

Poster Presentations

[MS24-P37] Pyrrolidine and its hydrates – *in situ* crystallization, structure and properties

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Tetrahydrofuran (THF) with water forms a stable clathrate hydrate with THF to water ratio equal to 1:17. The melting point of the crystals yields *ca.* +5°C. The host network built from water molecules incorporates guest THF molecules [1]. There are no hydrogen bonds present between host and guest moieties. What happens if we change THF to pyrrolidine – similarly in shape molecule? Is it possible to get clathrate of pyrrolidine or only hydrate? How many hydrates form pyrrolidine and how stable will be?

Presented here study concerns structural, spectroscopic and thermal investigations of pyrrolidine-water system. Pyrrolidine is a cyclic secondary amine with an aliphatic five-membered ring. This amine is liquid at ambient conditions with relatively low melting point (63°C). Although there are known two crystalline form of pyrrolidine – monoclinic and triclinic – [2] it is worth to look closer to pure amine. Thus experiments with attempts to obtain crystals of pure pyrrolidine were started at the beginning. Because this compound is a liquid to get suitable crystals for x-ray experiments it desire to use *in situ* crystallization technique supported by IR laser beam radiation [3]. The outcome of the experiment with pure amine was a new orthorhombic polymorph of pyrrolidine. Moreover there is a phase transition between known LT monoclinic polymorph and HT orthorhombic one related to reorientation of molecules in the crystal lattice.

As a result of crystallization of pyrrolidine with water (technique as above) two hydrates containing 0.5 and 6 H₂O molecules per one amine moiety were obtained. The hexahydrate

undergoes an order-disorder phase transition at about -78°C. These crystals are surprisingly stable with melting point around -3°C. In the crystal lattice amine molecules interact with the network of water molecules. In both hemihydrate and LT form of hexahydrate structures water molecules are fully ordered. This is not the case of HT form of hexahydrate. For all obtained systems (two polymorphs of pyrrolidine, hemihydrate and two polymorphs of hexahydrate) the crystal structure was determined using single crystal x-ray diffraction. What is interesting in both pyrrolidine and hexahydrate crystals the phase transitions is associated with twinning. In addition for all obtained phases Raman spectra were recorded using *in situ* confocal probe. In this study also x-ray powder diffraction and differential scanning calorimetry (DSC) techniques were used to better describe investigated systems.

References:

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Keywords: hydrates; in-situ experiments; Raman spectroscopy