonic water-ice crystal which may have started the formation of the clathrate solidification. At the other end of the scale, Tulk et al.[10] quenched THF solutions very quickly, forming glassy states; they then looked at the formation of clathrates from the glassy state as the temperature was raised.

Zhang et al.[11] have looked at the formation of hydrates with polarized light in a novel sample holder. They looked at various aspects of THF samples as they froze, including transmitted light intensity and the change in the polarizing state of the emerging light. They sought to quantify the levels of clathrate solids within a given sample tube by arguing that, since the crystals formed with THF clathrates are cubic and have optical birefringence (compared to the liquid water/THF mixture), the

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levels of clathrate in the tube should be quantifiable. They also argued that the device might provide information as to where in the sample the hydrate formation began. Their experiments were carried out between 272 and 274 K and so had low levels of supercooling (~4−6 °C). In that case, the freezing process itself was slower than when solutions are supercooled by 12−16 °C, as in our work.[2]

The work described below builds on the work of Zhang et al.[11] Initially we decided to use an ALTA-type arrangement to determine if we could see a difference in the optical properties of the solid phase between that of water-ice and that of THF/water solutions immediately following the nucleation event. We argued that since the solid clathrate is cubic and water-ice is hexagonal (we do not cool fast enough or to low-enough temperatures to get glass or ice 1c), the difference in birefringence would mean that for a given tube filled with polycrystals the transmission of polarized light may be quantitatively different, and we might have been able to tell without doubt whether the first few seconds of freezing were due to water-ice or THF clathrate.

We pass polarized light through the sample tube and then through a second polarizer at 45° to the first. Light intensity was measured as a function of time as the tube was cooled and the sample supercooled and froze. Regardless of whether hexagonal or cubic crystals formed, the occurrence of polycrystals meant that we were simply integrating the light levels transmitted through and scattered by many crystals. To our surprise the transmitted light signals themselves were markedly different for water-only samples and THF samples, that is, not simply the levels of transmitted light.

Materials and Methods

Our experimental procedure involves taking a small volume of solution in a glass tube and cooling it linearly to below its equilibrium melting point until it nucleates and freezes. A light beam is passed through the tube, and the transmitted light intensity is analyzed. The basic ALTA device is described by Wilson et al.[2] We used THF concentrations of 15 and 25 wt % THF with water, that is, either side of the stoichiometric ratio (of 19 wt % or 17:1 mole ratio) of the clathrate hydrate. The water used was Ultrapure reagent grade water (Merck, Germany) filtered through a 0.2-μm filter. The THF is reagent grade from Scharlau, Spain. All measurements were made at one atmosphere.

Sample volumes of 300 μL have been used in each case, and these were placed in custom-built sample tubes made from borosilicate glass with an outside diameter of 5.0 mm and a length of 65 mm. These glass tubes were inserted with a snug fit into a hole drilled into an aluminum sample holder in the ALTA. The aluminum block is cooled by thermoelectric units on either side, and the temperature control is by a PID package built into a Genie software package (Advantech Inc.) which controls the experiment via a multipurpose DAQ card and PC interfacing. A typical cooling rate of 4.5 K min^{-1} was used, and the light source was either a non-polarized red laser or a bright-white LED. A polarizer at 45° to the tube axis was placed immediately after the light source, and another was placed before the photodiode with its axis horizontal to the sample tube, as shown in Figure 1. Cooling rates a factor of 2 faster were also used for these experiments, and no differences in the results were found.

The photodiode output was fed to an analogue-to-digital converter (Powerlab, ADI Instruments, Dunedin, NZ), and the voltage was plotted in real time (as a function of time) as the

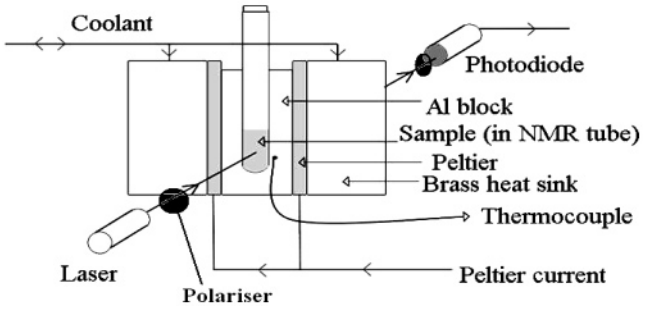

Figure 1. Experimental arrangement showing our ALTA setup and the positioning of the polarizing filters.

