

Scientific report:

“Dortmund-Innsbruck clathrate hydrate collaboration”

The purpose of the visit by Ph.D. student H. Nelson from the Dortmund group of R. Böhmer to the group of T. Loerting from Innsbruck University was twofold.

On the one hand, measurements carried out by both groups over the last year had to be discussed to obtain the same level of information for both groups. With this acquired knowledge measurements already done were evaluated and future steps of our collaboration could be planned.

On the other hand, several clathrate hydrate systems of the cubic sII structure were analyzed with respect to the amount of hexagonal ice formed during the crystallization of the hydrate samples. During the visit we carried out X-ray diffraction (XRD) measurements at 85 K and we focused on the previously applied cooling rate dependence of our clathrate samples in order to study the resulting mixing ratio of ice I_h with the clathrate hydrate.

Work description:

A whole series of XRD measurements on several hydrate systems was carried out. We analyzed in detail the following guest molecules (see Fig.1): Tetrahydrofuran (THF), Dioxolane (DXL), Tetrahydropyran (THP) and Dioxane (DXN). Cyclopentane (CP) hydrate samples were not measured in this context, as CP is not easily miscible with water and therefore needs a more complicated and time consuming crystallization procedure.

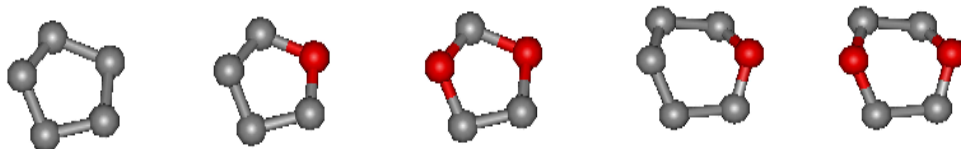


Fig.1: Cyclopentane – Tetrahydrofuran – Dioxolane – Tetrahydropyran – Dioxane
Red spheres: oxygen atom. Gray spheres: CH_2 group.

In order to compare different crystallization techniques we prepared samples with vastly different thermal histories.

1. We placed the stoichiometrically prepared growth liquid in a small glass bottle at $-20\text{ }^\circ\text{C}$ for 3 days (referred to as slowly cooled samples).
2. We quenched the growth liquid by inserting a small glass bottle in liquid nitrogen (referred to as rapidly cooled samples).
3. We introduced small drops of the growth liquid with a pipette into liquid nitrogen (referred to as quenched drop samples).

We carried out twelve individual XRD measurements on the samples produced by the three crystallization procedures mentioned above for the four hydrate systems (i.e., not for cyclopentane hydrate).

In addition NMR and dielectric spectroscopy data from measurements previously performed in Dortmund were exchanged, compared to calorimetric (DSC) and XRD measurements performed in Innsbruck, and thoroughly discussed.

Results:

During the crystallization of the hydrate solution by quenching small drops in liquid nitrogen, we encountered some difficulties. The quenched drop samples contained large amounts of ice I_h and very low amounts of hydrate crystals, see Fig. 2. This can be explained either by a phase separation of water and guest molecules or by a contamination with moisture. The two methods, that involved the sealing of our solution in glass bottles before the crystallization yielded samples that turned out to contain less ice impurities than the drop quenching method.

