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Mendeleev Commun., 2018, **28**, 211–213

Mendeleev Communications

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

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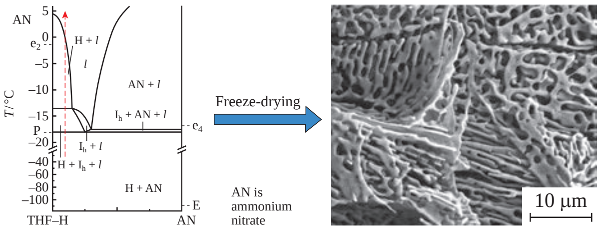
DOI: 10.1016/j.mencom.2018.03.035

Fine powders of ammonium nitrate were prepared by the freeze-drying of a solution in a THF–water mixture. Freezing gives a THF hydrate and dispersed ammonium nitrate particles; the THF hydrate can be then removed by sublimation to leave fine ammonium nitrate powder. To optimize the process, the stability of cubic structure II THF clathrate hydrate in the presence of ammonium nitrate was studied by X-ray diffraction and thermal analysis.



Ammonium nitrate is used as the main component of industrial explosives.[1] Milled ammonium nitrate is sometimes added to ready energetic compositions to achieve their target characteristics, in particular, to modify their properties without increasing significantly the critical diameter.[2] It is important to produce fine ammonium nitrate powders without milling in order to get very pure samples.

Cryotechnology is one of the main methods for obtaining fine powders.[3] A central process in this technology is the fast freezing of aqueous salt solutions of target components with the subsequent solvent removal. In contrast to cryoextraction that imposes strict restrictions on the solubility of salts in mixed solvents (such as ethanol–water) at low temperatures; the freeze-drying method makes it possible to remove a solvent by sublimation, so that no liquid phases are formed. As a result, the final fine powders have a high specific surface area and a uniform distribution of the components throughout the bulk sample.[4] The freeze-drying is a time- and energy-consuming process. It is therefore important to find the ways of its optimization.

Many aqueous-organic solutions form clathrate hydrates on freezing.[5] Clathrate hydrates are water-based crystalline compounds consisting of a lattice-like framework of hydrogen-bonded water molecules that form cavities, in which small (< 0.9 nm) nonpolar guest molecules of volatile organics are incorporated. A mixed THF–water solvent is of special interest for the preparation of ultrafine powders by freeze-drying since the THF clathrate hydrate formed in this system [cubic structure II (CS-II), *Fd*3*m*, *a* ~ 17.1 Å, THF : water molar ratio of 1 : 17; hereafter, THF hydrate] is stable up to high temperatures (it decomposes at +4.5 °C at ambient pressure of 1 bar).[5] Using a mixed solvent giving a clathrate on freezing is beneficial in terms of the significant shortening of a primary drying stage.[6]

The aim of this work was to study the stability of the THF clathrate hydrate in the presence of ammonium nitrate in order to optimize the conditions (the critical temperature of a primary drying stage) of the freeze-drying process giving fine ammonium nitrate powders.

The X-ray diffraction experiments (details are given in Online Supplementary Materials) have shown that the samples of frozen (at different cooling rates, see Table S1) aqueous solutions of ammonium nitrate with different concentrations in a temperature range from –120 to –20 °C are composed of the mixtures of ice I$_h$ and ammonium nitrate polymorph IV[7] [Figures 1,2(*b*)]. In the powder diffraction patterns obtained for the solution of ammonium nitrate in a THF–water mixture (19.6 wt% THF) frozen in the above temperature range, all the reflections belong either to the THF hydrate or to the polymorph IV of ammonium

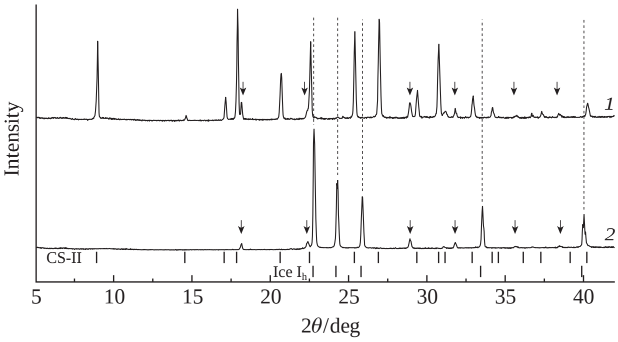


Figure 1 Powder diffraction patterns (–100 °C) of ammonium nitrate solutions in (*1*) the THF–water system (19.6 wt% THF) and (*2*) water. The reflections of the CS-II THF hydrate and ice I$_h$ are shown as ticks at the bottom. The strongest reflections of ammonium nitrate phase IV are pointed by arrows.

