CRYSTALLIZATION OF 1,1-DIAMINO-2,2-DINITRO-ETHYLENE (FOX-7)

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1 Introduction

The crystallization is a well-established method to obtain particulate products. The common ground of all crystallization methods is the need of a supersaturated phase which is received e.g. by cooling down a solution or evaporating the solvent. To accomplish a controlled crystallization, the solubility curve of the system is necessary. Nucleation and growth of the crystal lead to a reduction of the supersaturation.

While designing explosives it is important to get the desired particle size during the crystallization otherwise the product has to be ground afterwards. This is an energy extensive operation which can only be carried out under considerable safety precautions.

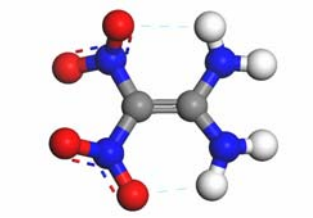
Parameters influencing the particle size and shape are for example the solvent, the cooling rate, additives, antisolvents and the stirrer speed. In this work, some of these parameters are investigated with respect to FOX-7 as particulate product.

This paper is a result of the cooperative project between FOI (Sweden) and Fraunhofer ICT (Germany). The main focus of FOI was the investigation of the particle shape and surface using different solvents and analyzing the thermal properties of the crystals. The main focus of ICT while crystallizing FOX-7 from different solvents was put on the particle size and rate of yield. The goal is also to develop an economic crystallization method to produce crystals with desired properties. Therefore, reproducibility of the experiments was also tested.

2 Materials

2.1 1,1-Diamino-2,2-Dinitroethylene

1,1-Diamino-2,2-Dinitroethylene (FOX-7) is a new explosive with high performance data and low sensitivity. In Figure 1 the molecular structure is shown and a comparison between FOX-7 and RDX is drawn concerning density, sensitivity and explosion heat.



	FOX-7	RDX [1]
Density [g/cm^3]	1,88*	1,82
Friction sensitivity [N]	216*°	120
Impact sensitivity [Nm]	15*°	7,4
Explosion heat [J/g]	4493*	5757

*measured at ICT, ° at 20°C, 30% relative humidity

Figure 1: molecular structure of FOX-7 and a comparison to RDX,

All experiments at FOI and ICT were carried out with FOX-7 from the same batch (Eurenco Bofors, Sweden). FOI used the wet raw material for crystallization. At ICT, the FOX-7 was dried before recrystallizing it to have a defined system.

2.2 Solvents

To influence the properties of the FOX-7 crystals, appropriate solvents are required. At FOI, experiments with a mixture of 1-methyl-2-pyrrolidone (NMP) and water, acetonitrile, γ-butyrolactone (GBL) and a mixture of dimethylformamide (DMF) and water were carried out.

At ICT, NMP, different NMP/water mixtures and DMF were used for crystallization. Water was used as antisolvent in some experiments.

3 Experimental setup

3.1 Solubility curves

To get the solubility curves, the different solvents have been saturated with FOX-7 at 20°C, 40°C, 60°C and 80°C. Samples of the saturated solutions have been taken and the solvent has been evaporated. The mass loss during the drying is equal to the mass of the evaporated solvent (m_{sol}), the evaporation residue is equal to the mass

of the FOX-7 (m_{FOX}) dissolved before. The mass concentrations are plotted against the temperatures (Figure 2).

