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Preparation of fine powders by clathrate-forming freeze-drying: a case study of ammonium nitrate

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Contents:

Materials

Peroxide-free twice-distilled THF and distilled water were used as solvents. Ammonium nitrate (AN) was of analytical grade and used as purchased without additional purification.

Low-temperature powder X-ray diffraction experiments

Powder X-ray diffraction experiments were carried out on a Bruker D8 Advance diffractometer (λ=1.5406 Å, tube voltage of 40 kV and tube current of 40 mA) equipped with an Anton Paar TTK 450 low temperature chamber. The vial with frozen solution was broken, the sample was gently ground in a mortar (all operations being performed at liquid nitrogen temperature) and placed onto a holder, which had been preliminary cooled to -100°C. Diffraction patterns were measured in the -100 - -5°C temperature range (2Θ scans from 3-45 degree, 0.02 degrees step).

Samples for low-temperature powder X-ray diffraction and freeze-drying

Starting solutions: aqueous AN solutions (10 wt %; 42.8 wt %) (reference solution), THF-water solutions (THF hydrate composition, 19.6 wt %) (reference solution), AN (10 wt %) in the THF/water co-solvent system (19.6 wt % of THF).

Freezing methods:

Method 1. Vials (Sci/Spec, B69308), 1,000 ml aliquots, air thermostat, 250 K.

Method 2. Vials (Sci/Spec, B69308), 1,000 ml aliquots, cryothermostat (KRYO-VT-05-02, TERMEX, Russia), 220 K.

Immediately after freezing the solutions a few vials were broken under liquid nitrogen temperatures, in order to extract the samples, which were thereafter kept in liquid nitrogen until diffraction experiments.

Method 3 (Spray freezing (SFD [1])).

The aqueous AN solution was sprayed into a vessel with liquid nitrogen (diameter of the capillary 0.4 mm, excessive pressure of the spraying gas 1.3-1.7 bar). The frozen solution was kept in liquid nitrogen before diffraction experiments.

Method 4 (Thin Film Freezing (TFF) [1])

Small amounts of solution were splashed onto a copper plate cooled to liquid nitrogen temperature. The frozen solution was gently ground manually at liquid nitrogen temperature and was kept in liquid nitrogen before diffraction experiments.

Samples prepared by Methods 3 and 4 were freeze-dried in drying trays.

Table S1. Compositions and freezing methods for AN solutions used for low-temperature powder X-ray diffraction and freeze-drying. * - eutectic composition in the AN-water binary system.

Mark	W_{10}	H_{10}	W_{SFD}	W_{20}	W_{50}	W_{TFF}
Solvent	water	THF/water co-solvent system (THF hydrate composition, 19.6 wt % of THF).	water	water	water	water
AN concentration in solution, wt %	10	10	10	42,8*	42,8*	42,8*
Freezing method	Method 1	Method 1	Method 3	Method 1	Method 2	Method 4

TA experiments

The TA experiments were carried out on the installation reported [2]. Each of two aluminum sample holders were loaded with four teflon cells filled with solutions (the volume of the samples were 1.000 ml; the thickness of the solution layer in each of the cells was 13 mm). Type K thermocouple was placed in each of the samples, the junction being approximately in the middle of the sample. The assembly of the samples was placed in the autoclave. Then the autoclave was cooled/heated (+20 °C → –30 °C → +30 °C) at the constant rates of 0.5 and 1.0°C/min at atmospheric pressure. The temperatures in each of the samples were digitally recorded. The absolute temperature uncertainty was ±0.2°C. The formation of the ice I*h*, THF hydrate and the AN-ice eutectic on freezing (nucleation) as well as melting of the ice I*h*, THF hydrate, AN-water eutectic, ternary peritectic on heating were revealed by heat effect registered with the thermocouple. All measurements were performed in triplicate.

SEM experiments

Morphological examination of the AN samples obtained by freeze-drying of aqueous AN solutions and AN solution in the THF/water co-solvent system (19.6 wt % of THF) were carried out with a TM-1000 (Hitachi) scanning electron microscope. The samples were mounted on a SEM stub with double-sided carbon tape and coated with gold to a thickness of about 8 nm with a JFC-1600 Auto Fine Coater (Jeol). All samples were studied immediately after removal from the freeze-dryer.