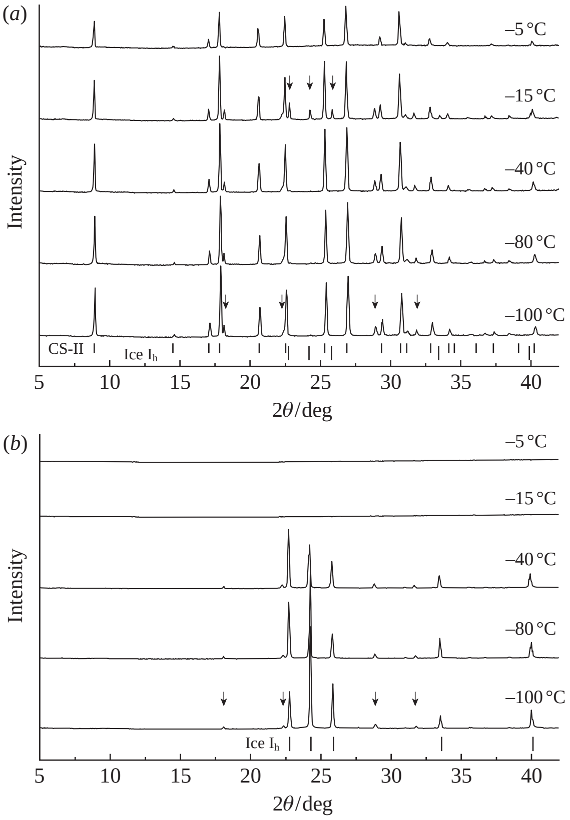


Figure 2 Powder diffraction patterns of ammonium nitrate solutions in (*a*) the THF–water system (19.6 wt% THF) and (*b*) water at different temperatures. The the reflections of the CS-II THF hydrate and ice I_h are shown as ticks at the bottom. The strongest reflections of ammonium nitrate phase IV are pointed by red arrows. The reflections of ice I_h are pointed by blue arrows.

nitrate (see Figure 1). Thus, the formation of the THF hydrate under the standard conditions of laboratory freeze driers is selective and complete also in the presence of ammonium nitrate. When the sample is heated, the first reflections of ice I_h appear at –15 °C. Simultaneously, the intensities of reflections corresponding to the THF hydrate start to decrease. On further heating of the sample, the diffraction pattern measured at –5 °C has only the reflections of the THF hydrate, but not of ammonium nitrate. The background increases giving evidence that a liquid phase is formed [Figure 2(*a*)]. Meantime, the diffraction patterns of the aqueous ammonium nitrate solutions obtained at the same temperatures do not contain any reflections corresponding to a crystalline phase [Figure 2(*b*)]. This is related to the melting of these samples (the temperature of the eutectic melting in the water–ammonium nitrate system is –16.7 °C[8,9]).

To determine the critical temperature of the primary drying stage of freeze-drying, comparative thermal analysis (TA) experiments (details are given in Online Supplementary Materials) have been carried out with the samples of 10 wt% ammonium nitrate solutions in pure water and in the THF–water solvent (19.6 wt% THF). The cells were described elsewhere;[10] the signals were measured using a TERCON precision converter of signals of resistance thermometers and thermocouples with a TERCON-K switch of input signals (TERMEX). The TA curves measured on heating the frozen ammonium nitrate aqueous solution show two thermal effects that correspond to eutectic melting at –16.8 °C and to a liquidus point (Figure S1).[7,8] In contrast, the TA curves measured on heating the frozen solutions of ammonium nitrate in the THF–water mixture show three thermal effects in the same temperature range (Figure S1, Table S2).

The results of X-ray diffraction and TA experiments cannot be explained assuming that the THF hydrate–ammonium nitrate polythermal section of the state diagram of the THF–water–ammonium nitrate ternary system is quasi-binary (Figure S2). Recently, it was shown that the addition of the third component changes the melting behavior of the THF hydrate (THF–water binary system: congruent melting of THF hydrate; ternary system: incongruent melting of THF hydrate) [Figure 3(*a*)].[6] Thus, the first thermal effect (–17.5 °C) corresponds to a four-phase peritectic reaction $H_{(solid)}$ + ammonium $nitrate_{(solid)}$ = ice $I_{h(solid)}$ + *l* (where H is the THF hydrate, and *l* is liquid). The second effect (–13.5 °C) corresponds to the secondary melting[11] of the THF hydrate–ice I_h

