Crystallization of Ammonium Dinitramide – Part 1: Solvent Screening

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Introduction

Ammonium dinitramide (ADN) from synthesis is of an irregular, flat morphology and is thus not suitable for a further processing. Up to now, the formation of spherical ADN particles is done by emulsion crystallization processes. A solvent crystallization process is aimed for the generation of compact ADN crystals.

Aim

The aim of this work is to find a solvent that is applicable for the recrystallization of ADN. It is also important that no decomposition of ADN is occurring.

Materials

Ammonium dinitramide was purchased from NEXPLO Bofors.
The screening of the solvents was carried out by using a Quest 210 (Argonaut Technologies, Figure 1). It was designed to perform solution or solid phase organic chemistry reactions. Two banks of ten reaction vessels allow up to 20 reactions in parallel. Each bank of reaction vessels has an integrated heating/cooling block. The reaction vessels are made of clear Teflon. A Teflon µFrit with 7µm porosity is used in the bottom of each reaction vessel to allow solutions to drain. The mixing is done by Teflon-encapsulated magnets placed in the reaction vessels. They are attracted to a magnet bar and are following its up-and-down movements, thereby mixing the contents.
The solvents that have been used for the screening are listed in Table 1.

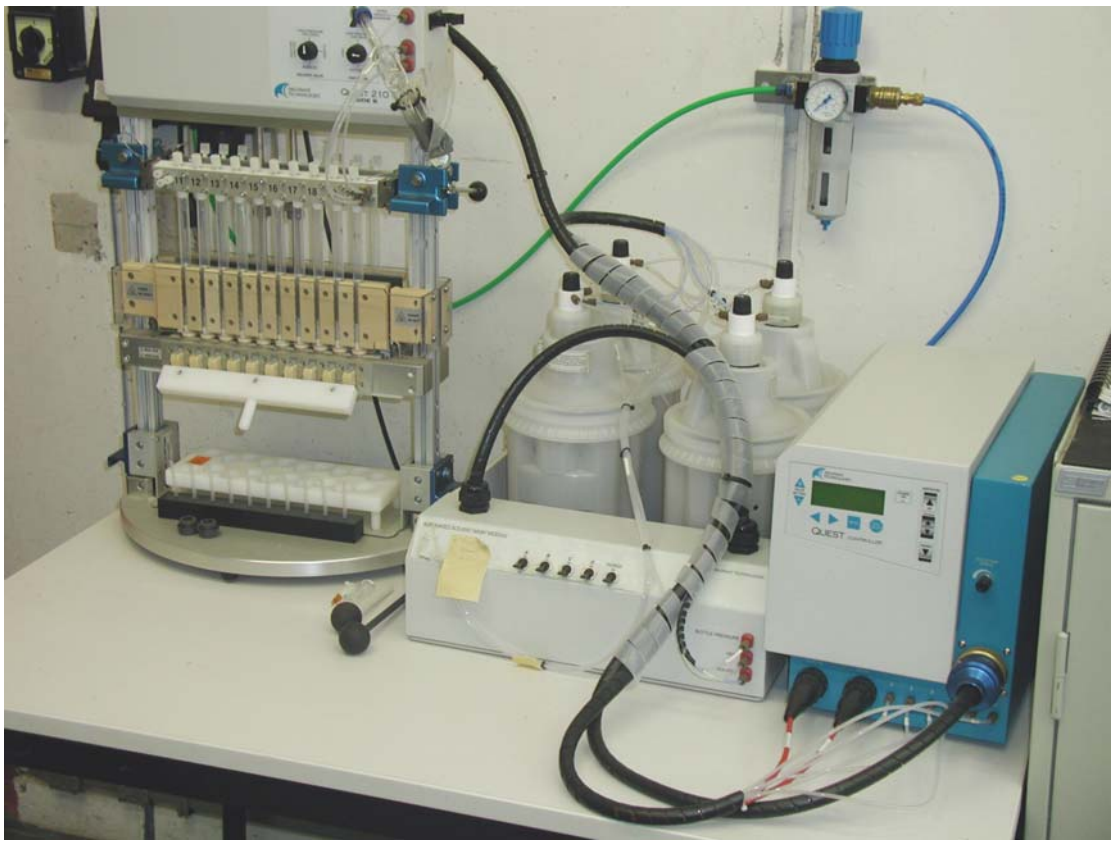

Figure 1: Quest 210

Table 1: Solvents used for screening

#	solvent		#	solvent
1	propylene carbonate		21	acetone
2	1-propanol		22	methanol
3	1-pentanol		23	ethanol
4	1-octanol		24	ethyl methyl ketone
5	benzyl alcohol		25	tetrahydrofuran
6	2-methyl-2-pentanol		26	trichlormethane
7	ethylene glycol		27	1,2-dichlorbenzene
8	2-propanol		28	benzonitrile
9	methyl acetate		29	diethyl carbonat
