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Study of a recrystallization process for triaminoguanidinium azotetrazolate
Badanie procesu rekrystalizacji azotetrazolanu di(triaminoguanidyny)

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Abstract: *The aim of this work was the development of methods designed to change the crystalline form of triaminoguanidinium azotetrazolate (TAGAZ). The solubility of the compound was determined in several solvents and new crystallization methods were proposed and tested. The morphology and structure of the produced crystals was analyzed using optical microscopy.*
Streszczenie: *Celem niniejszej pracy było opracowanie metod zmiany formy krystalicznej azotetrazolanu di(triaminoguanidyny) (TAGAZ). Określono rozpuszczalność substancji w wybranych rozpuszczalnikach i zaproponowano nowe metody rekrystalizacji. Zbadano morfologię oraz strukturę uzyskanych kryształów za pomocą mikroskopii optycznej.*

Keywords: *explosives, TAGAZ, triaminoguanidinium azotetrazolate, crystallization, LOVA*
Słowa kluczowe: *materiały wybuchowe, TAGAZ, azotetrazolan di(triaminoguanidyny), krystalizacja, LOVA*

1. Introduction

An interesting group of chemical compounds which can be applied in novel gun and rocket propellants are high nitrogen explosive materials (HNEM). The presence of many N-N and C-N bonds in their structure results in them having a high standard enthalpy of formation. The large number of nitrogen molecules in HNEM, reaching more than 70%, results in a significant quantity of gaseous combustion products and a decrease in their temperature. The low carbon and hydrogen content prevents formation of solid particles and corrosive compounds. As a result, HNEMs are known as "green" explosives.
Triaminoguanidinium azotetrazolate (TAGAZ) is a HNEM with one of the highest nitrogen contents (82.3%) [1-10]. TAGAZ is characterized by good detonation parameters (calculated), is stable to 195 °C and decomposes without melting. Its synthesis is not expensive and does not generate any difficulties. Due to its many advantages, TAGAZ is proposed as an ingredient in future smokeless gun and rocket propellants.
TAGAZ consists of two flat triaminoguanidinium cations and a flat azotetrazole anion, between which are three-dimensional intermolecular hydrogen bonds [8-10]. The TAGAZ molecule does not contain oxygen and therefore the energetic transformation mechanism is different from typical mechanisms in explosive materials. Where the energy of a molecule is low because of a large number of N-N bonds (a single N-N bond has an energy of 163 kJ/mol), and the energy of gaseous products is high (N_2 molecules with a triple bond have an energy of 946 kJ/mol energy), the difference is realised during burning. The specific structure of TAGAZ has an effect on the creation of a high amount of gas per unit mass and causes a high standard enthalpy of formation, whose value is 1076 kJ/mol [1-9]. The structure of the compound is shown as Fig. 1.

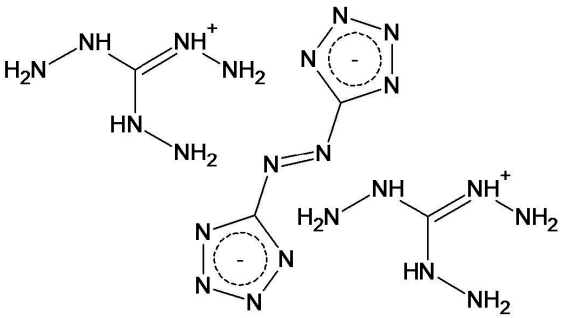


Fig. 1. Structure of TAGAZ molecule

The occurrence of extensive π-electron conjugations and ionic bonds results in TAGAZ having good thermal stability. Its thermal properties were investigated using differential thermal analysis and thermogravimetric analysis (DTA/TGA). It decomposes at 194 °C [12]. TAGAZ has low sensitivity to mechanical stimuli. Determining the sensitivity to friction on the Julius Peters apparatus, the compound underwent initiation at 230 N. Impact sensitivity was determined using 2 kg drop hammer. The value was expressed as drop height at which 50% initiation or explosion occurs (h_{50}) and it was equal to 25 cm [3]. Sensitivity to electrostatic discharge was equal to 0.312 J.