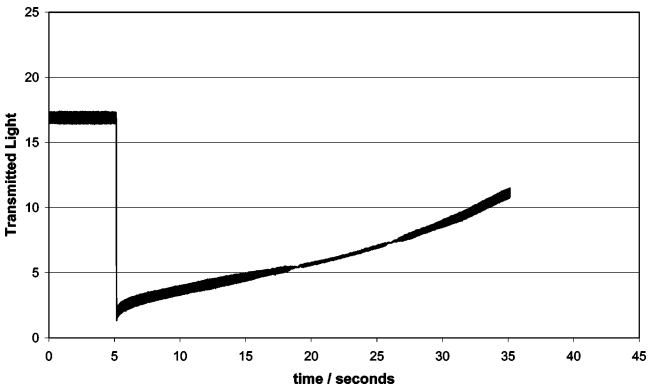

Figure 2. Transmitted light intensity as a function of time after the nucleation event for water-only freezing. The rising curve indicates increasing transmittance and is probably due to recrystallization of the polycrystalline water-ice. The photodiode signal is only a few millivolts, and the obvious noise can be filtered out with the Powerlab instrument, as shown in Figure 3.

sample was cooled to well below its melting point. At some time (and so temperature, since cooling was linear with time) the tube froze, and our results below show the light intensity before and after this freezing event. The feedback loop in ALTA ensures that cooling is linear, and we continued to cool even after the freezing event. This was not perfect, however, since the freezing event at say −12 °C liberated latent heat into the sample tube, and the temperature then rose slightly and plateaued before beginning to fall again. However, this fluctuation was deemed not serious since the temperature was already many °C below the melting point of the solutions, and the maximum cooling power (160 W) was sufficient to regain the linear cooling curve within a few seconds.

Results

All of the traces presented below show time on the horizontal axis and have small divisions of 1 s. The vertical axis is photodiode voltage (i.e., light intensity) and in arbitrary units. Figures 2 and 3 show water-only cooled and frozen. The rising curve after the initial freeze is, we believe, recrystallization of the polycrystalline ice, and this is discussed further below.

Figure 3 shows another sample of water-only, and this time the filters in the Powerlab electronic chart recorder were set to minimize the noise on the voltage signal from the photodiode. The results show a trend similar to that seen in Figure 2, again suggesting increased transmission of light by less scattering as the average ice crystal size increases with time at this subzero temperature. We did 12 runs with water at various cooling rates, and the results were all very similar to those seen in Figure 3.

The THF/water solutions used were either 15 or 25 wt %, and we found no difference between the two. Figures 4−6 show

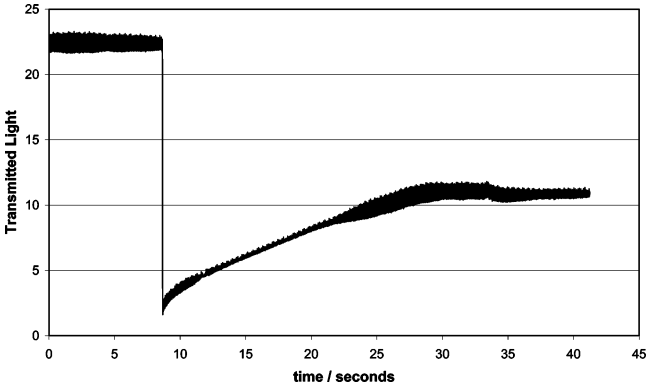

Figure 3. Transmitted light intensity as a function of time for water-ice with the ADI instruments filters set to reduce noise on the voltage signal.

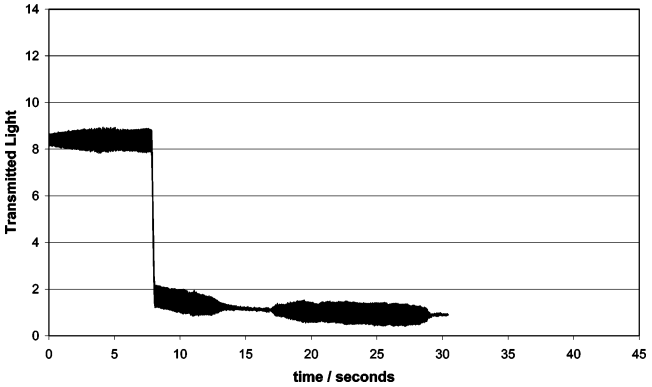

Figure 4. This plot shows 15 wt % THF/water during the freezing event. The light level remains approximately constant for the first 20 s and beyond (as shown below in Figure 6), and the fluctuations in the signal at 15 s are electrical noise which was unrelated to the light levels.

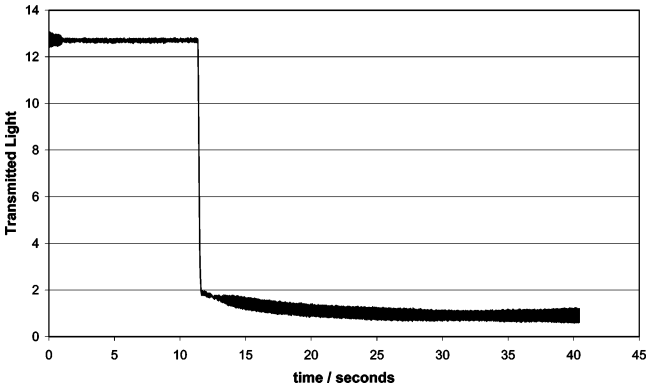

Figure 5. The plot for 25% THF/water at the time of freezing shows the light levels actually decreasing slightly after the nucleation/solidification event.

typical results at a cooling rate of 4.5 K/min, and we found that the results at twice this cooling rate were very similar. As seen in Figure 4, there is clearly no increasing light transmission immediately following the freezing event, and we take this to mean no recrystallization of the cubic clathrate structure.