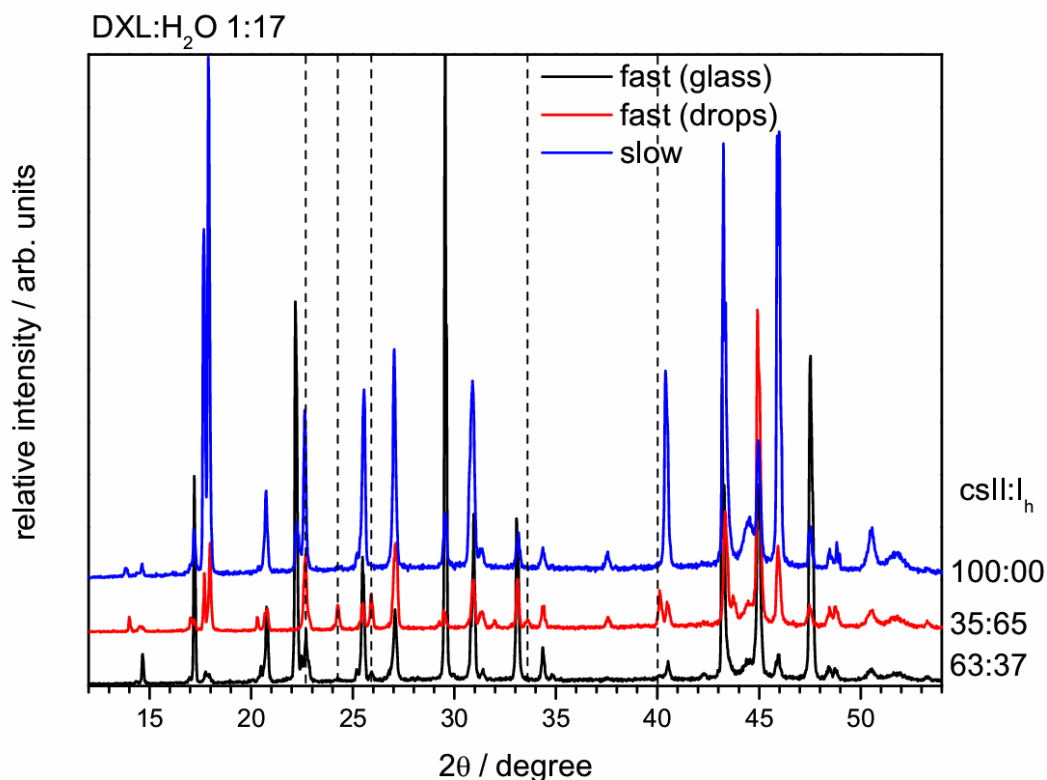


Fig. 2: X-ray diffractogram of $\text{DXL} \cdot 17\text{H}_2\text{O}$ samples cooled with different rates. Slowly cooled (blue), rapidly cooled (black) and quenched drops (red). The peak positions expected from ice I_h are shown as dotted lines at $2\theta \approx 23^\circ$, 24° , 26° , 33° and 40° . The slowly cooled DXL hydrate shows no ice impurities. The rapidly cooled sample contains 37 % ice and the quenched hydrate drops contain 65 % ice.

In Fig. 2 the three different crystallization procedures are compared for the hydrate $\text{DXL} \cdot 17\text{H}_2\text{O}$. The Bragg reflections for the cubic clathrate structure sII are present for all measurements. The vertical dotted lines show the main peak position of hexagonal ice. The

diffraction peaks were fitted and analyzed with the XRD software *Powder Cell*. For the DXL hydrate the ice to hydrate ratios are as follows (uncertainties are $\pm 5\%$):

Slowly cooled:	hydrate: 100 %	ice: 0 %
Rapidly cooled:	hydrate: 63 %	ice: 37 %
Quenched drops:	hydrate: 35 %	ice: 65 %

For the three other hydrate systems the resulting ice content was always higher compared to DXL $\cdot 17\text{H}_2\text{O}$. A quantitative analysis was not possible for THP and DXN hydrate samples so far, because crystallized guest molecules seem to create additional diffraction peaks around $2\theta = 20^\circ$, see Fig. 3.

In this figure we compare the data measured for slowly and rapidly cooled DXN hydrates with data for the ideal sII hydrate structure calculated from the oxygen atoms of the water molecules and ice I_h . It should be noted that also for the slowly cooled sample a significant amount of ice impurities was detected. But, as can be seen at the peak around $2\theta = 40^\circ$, the fraction of ice crystals in the sample is strongly reduced in the slowly cooled sample.