In literature there is no information about any experimentally measured detonation parameters. There is only published data obtained by numerical methods. The calculated velocity of detonation is 9050 m/s and the detonation pressure is 29**.**2 GPa [15]. These parameters, in combination with the sensitivity results, means the material is classified as powerful secondary explosives.

It's compatibility with other materials, low temperature of gaseous products, high linear burning rate and lack of solid in the decomposition products, suggests that propellants based on this material will have better ballistic characteristics than gun and rocket propellants currently in use. For these reasons, TAGAZ could be used in modern low vulnerability ammunition (LOVA).

An important advantage of this material is that it burns without flame [3]. It certainly would be appreciated by ammunition designers, due to the possibility of making gun propellants which burn in the barrel without flash.

In spite of many advantages, TAGAZ has a major flaw – its crystals have long needle-like or rod-like shapes, which makes it impossible to utilise in explosive compositions or propellants, mainly because of low density and the lack of homogeneity in the resulting compositions.

As a typical example of a HNEM, mainly due to its low burning temperature, generation of only gaseous products and low erosiveness, potentially it is a perfect ingredient for contemporary explosive compositions. In civil technology, TAGAZ is proposed as a substitute for sodium azide in gas generator devices [3-6, 11-13]. It could be used in car airbags and in environmentally friendly pyrotechnic compositions.

2. Experimental

2.1. Synthesis of triaminoguanidinium azotetrazolate

Synthesis of triaminoguanidinium azotetrazolate proceeds in two-steps [9-14]. The substrate in TAGAZ synthesis – 5-aminiotetrazol (5-AT) is commercially available. At elevated temperatures (60 °C), in the presence of NaOH and $KMnO_4$, oxidative conjugation results in disodium azotetrazolate pentahydrate (SAZ) being formed. In the second step SAZ and triaminoguanidinium hydrochloride react by the exchange of the sodium cation with the triaminoguanidinium cation taking place. The process was conducted at 80-90 °C. After the reaction was complete, the system was cooled to 5 °C and the solid precipitate filtered off and air dried at 50 °C.

Sample preparation is as follows. To a 500 cm^3 three-necked round-bottom flask 300 cm^3 2M NaOH was poured. This was heated to 60 °C and 10.3 g of 5-aminotetrazole (5-AT) was added. After 15 minutes 12.0 g of powdered

$KMnO_4$ was added incrementally and the solution was stirred for 10 minutes. Excess oxidizer was neutralized with 9 g of Na_2SO_3. The deposited manganese(IV) oxide was removed by filtration. The filtrate solution was kept at a temperature of 0-4 °C for 24 hours. Afterwards, the 21.5 g of sodium azotetrazolate (SAZ), as yellow crystals, was filtered and dried at 50 °C in air. The yield was about 71%.

The next step was the synthesis of TAGAZ. Into a round-bottom flask 5.0 g of SAZ and 60 cm^3 of water was poured. The mixture was heated to 85 °C. When the SAZ was dissolved, 7.0 g of triaminoguanidine hydrochloride was added. The mixture was stirred for 10 minutes and then cooled to 5 °C. The yellow precipitate was filtered off and dried in air. 7.7 g of needle shaped product was obtained (yield equivalent of 83%).

