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**SOLUBILITY REPORT OF 1-METHYL-3,5-DINITRO-1*H*-1,2,4-TRIAZOLE
(MDNT) AND 2-METHYL-4,5-DINITRO-2*H*-1,2,3-TRIAZOLE 1-OXIDE (MDNTO)
FOR CO-CRYSTALLIZATION SCREEN**

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November 2015



U.S. ARMY ARMAMENT RESEARCH, DEVELOPMENT AND
ENGINEERING CENTER

Munitions Engineering Technology Center

Picatinny Arsenal, New Jersey

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PREFACE

The purpose of this research was to determine the solubility of 1-methyl-3,5-dinitro-1*H*-1,2,4-triazole (MDNT) and 2-methyl-4,5-dinitro-2*H*-1,2,3-triazole 1-oxide (MDNTO) in various solvents for eventual co-crystallization. Dr. Reddy Damavarapu is to be thanked for guidance and materials.

INTRODUCTION

Co-crystallization is a technique that has been widely used in the pharmaceutical industry as a method to deliver co-drugs or improve physicochemical or pharmaceutical properties (ref. 1). New molecular architectures synthesized by assembling organized co-formers through noncovalent forces in novel crystalline lattices allow for tailorable properties of co-crystalline compounds such as melting point and solubility. These properties are unique from those exhibited by either co-former or a discrete mixture of individual co-formers. Recent research and development of new co-crystallization techniques has brought attention to the benefits of co-crystallization in the area of energetic materials (refs. 2 and 3).

Rather than synthesizing new energetic materials by introduction of functional groups on oxidizable backbones or heteroatomic ring systems, co-crystallizations allows for combinatorial effects of existing compounds through simplified synthetic techniques such as solution crystallization, grinding, and melting. Successes of energetic co-crystallizations have been reported through the synthesis of a HMX/AP co-crystal that was not water soluble by Levinthal (ref. 4) and less sensitive 2CL-20:HMX co-crystals reported by Matzger (ref. 5).

Essential to the formation and property predictions of energetic co-crystals is an understanding of the intermolecular forces between co-formers and how these interactions affect explosive properties. As an example, the extensive inter- and intra-molecular hydrogen bonding in a 2,4,6 triamino-1,3,5-trinitrobenzene crystal lattice is attributed to excellent thermal stability, reduced sensitivity, and low solubility in all solvents (ref. 6). The potential for hydrogen bonding is vast in the area of energetic materials from the prevalence of amino and nitro functional groups, and it is predicted that the extension of additional intermolecular hydrogen bonding in co-crystal lattices will have a similar effect on energetic co-crystalline materials. Additional noncovalent forces that can be attributed to the formation of co-crystals are π - π stacking and van der Waals, both of which are capable of contributing to greater crystal packing and density that lead to higher predicted performance.

Proper selection of co-formers is essential not only for the synthesis of the resulting co-crystal due to noncovalent bonding forces but also for prediction of explosive performance. Properties such as the type and extent of noncovalent bonds formed in the co-crystal, molecular composition of individual co-formers and their ratios in the co-crystal, co-former and co-crystal polymorphs, sensitivity and performance of co-formers amongst others all have the capability of affecting explosive performance of the co-crystal. It is for these reasons that 1-methyl-3,5-dinitro-1*H*-1,2,4-triazole (MDNT) and 2-methyl-4,5-dinitro-2*H*-1,2,3-triazole 1-oxide (MDNTO) were selected for study as co-crystal co-formers. Both compounds are high energy Composition B and RDX replacements, melt-castable materials with melting points of 98° and 130°C for MDNT and MDNTO respectively, and exhibit increased insensitivity with respect to RDX. Of importance is that they are not nitramine materials that have mainly been studied in the past for energetic co-crystallization, possess no known polymorphs, and their corresponding molecular structures complement each other well with regards to potential π - π stacking and hydrogen bonding. Additionally beneficial is the wide range of solubility expressed by each compound in organic solvents that make them ideal candidates for solvent-based co-crystallization methods (fig. 1).