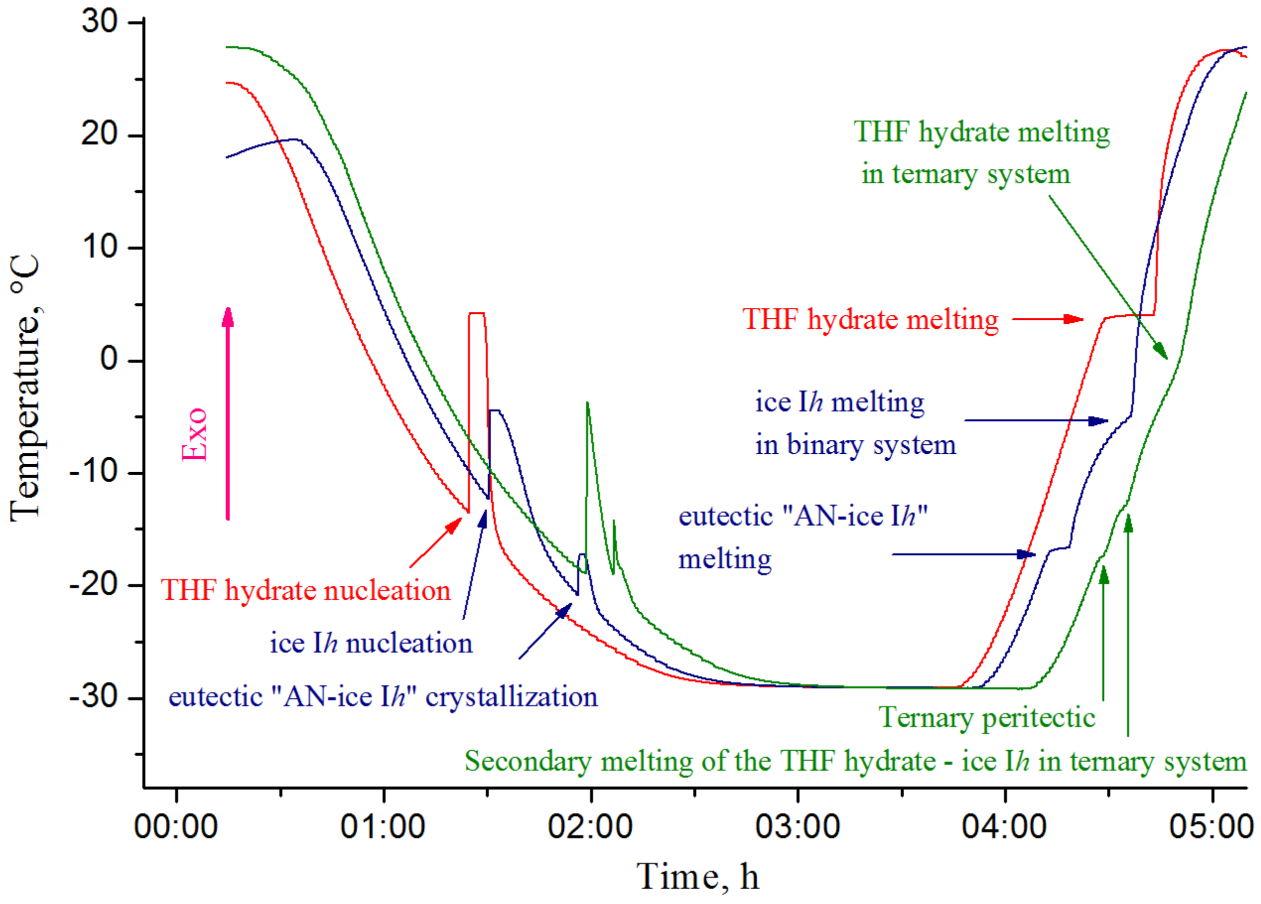

Figure S1.

Typical experimental curve obtained in TA experiments (cooling and subsequent heating).

Designations: AN – ammonium nitrate.

Red line - THF-water solution (THF hydrate composition, 19.6 wt % of THF) (reference solution);

Navy line - aqueous AN solution (10 wt %) (reference solution);

Green line - AN (10 wt %) in the THF/water co-solvent system (19.6 wt % of THF).

Table S2.

Results of the TA experiments.