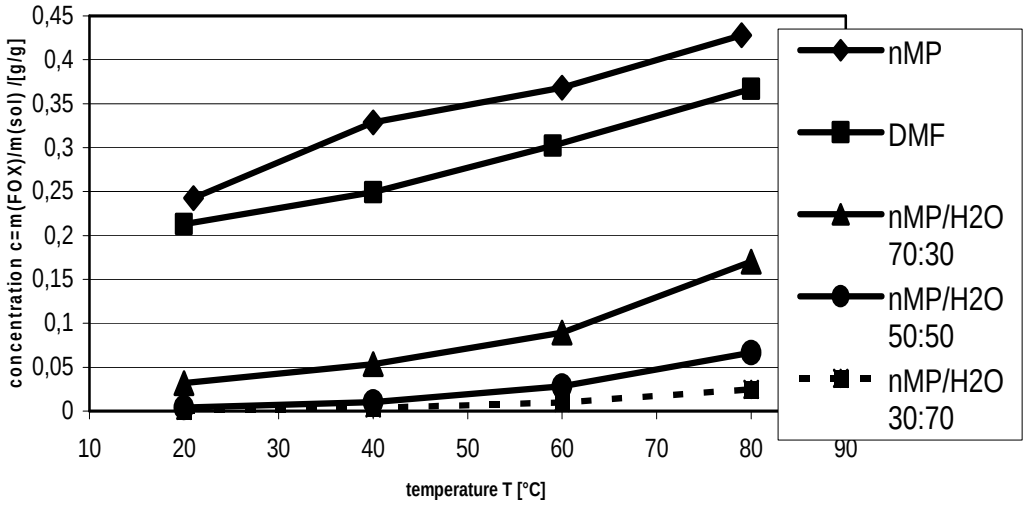


Figure 2: Solubility curves of FOX-7 [ICT]

*3.2 **Crystallization***

Cooling crystallization was done at FOI and ICT.

At FOI, FOX-7 was dissolved in the solvents mentioned above by heating up the mixture. Then, the system was cooled down to room temperature with cooling rates of approx. 12 K/h at the beginning and 1.2 K/h at the end of the process. The slurries were agitated at 150 rpm during the process. The slurry was then filtrated and the crystals were washed with water (experiment with NMP/water as solvent) or with a small volume of the same type of solvent as was used for the recrystallization.

At ICT, a jacked 300 ml reactor with a defined temperature run was used. The stirrer speed was 200 min^{-1}. The concentration at the saturation point was determined at 60°C by means of the solubility curve of the corresponding system. To be sure that all crystals are dissolved before recrystallization, the temperature was first increased to 70°C for 15 minutes and then decreased to 60°C. Now, the cooling process took place with a cooling rate of 10 K/h for four hours. At 20°C, the crystallization process was accomplished. Cooling crystallization with and without antisolvent was done. The additive was dosed with a HPLC-pump. On one hand, it served to reduce the solubility of FOX-7 in the solvent; on the other hand it was useful to initialize the nucleation. The received crystals were filtered. To get rid of remaining solvent, the product was washed with acetone.

3.3 Characterization

Because of the different but complementary main focuses FOI and ICT worked on, the characterization of the crystals was different.

FOI was interested in size, shape and surface of the crystals as well as in the thermal properties of the recrystallized material. The thermal properties of the recrystallized FOX-7 were determined using a Mettler DSC 30 working under a nitrogen atmosphere (50 ml/min). The samples were sealed in 40µl aluminium pans with pierced lids. The sample weight was approximately 2 mg. Calibration was made with indium (Tm = 156.6°C). The TG/DTA used by FOI is a Mettler TGA 850. All tests were performed in a nitrogen atmosphere. The samples were put into alumina cups and the flow of nitrogen was approximately 25 ml/minute. The TG/DTA was calibrated by melting indium and aluminium standards. The DSC analyses has been performed between 30°C to 400°C with a heating rate of 10°C/min. Cyclic DSC and TG analysis has also been performed between 30°C and 185°C at a rate of 5°C/min and back to 30°C at a rate of -5°C/min. The cycle has been repeated four times in the DSC and three times in the TG. The particle size, shape and surfaces have been analysed using a JEOL 6400 scanning electron microscope (SEM).

At the ICT analyzed the product by light microscopy and by particle size measurements (laser diffraction, Malvern Mastersizer S). The mass of the washed and dried crystals was determined and out of it the rate of yield.

4 Results and discussion

4.1 FOI

A tabular overview of the accomplished experiments is given in Table 1:

#	solvent	T_{start}=T_{end}	T_{max}
1	NMP/Water (50/50 vol%)	RT	95°C
2	acetonitrile	RT	70°C
3	DMF/water (75/25 vol%)	RT	95°C
4	GBL	RT	95°C
5	Filtrate of GBL containing some FOX-7 crystals obtained from crystallization, left for 2 months in an open beaker at RT		

Table 1: Overview: Experiments carried out at FOI

Crystals recrystallized in NMP/water (#1), Figure 3, and obtained from Eurenco Bofors were in a range of 250 µm to 400 µm. The recrystallization of FOX-7 in

acetonitrile (#2) produced relatively small crystals, Figure 3. Crystals of < ~50 µm were obtained. The mixture of DMF and water (#3), Figure 4, produced crystals of approx. 55µm to 110µm. In GBL (#4) a broader range of crystal sizes were obtained, measuring approx. 50µm to 185 µm. After growing in the GBL filtrate (#5) crystals up to a size of ~500µm were obtained, Figure 4. A compilation of the size of the crystals is seen in table 1.