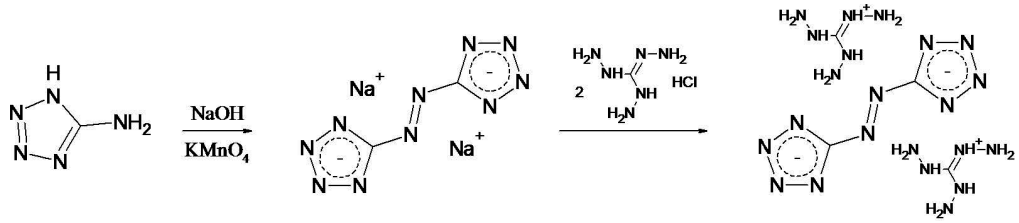


Fig. 2. Scheme of synthesis of triaminoguanidinium azotetrazolate

2.2. Solubility of TAGAZ study

To start the recrystallization process, the solubility of TAGAZ in various solvents was determined. To a round-bottom flask with attached stirrer and thermocouple, 100 ml of solvent or solvent mixture and 0.1 g of TAGAZ were added. If it dissolved during stirring, the amount was increased by another 0.1 g of substance until a saturated solution was obtained. If it did not dissolve in 25 °C, the flask was heated to the boiling point of the solvent. If dissolution was not observed, TAGAZ was considered to be sparingly soluble in that solvent and further examination was discontinued. Results are shown in Table 1.

Table 1. Solubility of TAGAZ in various solvents

Solvent	S [g/100 cm^3]	
	25 °C	Boiling point
Methanol	< 0.1	< 0.1
Ethanol		
2-Propanol		
Acetone		
Methylene chloride		
Methyl chloride		
Tetrahydrofuran		
Diethyl ether		
Ethyl acetate		
Acetonitrile		
Dioxane		
n-Hexane		
NMP[a)]		
Cyclohexane		
Pyridine		0.2
Morpholine		
Glycerin		10.0[b)]
Water	1.4	44.6

a) N-methyl-2-pyrrolidone; b) 93 °C

From the above, it is known that triaminoguanidinium azotetrazolate is sparingly soluble, both at 25 °C and at the boiling point of the chosen solvents. In each case solubility was slightly less than 0.1 g in 100 cm^3 of solvent at room temperature. The only solvents in which TAGAZ dissolved were water and glycerine. Solubility increases considerably when temperature increases – from 1.4 g in 25 °C to 44.6 g in 100 °C for water and from 0.1 g in 25 °C to 100 cm^3 in 93 °C for glycerine. To determine the dependence of solubility with temperature, the curve of solubility of TAGAZ in water was determined. Results are shown on Fig. 3.

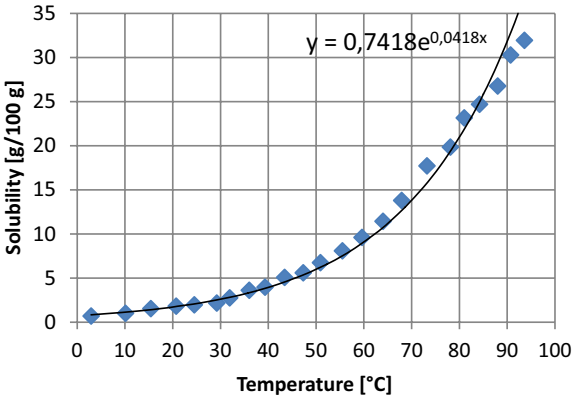


Fig. 3. Temperature dependence of TAGAZ solubility in water

Due to the fact that, of those tested, water and glycerine were the only proper solvents, solubility was determined when these were mixed with other solvents. The procedure was the same as that used previously. Results are shown in Table 2.

Table 2. Solubility of TAGAZ in mixed solvents at 50 °C

Solvent mixture [v/v][a)]	S [g/100 cm^3]
NMP/H_2O [4/1][b)]	< 0.2
NMP/H_2O [3/2][b)]	3.8
NMP/H_2O [3/1][b)]	< 0.2
NMP/hexane/THF [1/1/1/]	< 0.2
NMP/hexane/THF/H_2O [13/1/1/6]	0.4
NMP/CH_3OH/H_2O/hexane [7/1/6/1]	0.3
NMP/CH_3OH/H_2O/hexane [7/1/8/1]	3.5
NMP/CH_3OH/H_2O/hexane [10/1/6/1]	3.8
Morpholine/H_2O [3/2]	4.9
Glycerine/H_2O [1/1]	3.0

a) volume ratio; b) mass ratio (w/w)

The study permitted the selection of mixtures of solvents which could be used in the recrystallization of TAGAZ. The best systems were found to be NMP/H_2O (3/2) and glycerine/water (1/1) for which TAGAZ solubility is more than 3.0 g in 100 cm^3 of solvent at 50 °C.