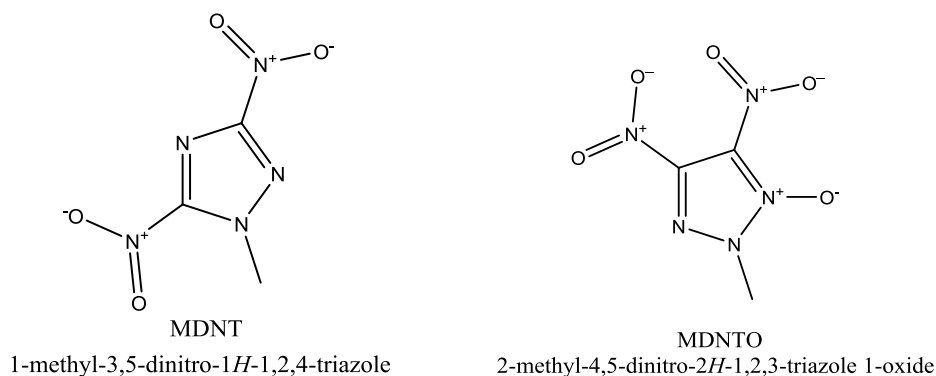


Figure 1
Molecular structures of MDNT and MDNTO

In order to prepare energetic co-crystals, detailed screening techniques are necessary, especially for solution preparation methods that are generally done from saturated solutions of the pure components. For this reason, solubility curves and van't Hoff plots of the two selected co-formers were experimentally determined. These results will be used to predict ideal solvents, co-former ratios, and temperatures for co-crystal formation.

EXPERIMENTAL PROCEDURES

Materials

The MDNT (ref. 7) and MDNTO (ref. 8) were synthesized at the U.S. Army Armament Research, Development and Engineering Center, Picatinny Arsenal, NJ, and determined pure by both nuclear magnetic resonance (NMR) and melting point. Solvents used for solubility experiments were purchased from commercial sources and used without further purification. Reagent grade acetone and methanol were purchased from Pharmco-AAPER, Brookfield, CT. Ethyl Acetate (99.99% extra dry AcroSeal from Acros Organics, Belgium) was purchased from Fisher Scientific, Pittsburgh, PA. Methanol (anhydrous, 99.8%), 1-butanol, isopropanol and ethanol (200 proof) were purchased from Sigma Aldrich, St. Louis, MO. Methanol- d_4 with +0.05% V/V TMS was purchased from Cambridge Isotope Laboratories, Inc., Tewksbury, MA