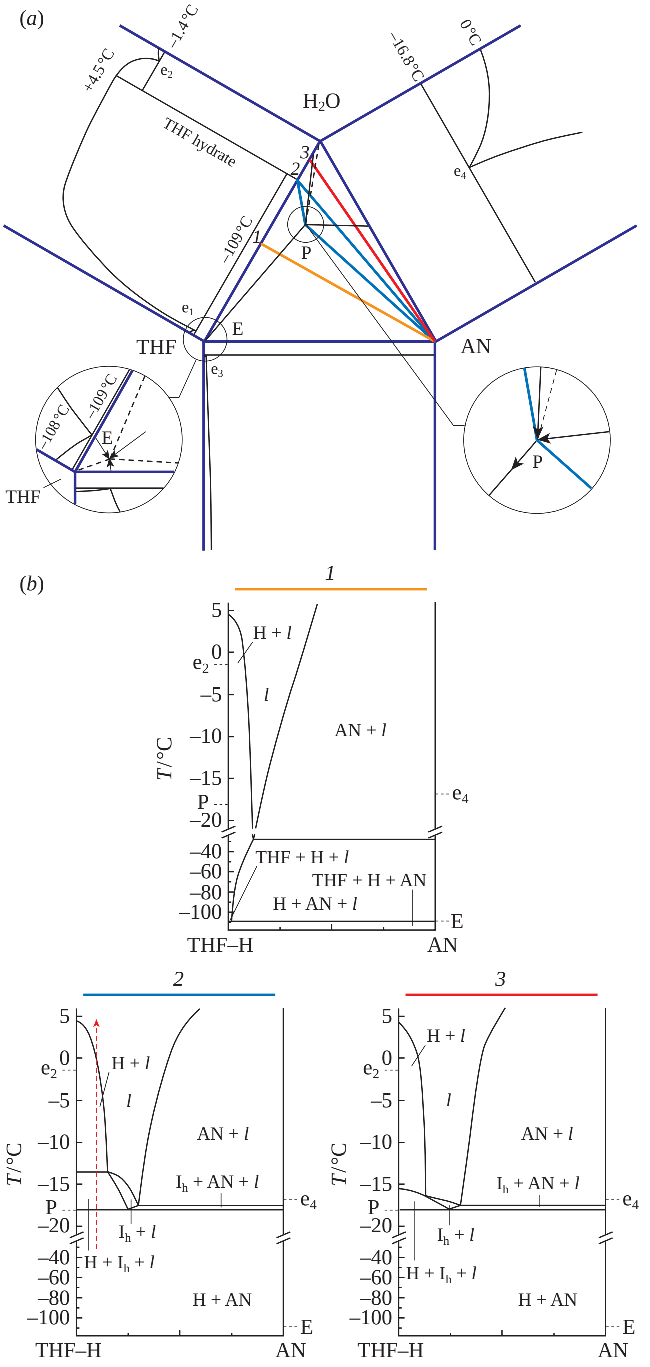


Figure 3 (*a*) Projection of the temperature-composition state diagram for the THF–water–ammonium nitrate (AN) ternary system (modeled based on published data[5,7,8,12]) on the composition triangle. Arrows in callouts designate the lowering of the temperatures of binary eutectics near the ternary peritectic and the ternary eutectic. Color lines *1*–*3* are the projections of polythermic sections. (*b*) Polythermic sections of the state diagram of the THF–water–ammonium nitrate ternary system: THF–H subsystem–ammonium nitrate (line *1*); H–ammonium nitrate (line *2*); H–water subsystem–ammonium nitrate (line *3*). Dashed line illustrates thermal effects observed in TA experiments.

in the ternary system: $H_{(solid)}$ + ice $I_{h(solid)}$ = l. The third thermal effect (–1.2 °C) corresponds to the melting of the THF hydrate in the ternary system (in the THF–water system, the melting point of the THF hydrate is +4.5 °C): $H_{(solid)} = l$ [Figure 3(*b*)]. The limiting stage of freeze-drying is now the removal of the THF hydrate by sublimation at temperatures below the temperature of the four-phase peritectic reaction (–17.5 °C).

The rate of drying (the primary drying time) was measured with a laboratory-scale freeze dryer (one processing shelf, 250 × 350 mm, with a temperature range of –30 to +80 °C) (NIIC SB RAS, Russia).[6] Convection-enhanced Pirani gauges (275 Mini-Convectron®, Granville-Phillips®) were used to monitor chamber and condenser pressures. The shelf was equilibrated at –20 °C before vials (Sci/Spec, B69308; 10 vials in a series; 1.000 ml aliquots) with frozen ammonium nitrate solutions (Table S1) were loaded. The chamber pressure (P_{start} ~ 50–53 mTorr) was determined at regular intervals (~30 min) until the pressure dropped to $P_{end} < 14$ mTorr (empty drying chamber at a condenser pressure of 8 mTorr). After that, the shelf temperature was increased to 30 °C and held for 2 h. The pressure in the freeze dryer was subsequently increased to $P = 1$ bar by filling it with dry nitrogen. The most important result of this work is that the duration of the first stage of the freeze-drying is twice less if mixed THF–water solutions are used, as compared to the freeze-drying of the ammonium nitrate solutions of the same concentration in pure water (10 vials in series: less than 5 h *vs*. > 10 h, respectively). Keeping in mind the estimated value of the sublimation enthalpy of the THF hydrate,[6] we attribute the shortening of the primary drying stage to a smaller required heat transfer to the samples for a given shelf temperature.

