

Experiment Report Form



	Experiment title: Clathrate hydrate phase diversity and transformations in $R_4\text{NBr}-\text{H}_2\text{O}$ ($R=\text{C}_4\text{H}_9$, $i\text{-C}_5\text{H}_{11}$) systems	Experiment number: CH-5516
Beamline: ID22	Date of experiment: from:9.11.2018 to:12.11.2018	Date of report: 12.02.2019
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The aim of this project was to investigate in detail the diversity of clathrate hydrate phases in $R_4\text{NBr} - \text{H}_2\text{O}$ ($R=\text{C}_4\text{H}_9$, $i\text{-C}_5\text{H}_{11}$) systems and influence of crystallization conditions and different admixtures on their formation. Clathrate phases in these systems are water-reach compounds with low melting temperatures (less than 13°C and 31°C correspondingly). Investigation of these systems is complicated by the tendency of metastable phase formation and existence of structurally-relative phases.

Diffraction pattern measurements were done using $\lambda=0.400054(4)$ Å radiation in \varnothing 1.5mm kapton capillaries for ambient pressure experiments and \varnothing 0.5mm thick-walled quartz glass capillaries for high-pressure (up to 50 bar) experiments. Samples were prepared by dissolving of 5–60 wt% of clathrate former ($R_4\text{NBr}$) in pure deionized water, or water solutions of admixtures (5–40 wt% of NH_4Br , 5 wt% of $(\text{C}_4\text{H}_9)_4\text{NBr}$ and 5 wt% of $(\text{C}_4\text{H}_9)_4\text{PBr}$). The samples were placed in capillaries at room temperature in form of liquid solutions for $(\text{C}_4\text{H}_9)_4\text{NBr}$ samples and wet paste for $(i\text{-C}_5\text{H}_{11})_4\text{NBr}$ ones. Special samples were prepared in He, CO_2 , and Ar atmospheres from degassed water and clathrate formers using Schlenk technique.

During the experiment, different crystallization techniques were tested:

- (1) temperature cycling – cooling of a sample from 295 K to 220 K and back at 360 K/hour rate; 6 samples;
- (2) slow quenching – cooling of a sample from room temperature to 150 K in about 10 seconds (time of cryostat nozzle moving to work position); 57 samples;
- (3) fast quenching/annealing – cooling by liquid N_2 during about 10 seconds with further annealing at 272 and 274 K; 23 samples.

The 1st way was found to be time-consuming and gives large crystals, which worsen intensity statistics. Attempts to improve the intensities by addition of amorphous sample carriers (amorphous boron, ground glass and filter paper were used) failed because of increase of background, masking details of diffraction patterns. The 2nd and 3rd ways gave appropriate samples. While there still were irregularities of phase composition on 1 mm scale, the measurements over a number of capillary positions were used to obtain representative set of diffraction patterns.

Indexing and Pawley refinement (Topas Academic v.6) of the obtained diffraction patterns showed formation of hydrates of cubic structure 1 (CS1) and tetragonal structure 1 (TS1) host frameworks for $(\text{C}_4\text{H}_9)_4\text{NBr}$ hydrates and orthorhombic structure 5 (OS5, novel unpublished structure type, oF 47.471, 21.664, 11.930 Å at 150K) for $(i\text{-C}_5\text{H}_{11})_4\text{NBr}$ hydrates. No difference in unit cell parameters were found for the samples obtained with different clathrate former content. In addition, no influence of both atmosphere composition at ambient pressure and admixtures of NH_4Br on hydrates unit cell parameters was found. However, admixtures of $(\text{C}_4\text{H}_9)_4\text{NBr}$ and $(\text{C}_4\text{H}_9)_4\text{PBr}$ to $(i\text{-C}_5\text{H}_{11})_4\text{NBr}$ samples bring in some diversity to the phase composition: in the first case formation of new phase (cP , c.a. 25.15 Å) with unknown structure type and variable unit cell parameters in addition to OS5 one is observed; in the second case formation of a variety of phases were detected. Notable, that unit cell parameters of OS5 stayed constant, which indicates absence of solution of admixtures in it.