2.3. Recrystallization of TAGAZ

2.3.1. Recrystallization from water and glycerine

The recrystallization of TAGAZ was carried out by solvent cooling. A sample of 3.0 g was dissolved in 60 cm^3 of water at 50 °C, cooled at a rate of 2 °C/min to 5 °C and kept overnight in a 5 °C. Crystals were filtrated off

and dried at 60 °C. The product weight of 2.49 g is equivalent to a yield of 83%. The TAGAZ crystals were of a needle-like shape. The process was carried out with glycerine as a solvent under analogous conditions. The 0.63 g obtained (21% yield) were of a needle-like shape.
Regardless of the cooling rate, recrystallisation from water produced lengthened rod-like shaped crystals. When the solvent was changed for glycerine under slow cooling conditions a significant decrease in crystal dimensions and a change of crystal form into needles was observed.

2.3.2. Recrystallization from NMP/water system with antisolvent

To a round-bottom 100 cm^3 flask 25 cm^3 of NMP/H_2O (3/2 w/w) mixture was poured and heated to 50 °C. In this solution 0.9 g of TAGAZ was dissolved. The resulting solution was poured into 100 cm^3 of antisolvent. The process was carried out for various antisolvents at different temperatures: +20 °C, -10 °C, -30 °C. The results are shown in Table 3.
TAGAZ crystals produced in the process of crystallization from NMP/water – antisolvent system had needle- or rod-like shape. The exception was with hexane and tetrahydrofuran (-30 °C), which resulted in a decrease in the dimensions of the crystals which aquired a cubic shape.

Table 3. Results of crystallization with antisolvent at +20 °C, -10°C, -30 °C

Antisolvent	Yield, α [%]			Crystal shape		
	+20 °C	-10 °C	-30 °C	+20 °C	-10 °C	-30 °C
n-Hexane	0.1	53.3	44.4	needle	cubic	needle
Chloroform	17.7	70.0	65.6	rod	rod	
Methanol	11.0	80.0	73.2			
Diethyl ether	13.3	52.2	48.8			
Cyclohexane	6.6	-	-		-	-
Benzene	14.4	-	-		-	-
m-Xylene	12.2	-	-		-	-
Trichloroethylene	14.4	-	-		-	-
Diisopropyl ether	8.9	-	-		-	-
Tetrahydrofuran	93.3	94.4	92.2	needle	needle	cubic
Ethyl acetate	22.0	62.2	26.6			needle
Acetone	11.1	87.8	90.0			
Acetonitrile	83.3	91.1	82.2			
Methylene chloride	56.7	74.4	52.2			
2-Propanol	82.2	-	-		-	-
n-Butanol	67.8	-	-		-	-
tert-Butanol	83.3	-	-		-	-
n-Propanol	60.0	-	-		-	-
Isobutanol	83.3	-	-		-	-