Recrystallization of water-ice is well-known and is usually explained by the Kelvin Effect where smaller ice crystals, which have high curvature, have melting points below the set temperature. They melt, and the liquid they free up migrates to nearby larger crystals and then refreezes, because these crystals have melting points above the set temperature. The overall effect is that when the matrix is held at high subzero temperatures, one gets fewer larger crystals. We have seen traces such as

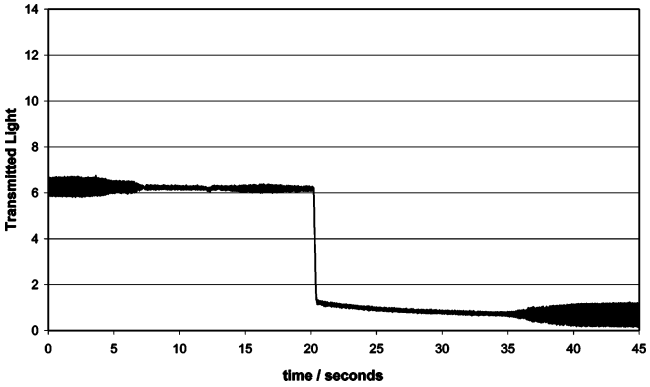

Figure 6. This plot shows THF/water (15 wt %) on an expanded scale. The sample had been liquid for 220 s, indicating that it froze at about −16 °C (at a cooling rate of 4.5 K/min). The voltage output was essentially horizontal for many more minutes, although we stopped the measurement at about −25 °C.

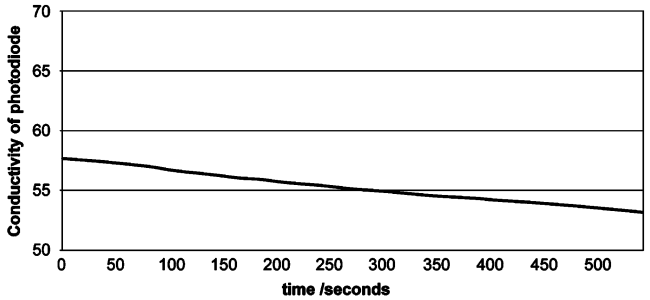

Figure 7. Trace from an optical recrystallometer with water frozen and held at −6 °C. The voltage output is inverted compared to the ALTA traces above; however, the increasing transmission indicates increasing average crystal size and so recrystallization of the ice.

Figures 2 and 3 before. Recently, an optical recrystallometer has been developed (by one of us, P.W.), and it has been used to quantify the levels of recrystallization in frozen solutions (PCT.NZ03/00201). This recrystallometer uses about 200 μL of sample, which is first quench-frozen at −80 °C in a small glass tube. The tube is transferred to the recrystallometer which has been set at, let's assume, −6 °C. The level of light scattering caused by the ice crystals is then measured while the frozen sample is held at this high subzero temperature. If the solution recrystallizes, the levels of transmitted light increase more or less linearly with time as the crystals increase in average size and cause less side and backscattering of the light. A typical trace from this device is shown in Figure 7.

It is worth noting here that, in these first experiments, the light beam is traversing about 4.2 mm of solid. This path length is sufficient to significantly lessen the level of transmitted light due to scattering of the light. It seems likely that, in the next round of experiments, a larger-diameter tube and thus a longer path-length would allow for even more-sensitive measurements since the ratio of scattering to transmission would increase. However, care would need to be taken that the solution/solid was still isothermal and lacked large gradients which would allow for more liquid surrounding crystals at the center of the tube, that is, farthest from where the heat is being removed from the sample.

Conclusions

These experiments are designed to test whether the differing birefringence of hexagonal water-ice and cubic clathrate may be used to determine the initial solid phase of a supercooled THF/water binary mixture. It was anticipated that the transmitted

light intensity between polarizers at 45° would show a signature determined by the structure of the solid phase. We are surprised to find that the signatures are markedly different in shape, not simply in intensity level. The fact that the signals are markedly different due to the recrystallization of the ice means that our results are consistent with the idea that the clathrate is the initial solid phase. This adds an important piece of data, not only for the particular case of nucleation of clathrates but also to the general problem of formation of an equilibrium solid from initial nonequilibrium (in this case metastable) equilibrium liquid.

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