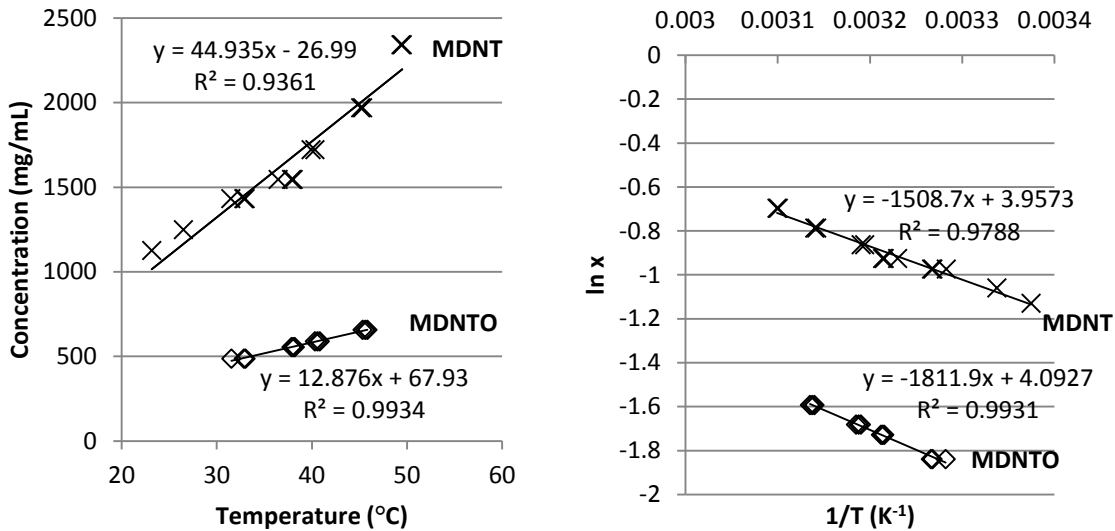
Solubility

Solubility determinations of the pure components were determined on an Avantium Crystal16™ and were analyzed using the CrystalClear software package. Solvents investigated were acetone, ethyl acetate, methanol, ethanol, isopropanol, and n-butanol. In each experiment, the solute was weighed into a small, clear, and colorless high performance liquid chromatography (HPLC) type vial equipped with a magnetic stir bar. Solvent was added and exact concentration recorded. The vials were placed into the Avantium Crystal16™, and temperature was cycled three times from 20° to 5°C below the boiling point of solvent with 90 min equilibration periods between heating and cooling. Ramp rates were 0.5° and -0.3°C/min.

The solubility of each vial solution was determined by identifying clear point temperatures, defined as the temperature at which the turbidity of the solution decreases upon heating and the solution becomes transparent. Graphing the clear point temperatures versus the concentration of the

solution yields a solubility curve and associated equation. Solubility data of the individual materials were then fitted to the van't Hoff equation as shown in figures 2 through 7.

Median standard deviation (MStdDev) was reported for error. This represents the median of clear point standard deviations in temperature at each concentration in which two or more measurements were made.

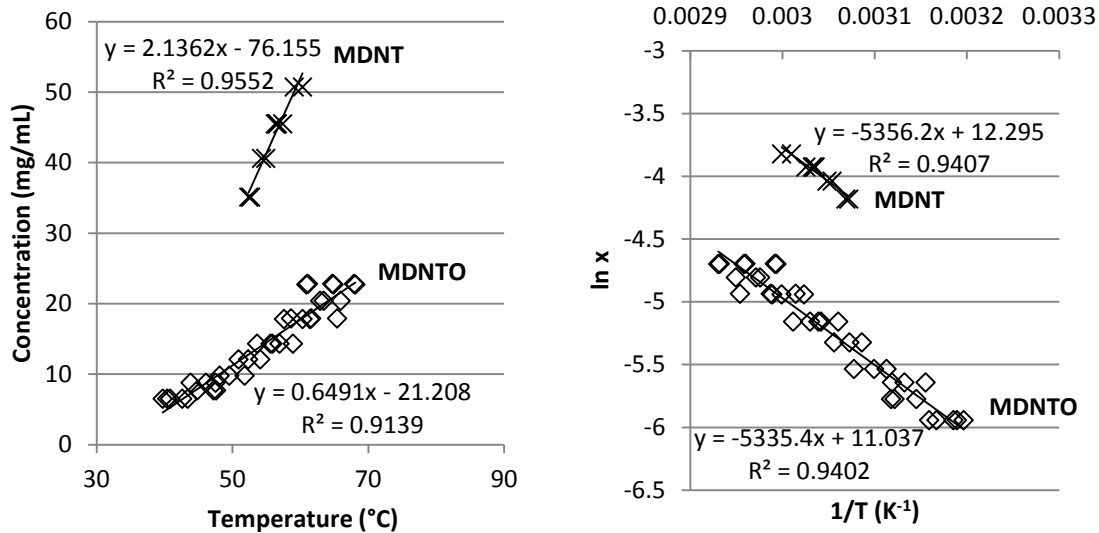


Note: The MDNT has a MStdDev of 0.28 and a range of 0.11° to 0.87°C. The MDNTO has a MStdDev of 0.25 and a range of 0.17° to 0.82°C.