Designations: H – THF hydrate; I*h* – ice I*h*; AN – ammonium nitrate; *l*- solution

Formulation	Melting temperature ± s.d., °C	Comments
THF-water (19.6 wt % THF)	4.2 ± 0.1 (+4.5°C [3]; +4.2°C [4])	Congruent melting of the THF hydrate
AN-water (10 wt % AN)	-16.7 ± 0.1 (-16.7°C [5, 6])	AN-water eutectic $AN_{(s)}$ + ice $Ih_{(s)} = l$
	-4.4 ± 0.3	Ice I*h* melting (liquidus line): $Ih_{(s)} = l$
AN-THF-water (10 wt % AN in THF/water co-solvent system (19.6 wt % of THF))	-17.5 ± 0.1	Ternary peritectic: $H_{(s)} + AN_{(s)}$ = ice $Ih_{(s)} + l$
	-13.3 ± 0.1	Secondary melting [7] of the THF hydrate - ice I*h* in the ternary system: $H_{(s)}$ + ice $Ih_{(s)} = l$
	-0.5 ± 0.1	THF hydrate melting: $H_{(s)} = l$

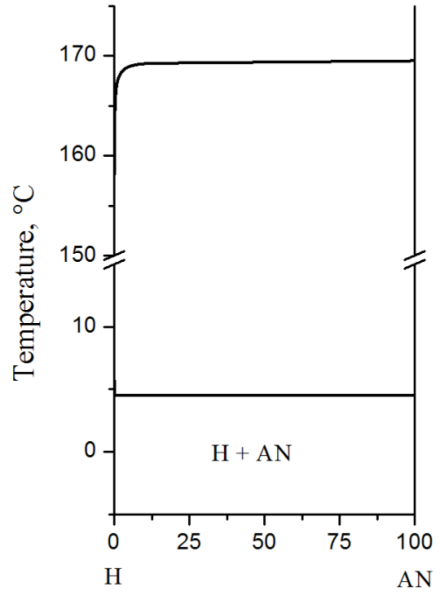

Figure S2.

Principal view of the “AN-THF hydrate” state diagram under assumption that the polythermal section “AN-THF hydrate” of the state diagram of the “AN-THF-water” ternary system is quasi-binary (AN is an indifferent phase relative to the THF hydrate). Designations: AN – ammonium nitrate; H - THF hydrate.

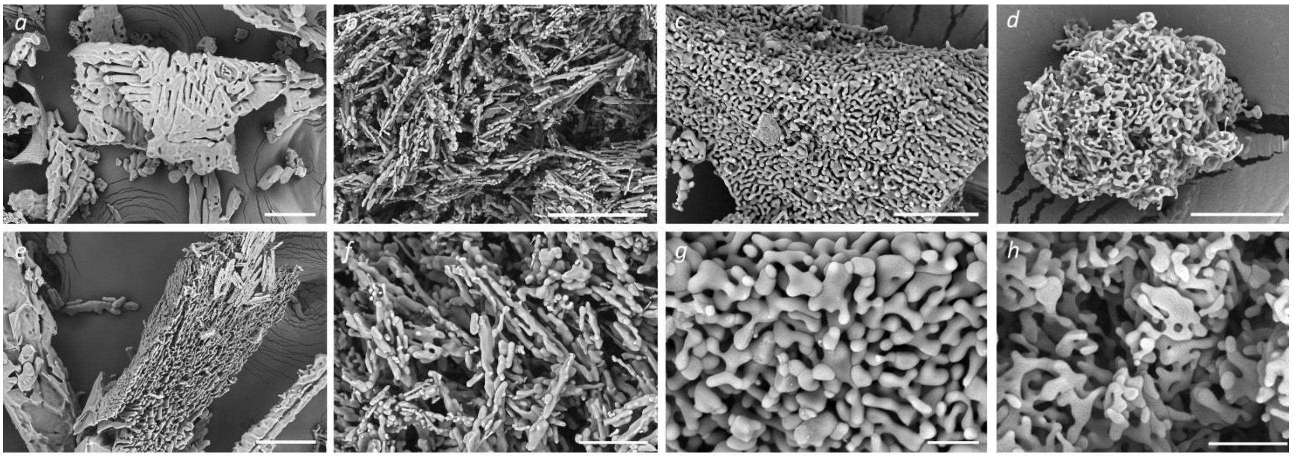

Figure S3.

SEM images of ultrafine AN samples, obtained by freeze-drying of aqueous solution. *a, e* – W_{20}; *b, f* – W_{50}; *c, g* - W_{TFF}; *d, h* - W_{SFD}. Scale bar: *a, b, e* – 100 µm; *c, f* – 50 µm; *d* – 30 µm *g, h* – 10 µm.

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