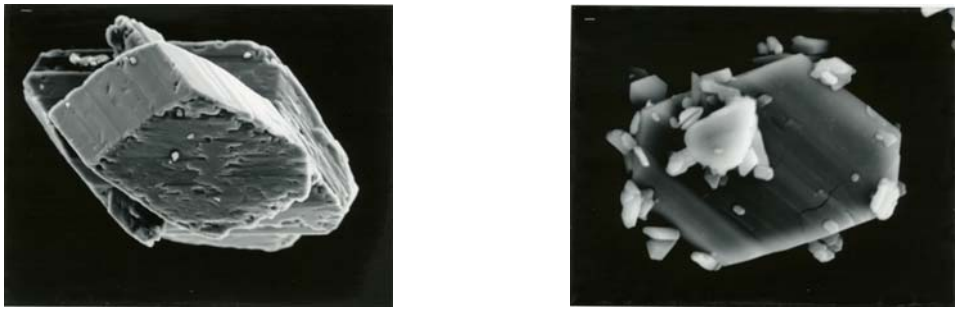


Figure 3: Crystals received from (#1) NMP/water (left) and from (#2) acetonitrile (right)

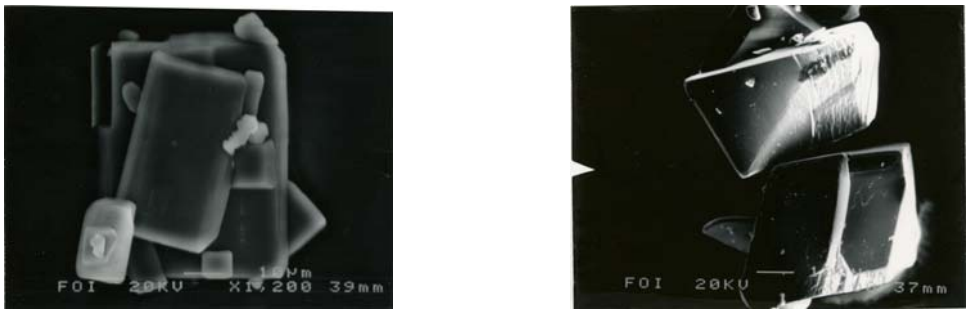


Figure 4: Crystals from (#3) DMF/water (left) and from (#5) GBL (right)

A comparison of the shape and surface of the larger crystals was made. Rhombic shapes in two dimensions are observed with crystals obtained from acetonitrile, the smaller fraction of GBL and NMP/water. The larger fraction obtained from GBL has a rhombic shape built in three dimensions. The crystals from DMF/water have a flat rectangular shape. The surfaces of the crystals obtained from GBL and DMF/water appears to be smoother than the surfaces observed at the crystals obtained from NMP/water. All surfaces are shown in Figure 5.

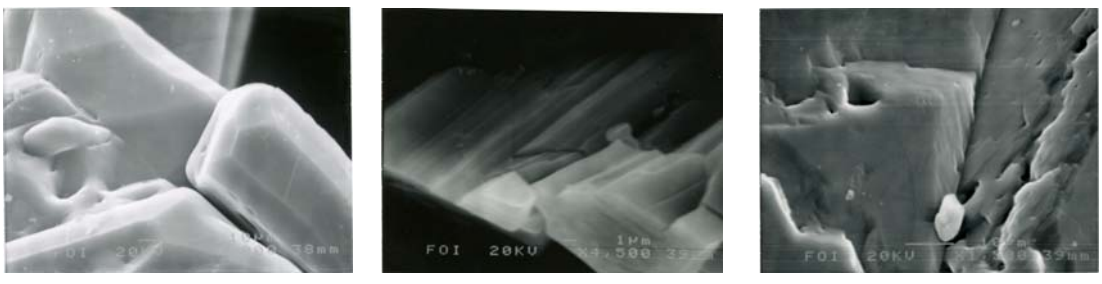


Figure 5: Surfaces of crystals obtained from (#5) GBL (left), (#3) DMF/water (middle), (#1) NMP/water (right)

The DSC measurements between 30°C and 400°C of the recrystallized FOX-7 all show at least one endothermic and two exothermal peaks. Recrystallized FOX-7 from NMP/water, DMF/water and the crystals grown in GBL produce a divided endothermic peak (illustrated in Figure 6) at approx. 160°C. The smaller crystals from GBL produce an endothermic peak around 160°C, however not divided. The crystals obtained in acetonitrile gives an indication of an endothermic peak around 160°C.