The particle size in ammonium nitrate samples (polymorph IV) obtained by the freeze-drying of aqueous solutions (W_{TFF}, W_{SFD}, W_{50}, W_{20}, see Online Supplementary Materials for details) decreased with raising the cooling rate and lowering the solute concentration (Figure S3).[13] The ammonium nitrate samples (W_{TFF}, W_{SFD}, W_{10}, H_{10}) are light fluffy powders with a bulk density (estimated immediately after removing from the freeze dryer by weighting in a calibrated cylinder) of ~0.1 or 0.25 g cm^{-3} for W_{TFF} and W_{SFD}, respectively. The bulk density values of ammonium nitrate samples obtained by the freeze-drying of solutions in water (W_{10}) and THF–water (H_{10}) throughout the volume of the cylinder of the product dried directly in the vials were ~0.1 g cm^{-3}. The samples of T_{10} and W_{10} after drying look like a dried porous cake (small pores were formed on removal of the THF hydrate by sublimation) with the size of the individual particles forming this cake samller than 200 nm (Figure 4).

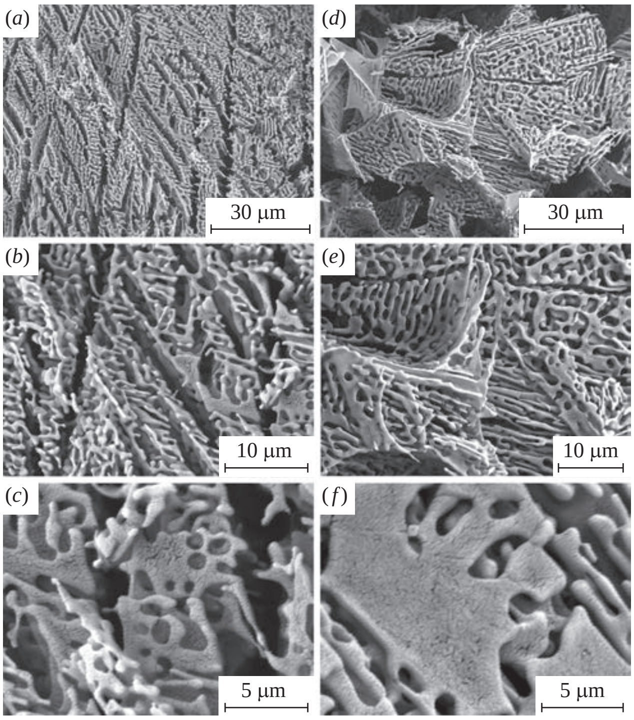


Figure 4 SEM images of ultrafine ammonium nitrate samples obtained by the freeze-drying of its (*a*)–(*c*) solution in THF–water system (H_{10}) and (*d*)–(*f*) aqueous solution (W_{10}).

Thus, using a case study of the water–THF–ammonium nitrate ternary system, we found that a mixed clathrate-forming solvent can be successfully applied in the freeze-drying technique in order to obtain ultrafine powders of inorganic salts with low temperatures of eutectic melting in the salt–water systems. The method has the following advantages: (i) the primary drying time can be significantly reduced, and this is important for technological applications; (ii) it is not necessary to use high cooling rates in order to achieve a small particle size.

In conclusion, the use of a mixed clathrate-forming solvent is beneficial for the significant shortening of the primary drying stage, as compared with pure aqueous solutions, and is of major importance for practical purposes. Potential applications include the production of [2.2]paracyclophane derivatives[14] as ultrafine powders for asymmetric catalysis, ion-selective electrodes, and molecular separation by binding suitably-sized guest molecules.

This study was supported by the Russian Foundation for Basic Research (project no. 17-03-00784-A). We are grateful to Professors E. V. Boldyreva and V. V. Boldyrev for initiating and ongoing moral support of this work and assistance in preparing this manuscript and to Professor S. V. Larionov for fruitful discussions. The NIIC team thanks Federal Agency for Scientific Organizations for funding.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2018.03.035.

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Received: 2nd October 2017; Com. 17/5363