10	ethyl acetate		30	propionaldehyde
11	n-butyl acetate		31	1,2-dichlorethane
12	gamma-butyrolactone		32	tert. butanol
13	diethylene glycol monoethyl ether		33	chlorbenzene
14	5-nonanon		34	triethylene glycol
15	cyclohexanone		35	acetic anhydride
16	toluene		36	n-methyl-2-pyrrolidinone
17	triethylamine		37	diethylene glycol
18	dimethyl sulfoxide		38	-
19	n,n-dimethylformamide		39	-
20	acetonitrile		40	-

Methods

Each reaction vessel was filled with 10 ml of a solvent and 2 g of ADN. The samples were heated up to 40°C. After a holding time of 20 min, the solutions have been drained through the Teflon frits and have been collected in small vessels. The solvents have been evaporated in a vacuum drying chamber and the concentration of ADN in each solvent at 40°C was determined.

To check the quality of the recrystallized ADN, the colours of the recrystallized ADN were checked and specified by numbers 0 (=bright white) to 7 (=dark brown). A dark colour is an indication for the decomposition of ADN. DSC measurements of the samples have also been carried out to see if the thermal behaviour has changed compared to the raw material

Solubility curves were determined for solvents from which ADN was recrystallized without a loss of quality. Solutions saturated at different temperatures have been prepared. The concentration of ADN has been determined as specified above.

Results

The ADN concentrations in the different solvents at 40°C (t=20 min) are reported in Diagram 1 and Diagram 2. Figure 2 shows five samples of recrystallized ADN. In Table 2, the results of the solvent screening are summarized (colour and shape of the crystals). DSC measurements of the ADN raw material, ADN from tetrahydrofuran and ADN from 1-propanol are shown in Figure 3, Figure 4 and Figure 5. Solubility curves of ADN/tetrahydrofuran and ADN/1-propanol are displayed in Diagram 3.