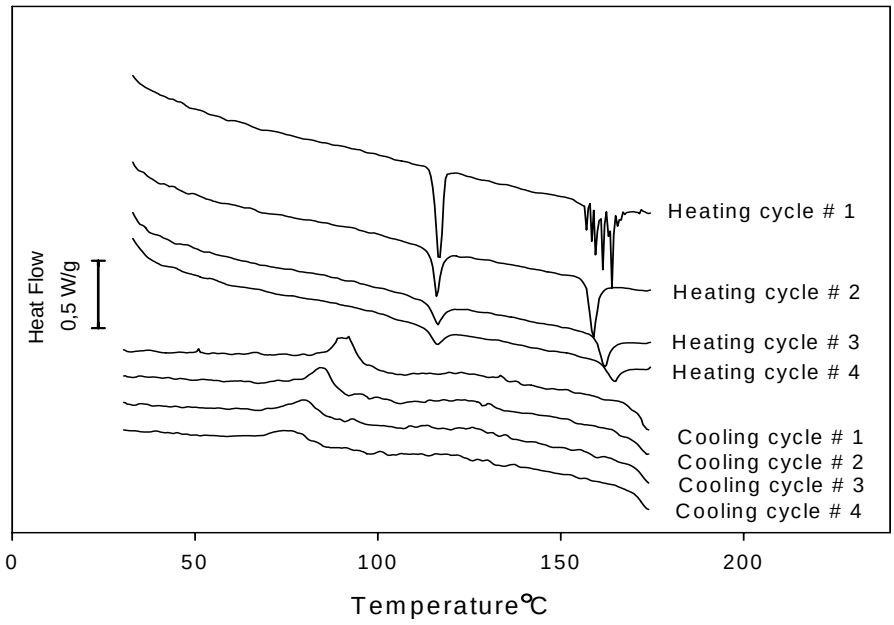


Figure 6: DSC thermogram of cyclic repeated heating of FOX-7 recrystallized in NMP/water

Cyclic repeated DSC analysis of crystals from NMP/water, DMF/water and the larger fraction from GBL show endothermic peaks during heating and one exothermal peak during temperature decrease. Figure 6 illustrates the profile of the thermograms from the cyclic repeated DSC analysis. The endothermic peaks appear repeatedly in each cycle. However, there are decreased peak areas for each cycle. The peak at ~117°C appears repeatedly at approximately the same temperature. The shape of the peak at ~160°C shifts from a divided peak in the first cycle to a single peak in the following cycles. However, compared to NMP/water and the larger GBL fraction the crystals from DMF/water show smaller peak areas and the last heating cycle does not show any peaks at all. The cyclic repeated DSC analysis of the smaller crystals recrystallized from GBL also show endothermic peaks at ~115°C and ~163°C. However, the peak at ~163°C is not divided but has a broad shape. Both peaks are repeatedly obtained with a decreased area in each new heating cycle. The repeated analysis of the crystals obtained from acetonitrile produces an endothermic peak at

~117°C in each heating cycle. A hint of an endothermic peak at ~170°C is also obtained during the first heating cycle but not in the following.

The repeated TG analyses of crystals from NMP/water and the larger fraction from GBL show weight losses in the first heating cycle, Table 2. The weight loss is registered at the corresponding temperature of the second endothermic peak in the DSC analysis. The NMP/water crystals have a weight loss of approximately 2 weight-% and approximately 1 weight-% is lost from the larger crystals obtained from GBL. A small weight loss of 0,1 weight-% is also obtained with the crystals from DMF/water. The cyclic repeated TG analysis of the small crystals obtained from GBL and acetonitrile does not show any significant weight loss at the corresponding temperature of the second endothermic peak obtained in the DSC analysis.

The crystals recrystallized from a mixture of solvent and water and the larger crystals from GBL produce a divided endothermic peak in DSC analysis whereas the smaller crystals from acetonitrile and GBL do not. The shape of the endothermic peak then shifts to a single peak in the following heating cycles. A possible cause of this phenomenon is solvent or water inclusion in the crystals. A fact that supports this is the weight loss registered during the first heating cycle of the repeated TG analyses of these crystals (Table 2). It appears at the temperature for the appearance of the divided peak in the DSC measurements.