2.3.3. Recrystallization from water/glycerine system with antisolvent

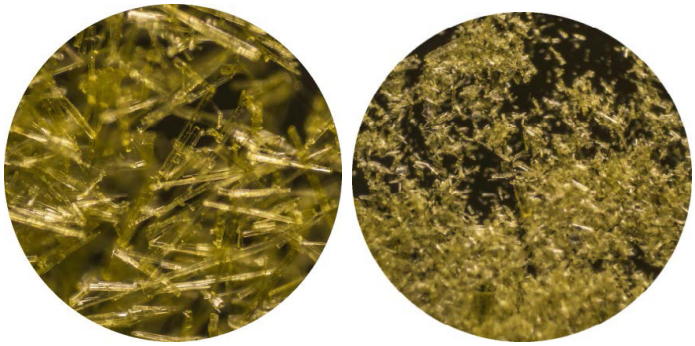
To a round bottom flask 3.0 g TAGAZ and 50 cm^3 water and glycerine mixture (1/1 v/v) was added. The system was stirred and heated to 50 °C. The resulting solution was poured quickly into 100 cm^3 of antisolvent at room temperature. Results of the crystallization are given in Table 4.
Good results for crystallization were achieved by oversaturation with antisolvent in water-glycerine solutions. Rod shaped crystals were obtained with methanol as the antisolvent. As for acetone, obtained crystals were in needle shape, as for 2-propanol needle-like shape, and for ethanol fine-crystallized product was obtained.

Table 4. Results of recrystallization from water/glycerine system with antisolvent

Antisolvent	Crystal shape
Methanol	rods
Ethanol	unknown
2-Propanol	needles
Acetone	cubes

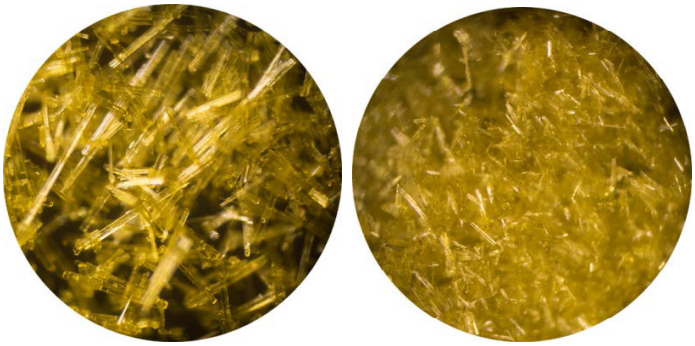
2.4. Optical microscopy

Pictures of crystals were taken with a BRESSER optical microscope at magnifications of x20, 80, 200 and 350. Crystallization from water resulted in long rod-like shape crystals (Fig. 4a.). An increase in the cooling rate to 27 °C/min is favorable for producing a decrease in the dimensions of the obtained crystals (Fig. 5b.). When the solvent was changed to glycerine, a significant decrease in the dimensions and a change of crystal form from rod to needle, was observed. When recrystallized from glycerine, under slow cooling conditions, the crystals formed as tiny needles. These crystals have smaller dimensions than crystals obtained from water. TAGAZ crystals resulting from recrystallization from water and glycerine are shown in Fig. 4.



a) b)

Fig. 4. TAGAZ crystals obtained after recrystallization process with slow cooling: a) after synthesis in water; b) from glycerine (mag. x200)



a) b)

Fig. 5. TAGAZ crystals after recrystallization in water system by cooling: a) with 2 °C/min rate; b) with 27 °C/min rate (mag. x100)

In crystallization from the water with antisolvent system there was an improvement in morphology. Crystal dimensions were reduced. With methanol, rods were obtained, with acetone, 2-propanol and ethanol – small

needles. These photos were shown in Fig. 6.