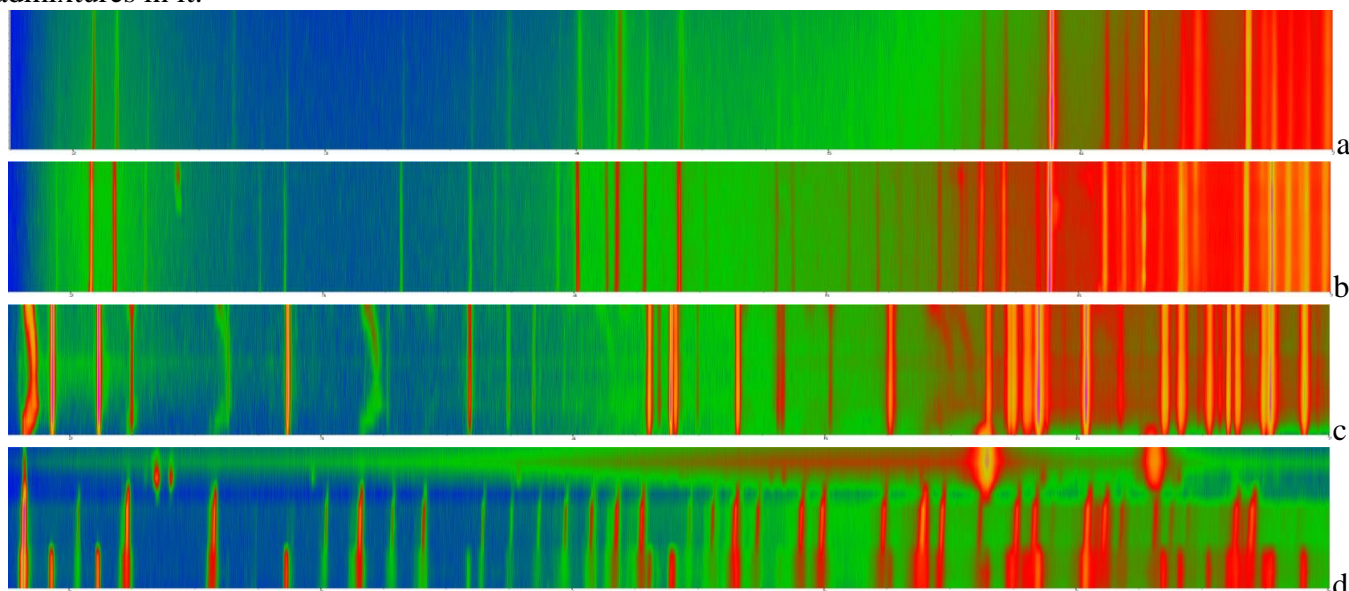


Figure. Series of diffraction patterns in $1.8\text{--}7.0^\circ$ 2θ obtained for (a) 45 wt% $(\text{C}_4\text{H}_9)_4\text{NBr}$ (CS1 hydrate phase); (b) 40 wt% $(\text{C}_4\text{H}_9)_4\text{NBr}$ (TS1 and CS1, formed after eutectic melting); (c) 40 wt% $(i\text{-C}_5\text{H}_{11})_4\text{NBr}$ + 5 wt% $(\text{C}_4\text{H}_9)_4\text{NBr}$ (OS5 and solid solution based on unknown hydrate phase); (d) 60 wt% $(i\text{-C}_5\text{H}_{11})_4\text{NBr}$ + 5 wt% $(\text{C}_4\text{H}_9)_4\text{PBr}$ (OS5 and three unknown hydrate phases).

High pressure experiments were conducted by stepwise increasing of CO_2 pressure over one $(\text{C}_4\text{H}_9)_4\text{NBr}$ (40 wt%) and two $(i\text{-C}_5\text{H}_{11})_4\text{NBr}$ (40 wt%) samples prepared using fast quenching/annealing technique. For the $(\text{C}_4\text{H}_9)_4\text{NBr}$ sample stabilization of TS1 phase respectively to CS1 at pressure increasing was observed. For the $(i\text{-C}_5\text{H}_{11})_4\text{NBr}$ samples the OS5 phase was stable up to 20 kbar, at further pressure increasing formation of phase with host framework of distorted hexagonal structure 1 (HS1, oP 21.722, 12.951, 12.081 Å) occurred. Heating of the $(i\text{-C}_5\text{H}_{11})_4\text{NBr}$ sample at 47 kbar CO_2 showed the higher thermal stability of HS1 mixed $(i\text{-C}_5\text{H}_{11})_4\text{NBr}\text{-CO}_2$ hydrate in comparison with ambient pressure $(i\text{-C}_5\text{H}_{11})_4\text{NBr}$ hydrates.

For the $(\text{C}_4\text{H}_9)_4\text{NBr}$ hydrates formation of bluish-black colored products of photodegradation at temperature below 120 K was found. Color changing is reversible and disappears on heating. The degradation, probably, is due to formation of free radicals, stabilized by host framework. In addition, a few degrees sample heating was observed for all $R_4\text{N}^+$ -containing samples, which manifested on peaks displacement during diffraction measurement and appearance of gaps in a sample if measurement were done near a melting temperatures. Since high thermal expansion of clathrate hydrates it results to noticeable widening of peaks on integral patterns. Building of experimental strategy reducing these effects let to increase the precision of unit cell parameters determination to distinguish highly relative clathrate phases.

The present work allows us to confirm existence of two (CS1 $(\text{C}_4\text{H}_9)_4\text{NBr}$ and OS5 $(i\text{-C}_5\text{H}_{11})_4\text{NBr}$) ionic clathrate were not sufficiently proved in the literature. In addition, formation of three new phases of $(i\text{-C}_5\text{H}_{11})_4\text{NBr}$ hydrates in presence of $(\text{C}_4\text{H}_9)_4\text{XBr}$ ($X = \text{N}, \text{P}$) admixtures was shown, at least one of which has unknown type.

The obtained experience allow developing experimental strategy for more precise diffraction data collection for ionic clathrate hydrate samples.