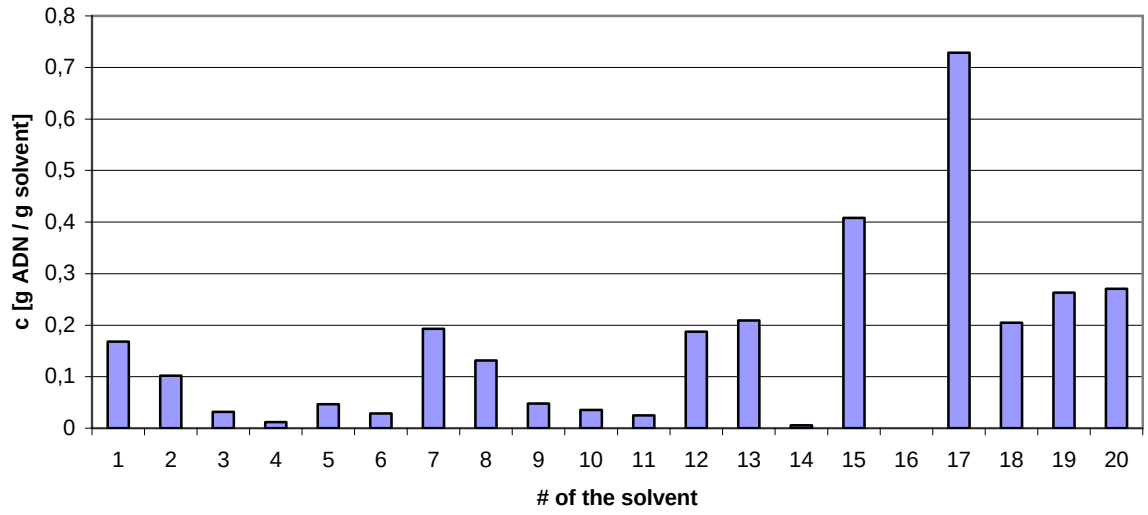

Diagram 1: concentration of ADN @ 40°C for solvents 1-20

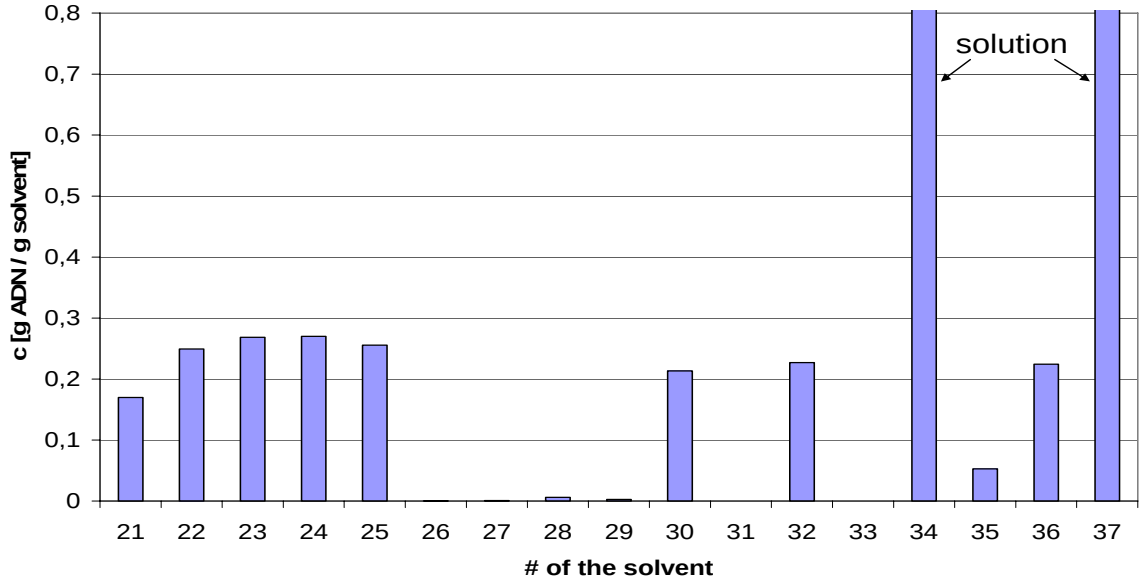

Diagram 2: concentration of ADN @ 40°C for solvents 21-37

Figure 2: ADN recrystallized from solvents 1 - 5

Table 2: ADN from different solvents, characterization

#	colour	notes		#	colour	notes
1	2	needle-shaped		21	1-2	
2	2	needle-shaped		22	0	white
3	2	needle-shaped		23	0	white
4	1	needle-shaped		24	3	-
5	3	short, compact needles		25	1	-
6	2	needle-shaped		26	-	no crystals
7	2	needle-shaped		27	-	no crystals
8	2	-		28	4	very little
9	1	-		29	3-4	very little
10	2	-		30	5	-
11	2	short needles		31	-	no ADN
12	2	long needles		32	1-2	a lot of ADN
13	4	needle-shaped		33	-	empty
14	7	solubility very poor		34	-	yellow solution
15	7	solvent did not evaporate		35	3-4	brown
16	-	no residue		36	3	-
17	6	solvent did not evaporate		37	-	clear yellow solution
18	1	-		38	-	-
19	2	-		39	-	-
20	1	-		40	-	-