(a)
The solubility curve of
MDNT (x) and MDNTO (◇)
in acetone

(b)
van't Hoff solubility plot of
MDNT (x) and MDNTO (◇)
in acetone

Figure 2
Experimental solubility curves for MDNT and MDNTO in acetone

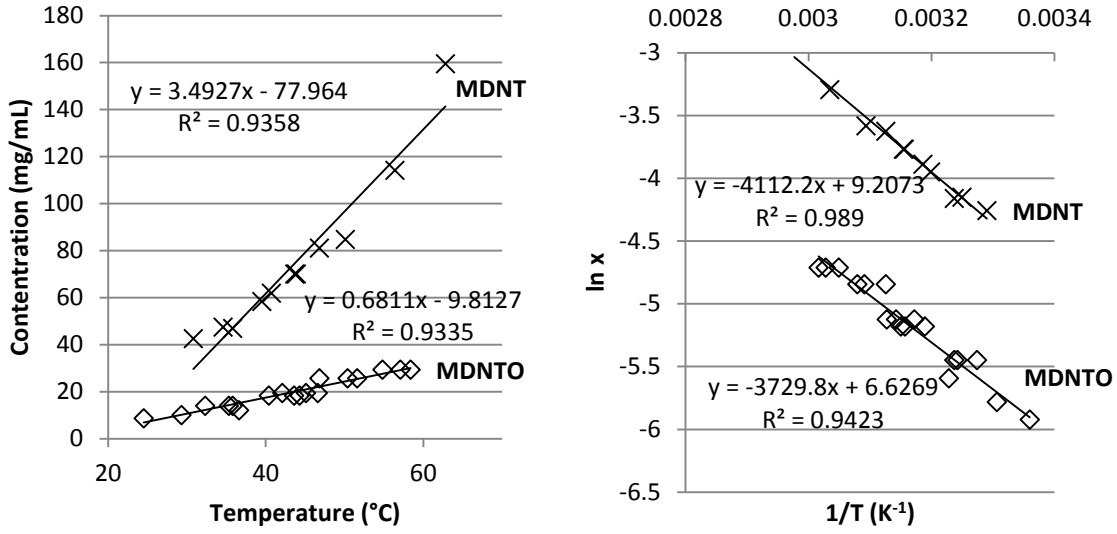


Note: The MDNT has a MStdDev of 0.32 and a range of 0.15° to 0.85°C. The MDNTO has a MStdDev of 1.87 and a range of 1.51° to 3.61°C.