Table 2: Weight loss of recrystallized FOX-7 in cyclic repeated thermogravimetric analysis

FOX-7 recrystallization solvent	**Weight loss during repeated heating cycles in TG analysis**			**Approximate crystal size (µm)**
	1st	**2nd**	**3rd**	
NMP/water	2 wt-%	-	-	250 - 400
GBL (larger crystals)	1 wt-%	-	-	<500
DMF/water	0,1 wt-%	-	-	55 - 110
GBL (smaller crystals)	-	-	-	50 - 185
acetonitrile	-	-	-	<50

The possibility of release of solvent or water from the crystal structure is produced due to a phase change. The profile of the divided peak reflects the release of solvent or water at the same time as the endothermic phase change is registered. The profile of the endothermic peak has changed to a single peak in the following heating cycles, hence only the phase change is then registered. The temperature at which

solvent or water loss is possible is dependent of the temperature at which the phase change occurs. The theory of water inclusion is supported by the fact that the water release would be complete during the first heating cycle. The phase change appears at a temperature approximately 60° higher than the boiling point of water which facilitates fast evaporation. NMP and GBL have boiling points at 202°C and 205°C respectively. This indicates a slow evaporation at the discussed temperature resulting in residue releases in the following heating cycles. Water inclusion is a possibility for all three types of crystals. Even though the GBL crystals were recrystallized in dehydrated solvent, the larger GBL crystals may have water inclusions as the growing was made in an open beaker in room temperature for a long period of time. The larger crystals in this study were recrystallized in GBL and in a mixture of NMP/water. Also the crystals from DMF/water show the same pattern but produces smaller peak areas than the other two. The weight loss is also smaller for DMF/water crystals than the other as can be seen in Table 2.

*4.2 **ICT***

4.2.1 FOX-7 from NMP

It was not possible to produce crystals by cooling the solution of FOX-7 and pure NMP with a cooling rate of 10 K/h from 60°C to 20°C.

4.2.2 FOX-7 from NMP/water (70/30 mass%)

By cooling a saturated mixture of NMP/water (70/30 mass%) the in Table 3 listed rates of yield and particle sizes (x_{50}-values) have been determined. Both, the rates of yield and the particle sizes are varying in a quiet broad range. Figure 7 shows the particles received from this test series.

Table 3: FOX-7 from NMP/water (70/30 mass%)

NMP/water (70/30 mass%), no antisolvent m(solvent)=150g, m(FOX-7) = 13 g		
#	Rate of yield (mass%)	x_{50}
7	34,6%	143,8µm
8	53,1%	244,1µm
9	47,7%	213,45µm

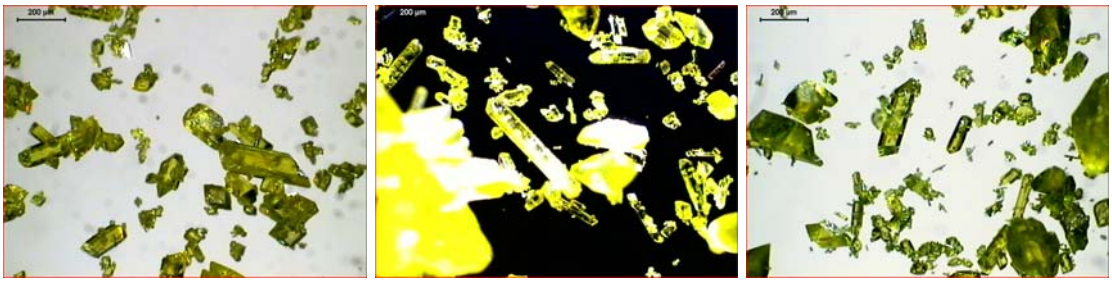


Figure 7: FOX-7 from the experiments #7 (left side), #8 (middle) #9 (right side)

By just cooling down the system, the rate of yield and the particle size are varying. This is caused by impurities which can not totally be avoided during the experiment. Depending on the amount and type of the impurity, nucleation is initialized uncontrolled at different points of the crystallization process.

4.2.3 FOX-7 from NMP/water (70/30 mass%), antisolvent

Here, water was used as antisolvent during the cooling process. The experiment was carried out three times (#10, #11, #12) to test reproducibility. The results are shown in Table 4 and Figure 8. The use of water as antisolvent causes a defined nucleation. This nucleation is hardly influenced by impurities and so a reproducible rate of yield and a particle size in a narrow range are achieved.