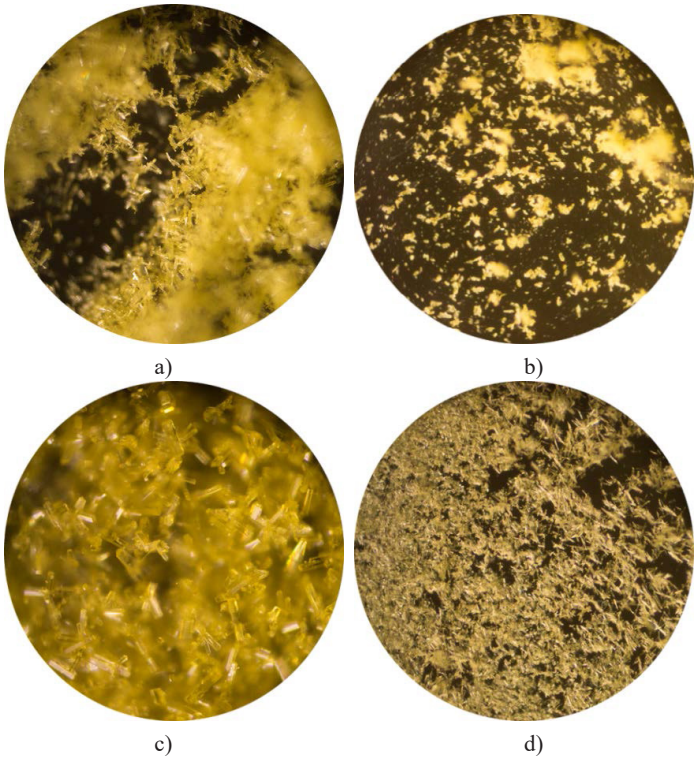


Fig. 6. TAGAZ crystals obtained from water and antisolvent: a) ethanol; b) acetone; c) methanol; d) 2-propanol

Studies of solvent mixture NMP/water (3/2 w/w) with antisolvent were also carried out. Following the recrystallization process the crystals had needle-like, rod-like and cubic shapes. A decrease in the antisolvent temperature, from 20 °C to –10 °C and –30 °C, resulted in a decrease of the crystals' dimensions. Crystals obtained at –30 °C had relatively small dimensions and a needle-like shape except for those obtained from tetrahydrofuran (Fig. 7c.). For crystallization at –10 °C, needle-like and rod-like crystals were produced, with an exception for hexane, which produced cubic shapes. Pictures of selected crystals are shown in Fig. 7.