(a)
The solubility curve
of MDNT (x) and MDNTO (◇)
in isopropanol

(b)
van't Hoff solubility plot
of MDNT (x) and MDNTO (◇)
in isopropanol

Figure 3
Experimental solubility curves for MDNT and MDNTO in isopropanol

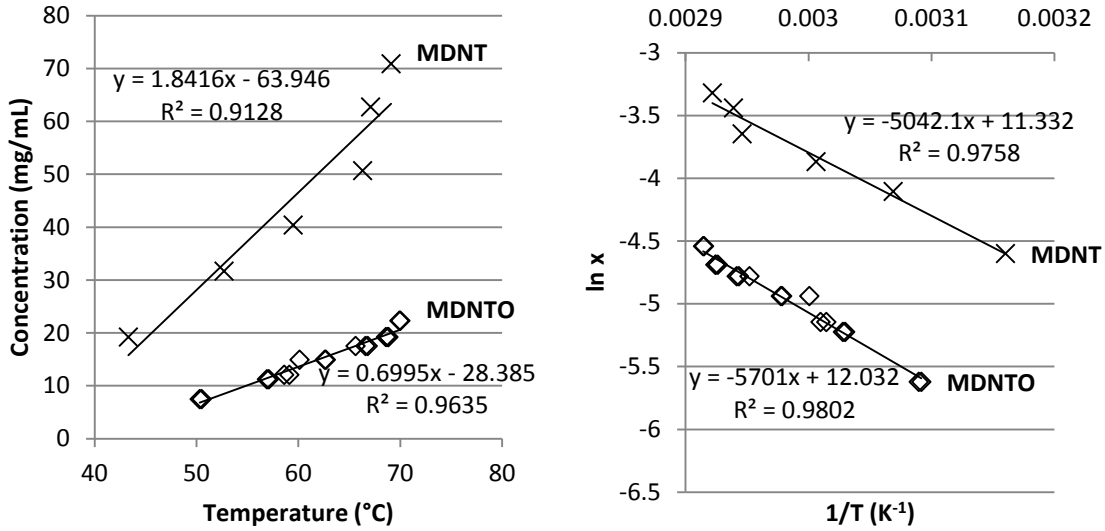


Note: The MDNTO has a MStdDev of 2.08 and a range of 1.82° to 2.50°C. No repeat measurements were present in MDNT.

(a)
The solubility curve of
MDNT and MDNTO in ethanol

(b)
van't Hoff solubility plot
of MDNT and MDNTO in ethanol

Figure 4
Experimental solubility curves for MDNT and MDNTO in ethanol

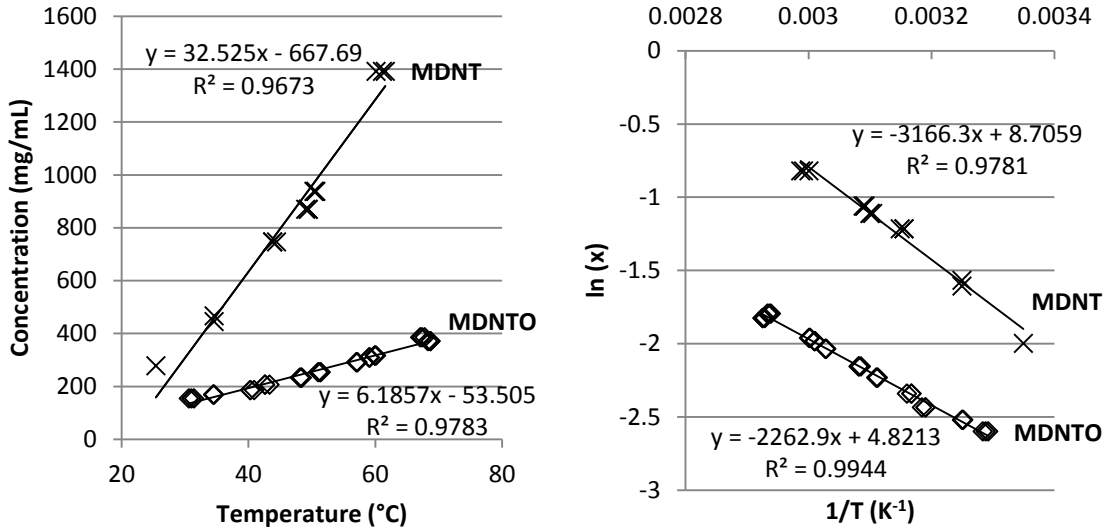


Note: The MDNTO has a MStdDev of 0.14 and a range of 0.07° to 1.47°C. No repeat measurements were present in MDNT.