Table 4: FOX-7 from NMP/water (70/30 mass%), antisolvent

NMP/water (70/30 mass%), water as antisolvent m(solvent)=150g, m(FOX-7) = 13 g			
#	m(antisolvent)	Rate of yield	x_{50}
10	66,6 g	89,2%	305,9µm
11	68,7 g	83,1%	286,6µm
12	66,8 g	89,2%	273,56µm

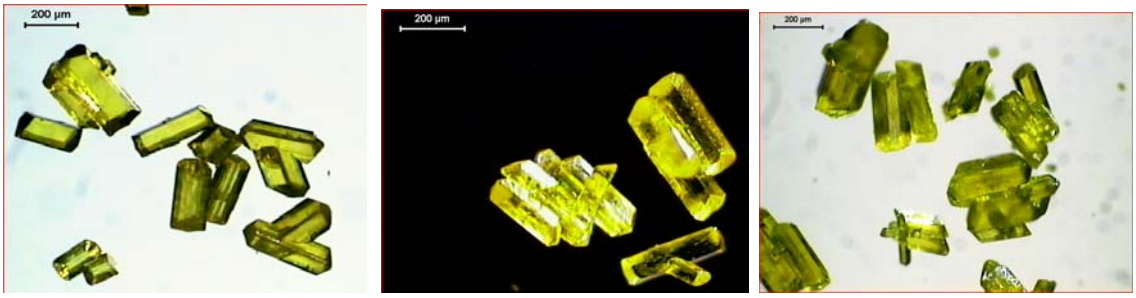


Figure 8: FOX-7 from the experiments #10 (left side), #11 (middle), #12 (right side)

4.2.4 FOX-7 from DMF

Beside NMP, DMF was also used as solvent. First, pure cooling crystallization was carried out. The temperature run was the same as in the other experiments. The rates of yield and particle sizes are shown in Table 5 and Figure 9. The experiments #14 and #15 show almost the same results in particle size and rate of yield. Experiment #13 suggests that unintentional nucleation caused by impurities took place during cooling. This led to a higher rate of yield and larger particles.

Table 5: FOX-7 from DMF, no antisolvent

DMF, no Antisolvent m(DMF) = 150 g, m(FOX-7) = 45 g		
#	Rate of yield	x_{50}
13	16,89%	130,52µm
14	4,44%	85,03µm
15	4,67%	98,67µm

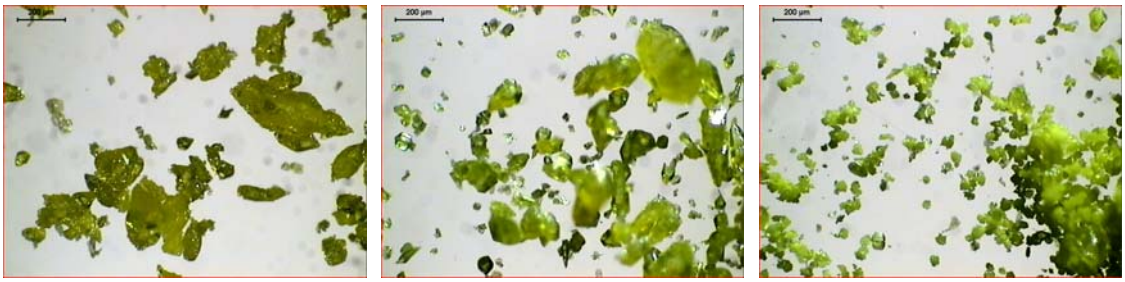


Figure 9: FOX-7 from the experiments #13 (left side), #14 (middle), #15 (right side)

5 Summary

The work has been accomplished in cooperation between FOI and ICT.

FOI investigated the shapes and surfaces of the FOX-7 crystals growing in different solvents. The larger crystals obtained from GBL, NMP/water and DMF/water have the same shape. Surface analysis of the larger crystals indicates a smoother surface of the crystals from GBL and DMF/water than from NMP/water. DSC and TG analyses of the larger crystals show divided endothermic peaks and corresponding weight losses at approximately the same temperature. The smaller crystals do not show any divided endothermic peaks or significant weight losses in the same temperature range. This may indicate a water inclusion during crystal growing that is independent of solvent type.

At the ICT, the goal of the work was to investigate the behaviour of FOX-7 during the crystallization process. The rates of yield and the particle sizes were of big interest. First, the solubility curves of FOX-7 and the different solvents have been worked out. Then, crystallization experiments have been carried out with a constant cooling rate. The characterization of the product included the rate of yield and the particle size. To ensure reproducibility, all experiments have been done three times.

6 Literature

[1] J. Köhler, R. Meyer: Explosivstoffe, 7. Auflage, VCH Verlagsgesellschaft mbH