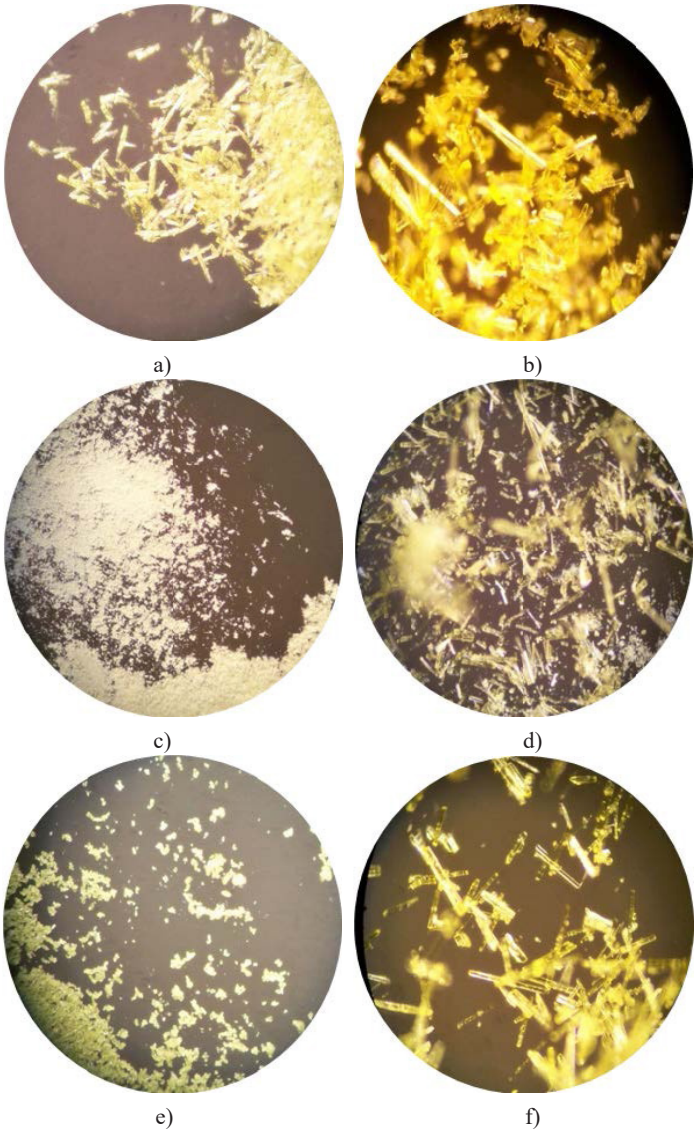


Fig. 7. Crystals obtained from mixture of solvent NMP/H_2O and antisolvent: a) acetone (–30 °C); b) acetone (20 °C); c) THF (–30 °C); d) THF (20 °C); e) hexane (–10 °C); f) hexane (–30 °C)

In water/glycerine (1/1) crystals were obtained with more favourable regular shapes and dimensions than in case of crystals following synthesis. An especially fine-crystalline product was formed, when ethanol was the antisolvent. When methanol was an antisolvent, larger, regular rod-like crystals were obtained. With acetone as an antisolvent, crystals had a cubic, rod-like and irregular shape. The results of study were shown in Fig. 8.

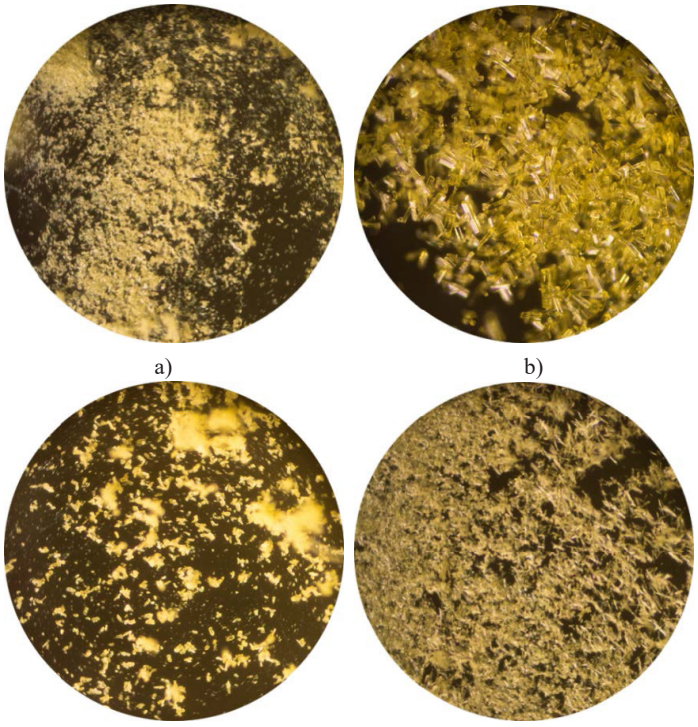


Fig. 8. Crystals obtained from water/glycerine system and antisolvent: a) ethanol; b) methanol; c) acetone; d) 2-propanol (mag. x200)

3. Summary

TAGAZ is not soluble in most of the investigated organic solvents. It can be dissolved only in water, glycerine and in the following mixtures: NMP/water (3/2 w/w) and glycerine/water (1/1 v/v). Mixtures of NMP/water and glycerine/water were the best systems for recrystallization with antisolvent. Needle-like and rod-like crystals were those most often obtained in recrystallization. In the experiments with hexane (–10 °C) and THF (–30 °C) in NMP/water solution the product had cubic shape of crystals. The use of the antisolvents methanol, ethanol, 2-propanol and acetone in glycerine/water mixture gave: rods, a fine crystalline product, small needles and cube-like crystals, respectively. The main advantage of small cubes with regular dimensions is a high bulk density of the product. Also cubic shape is better than needles for mixing with other ingredients of propellant compositions. Regarding lowest as possible toxicity of solvents and the best shape of crystals we can say that recrystallization of TAGAZ in glycerine/water with acetone as antisolvent is our method of choice.

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