(a)
The solubility curve
of MDNT (x) and MDNTO (◇)
in n-butanol

(b)
van't Hoff solubility plot
of MDNT (x) and MDNTO (◇)
in n-butanol

Figure 5
Experimental solubility curves for MDNT and MDNTO in n-butanol

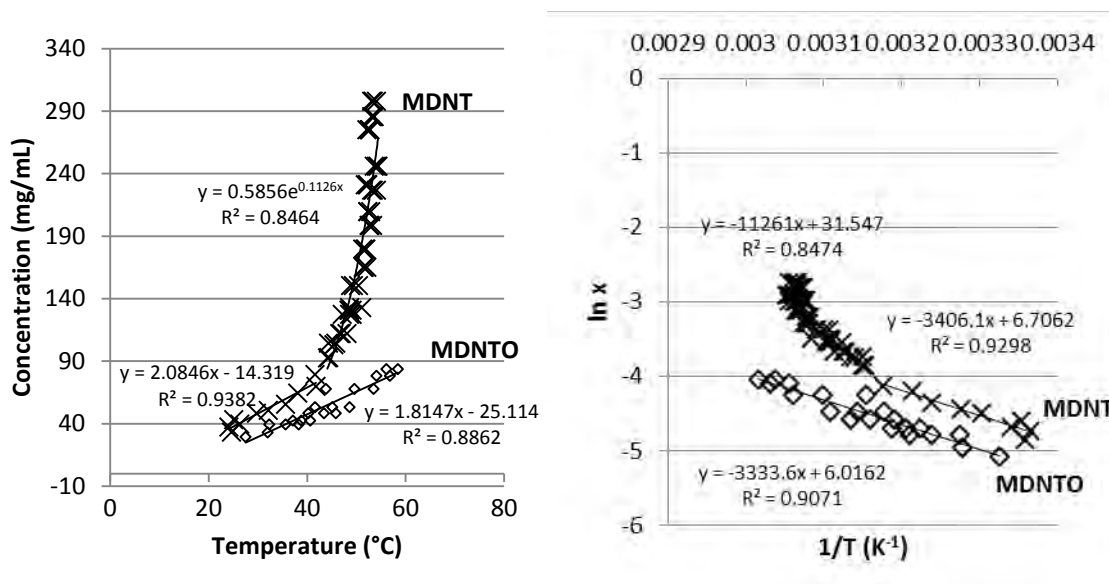


Note: The MDNT has a MStdDev of 0.29 and a range of 0.15° to 0.76°C. The MDNTO has a MStdDev of 0.21 and a range of 0.06° to 0.4 0°C.

(a)
The solubility curve
of MDNT (x) and MDNTO (◇)
in ethyl acetate

(b)
van't Hoff solubility plot
of MDNT (x) and MDNTO (◇)
in ethyl acetate

Figure 6
Experimental solubility curves for MDNT and MDNTO in ethyl acetate



Note: The MDNT is broken down into two temperature ranges of 24.6° to 41.6°C and 44.1° to 54.1°C correlating to the two different trendlines. The MDNT has a MStdDev of 0.38 and a range of 0.25° to 1.77°C. The MDNTO has a MStdDev of 2.81 and a range of 1.63° to 4.88°C.

(a)
The solubility curve
of MDNT (x) and MDNTO (◇)
in methanol

(b)
van't Hoff solubility plot
of MDNT (x) and MDNTO (◇)
in methanol

Figure 7
Experimental solubility curves for MDNT and MDNTO in methanol

Nuclear Magnetic Resonance

A Bruker 400 MHz NMR equipped with a PA BBO 400SB BBF-H-D-05 Z probe was used to conduct variable temperature measurements of MDNT in deuterated methanol. Proton spectra were collected with a conventional pulse program (zg30) with a 10.69 μ s pulse, 5.12 sec acquisition time and 1 sec pulse delay. Carbon-13 spectra were collected with a pulse program (zgpg30) with a 10.00 μ s pulse, 3 sec acquisition time with ^1H - ^{13}C decoupling and 2 sec pulse delay.

Temperature of the probe was precisely controlled, and the evaluated temperatures were set and allowed to equilibrate before spectra were acquired. The NMR was tuned, matched, and shimmed at each temperature to obtain quality data. Proton data was collected at 5°C intervals from 25° to 60°C. Carbon data was collected at 22° and 50°C. Carbon data was limited due to extended collection times at low concentrations.

The ^1H -NMR analysis sample preparation: The NMR sample was prepared by adding MDNT to an NMR tube with approximately 0.75 mL of deuterated methanol at ambient temperature. The NMR tube was inverted until a uniform solution was achieved. A blank sample of deuterated methanol was also prepared for direct comparison of solvent peak movement due to variable temperature.

The 22°C ^{13}C -NMR analysis sample preparation: 0.75 mL deuterated methanol was added to a small HPLC style vial at ambient conditions, MDNT was added until just below the saturation point. The solution was then transferred to a standard 5-mm NMR tube for analysis.