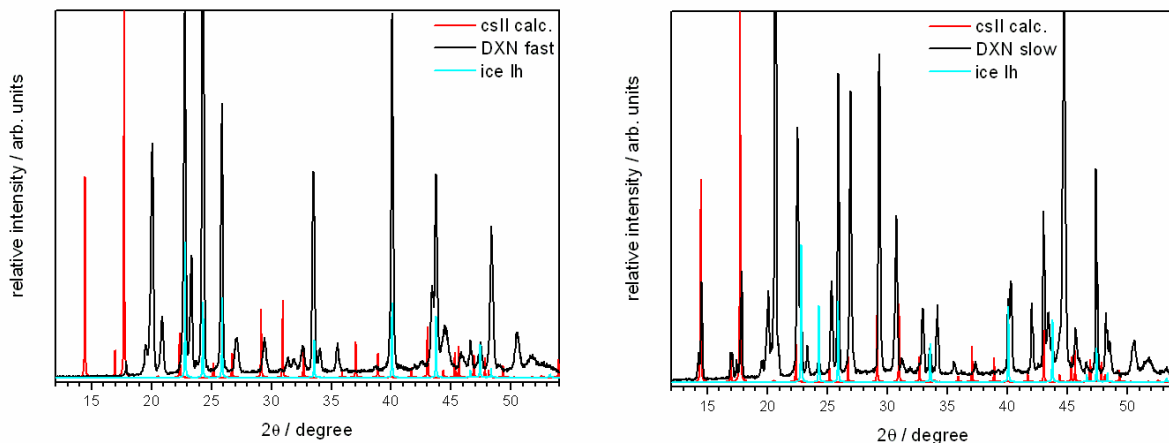


Fig. 3: X-ray diffractograms of DXN $\cdot 17\text{H}_2\text{O}$ (black) compared to calculated reflections for an ideal sII structure hydrate (red) and ice I_h (cyan). The rapidly cooled sample (left) shows no sign of hydrate crystals. Here a phase separation of water and DXN is likely.

In the slowly cooled sample (right) the Bragg peaks of a sII hydrate can be seen. In addition ice contamination of the hydrate is detected. Peaks that are believed to stem from crystallized DXN molecules around $2\theta = 40^\circ$ are present in both measurements.

To summarize, we find the slow-cooling crystallization method works best for all analyzed hydrate systems. For DXL and THF there is no detectable amount of ice impurities in the slowly cooled hydrates. In contrast for THP and DXN it was not possible to prepare pure, ice-free hydrate samples.

Future collaboration:

As a result of the visit of H. Nelson to Innsbruck we plan to perform several additional measurements:

In order to elucidate whether the deuteron spin-lattice relaxation time of $T_1=10$ s of amorphous TDF · 17H₂O hydrate measured at 100 K originates from guest- or host-molecule reorientation we plan to perform ²H-NMR measurements of THF · 17D₂O hydrates. The samples will be prepared in Innsbruck and transferred to Dortmund for the actual measurements.

DSC measurements on amorphous THF · 17H₂O hydrates will be performed in Innsbruck to check whether a glass transition exists around 110 K as predicted by dielectric spectroscopy.

Trimethylene oxide is capable to form both cubic clathrate structures sI and sII and is therefore well suited to investigate further the guest-host interaction in clathrate hydrates. The possibility to analyze the same guest molecule in two different cage structures is a very interesting aspect in our research ambitions.

Projected publications:

Our collaborative effort has already brought to bear a number of important scientific aspects on icy solids which need further clarification and extension, as mentioned above, and will form the groundwork of a joint future publication. We expect that for example DSC studies on relaxation processes or phase transitions in amorphous clathrates can be published in due course. Also NMR and dielectric spectroscopy studies on dynamics in amorphous clathrates yield valuable insights. In addition the XRD measurements performed during this visit constitute a valuable contribution to the Ph.D. thesis of H. Nelson.