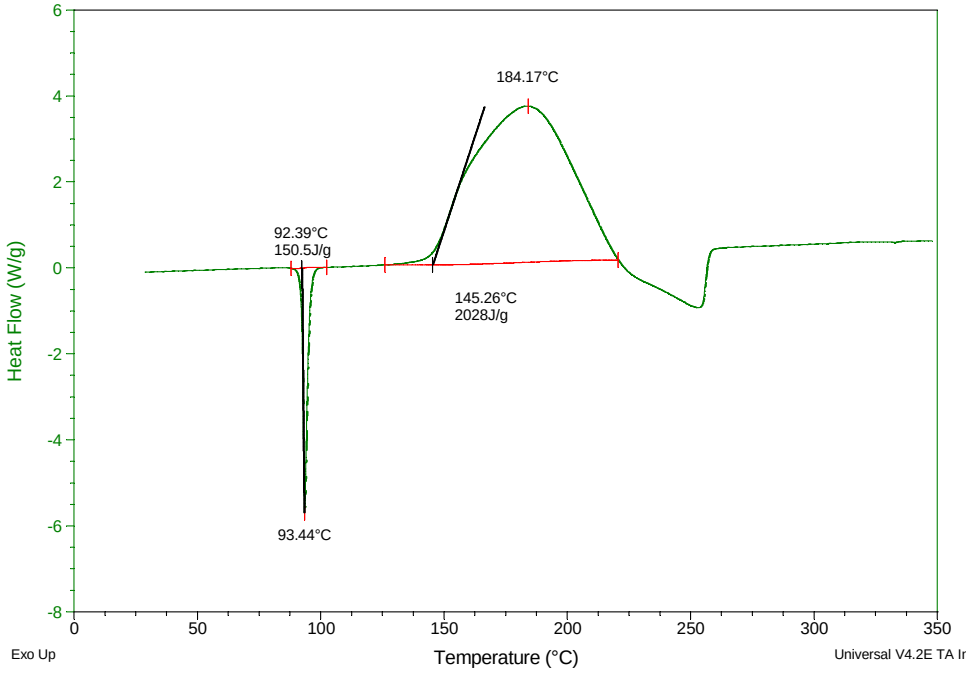

Figure 3: DSC of raw ADN

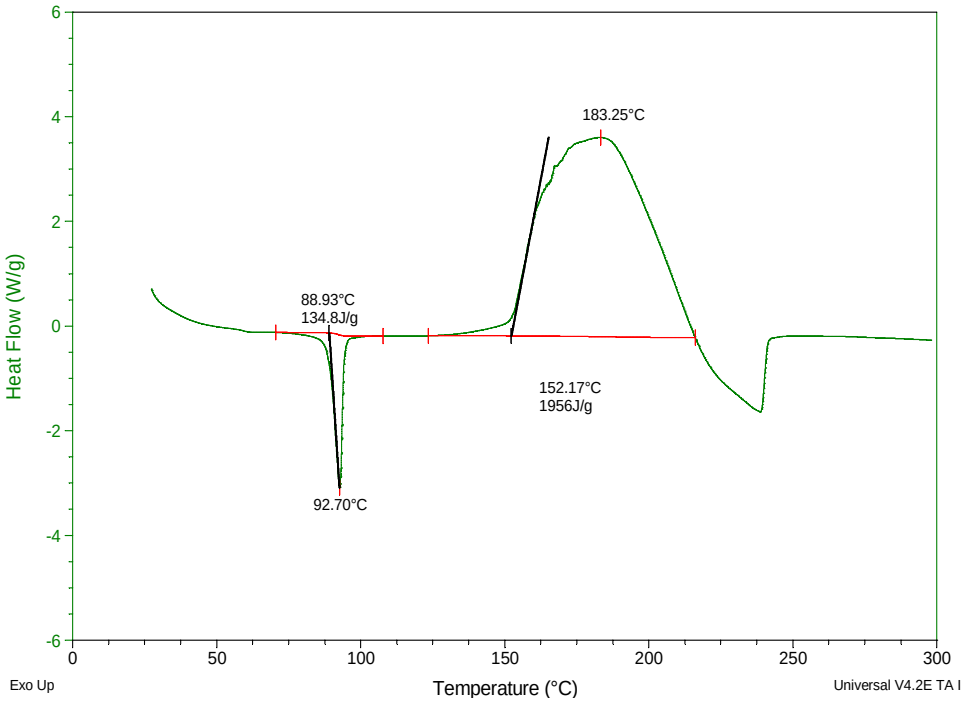

Figure 4: DSC of ADN from tetrahydrofuran

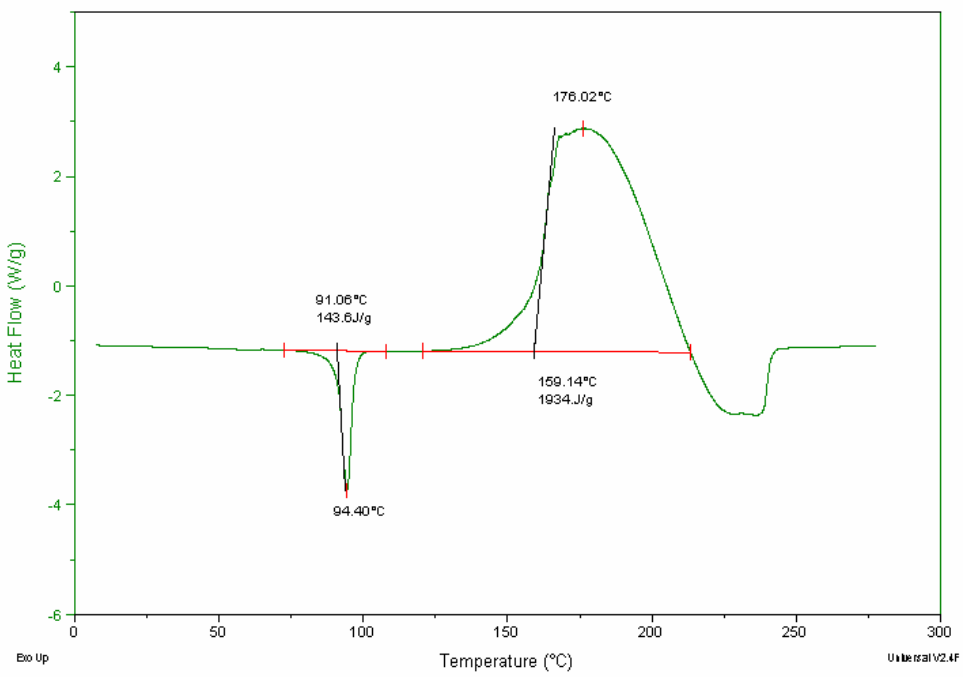

Figure 5: DSC of ADN from 1-propanol

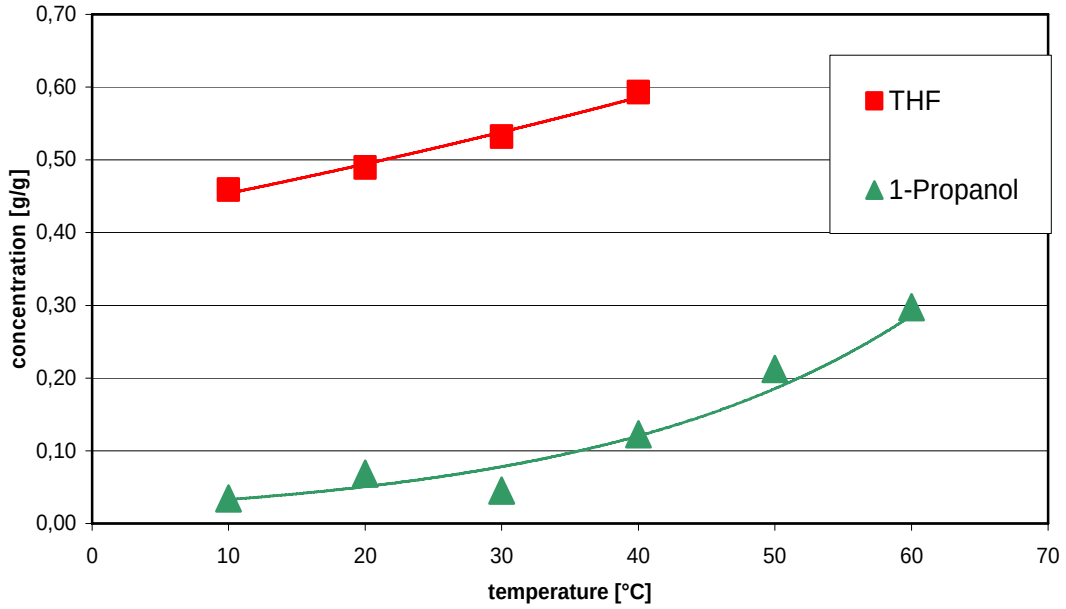

Diagram 3: Solubility curves

Discussion

Both tetrahydrofuran (THF) and 1-propanol show a good solubility for ADN. The temperature dependency of the solubility of THF/ADN is very poor. Therefore, THF can only be used in evaporation crystallization. The main focus will be on the crystallization of ADN from 1-propanol which shows excellent temperature dependant solubility. From the solvent screening, needle-like crystals are obtained by using 1-propanol. This particle shape is not the desired one so by using 1-propanol as a solvent it may be necessary to use morphology-influencing additives.

Outlook

The acquired results are the basis for further crystallization experiments. The aim is to receive crystals of a compact shape. If this is not possible by the choice of the solvent a screening for a suitable additive will be done. The investigation of crystallization parameters (e.g. cooling / evaporation rate, initiation of the nucleation) on the particle size distribution is also important to get a usable product.