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50°C ¹³C-NMR analysis sample preparation: MDNT (~200 mg) was added to 0.75 mL deuterated methanol in a vial and was subsequently heated to 60°C until all MDNT was dissolved. The solution was then transferred to a standard 5-mm NMR tube for analysis. All MDNT remained in solution.

RESULTS AND DISCUSSION

To interpret the data as an ideal system for better extrapolation or interpolation values, a van't Hoff plot was calculated from each solubility curve

$$\ln x = -\frac{\Delta H}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \quad (1)$$

where x is the component mole fraction, ΔH is the dissolution enthalpy, T_0 (K) is a set-point temperature, and T (K) is the saturation temperature of the mole fraction x (ref. 1). As shown in figures 2 through 6, solubilities of MDNT and MDNTO in acetone, ethyl acetate, ethanol, isopropanol, and n-butanol are well correlated by the van't Hoff equation. Although MDNTO solubility exhibits a linear van't Hoff plot in methanol, MDNT shows two distinct linear regions upon temperature increase indicating possible solvation, tautomerization, or polymorphism. To better understand the chemical changes occurring in the MDNT/methanol solute solvent interactions, a temperature dependent NMR study was performed.

Figure 8 is a comparison of the solubilities of MDNT and MDNTO in the various organic solvents investigated. These plots are based on the model trendlines that were constructed from the experimental data. It can be seen that MDNT is highly soluble in both acetone and ethyl acetate and exhibits lower solubility levels in the remaining solvents (fig. 8) (table 1). It can also be noted that the solubility of DNMT is consistently higher in each solvent than that of DNMTO (fig. 9) (table 2).

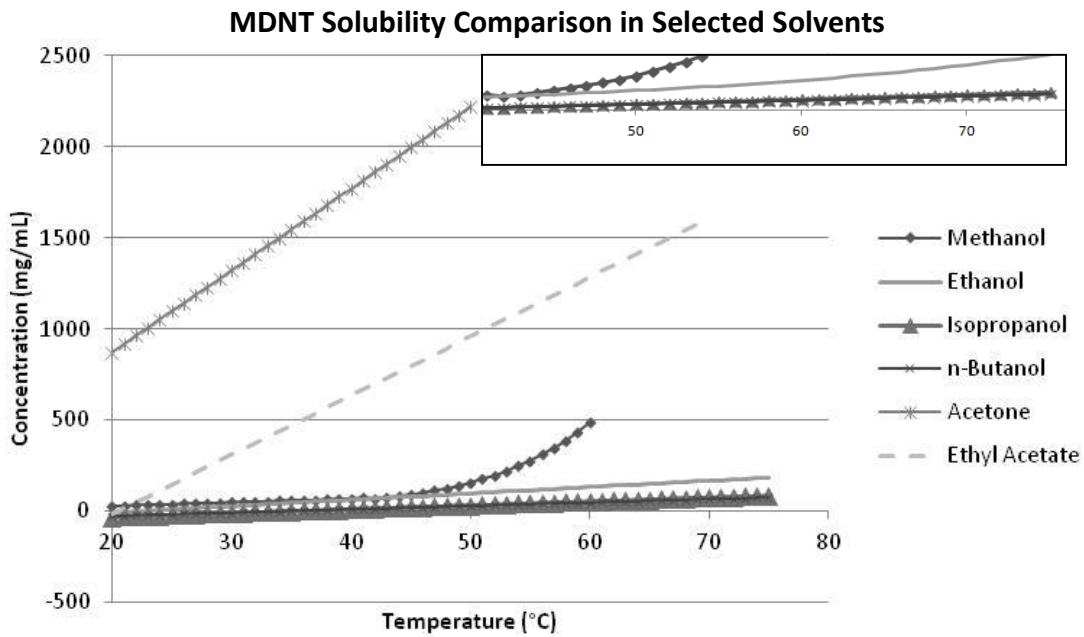


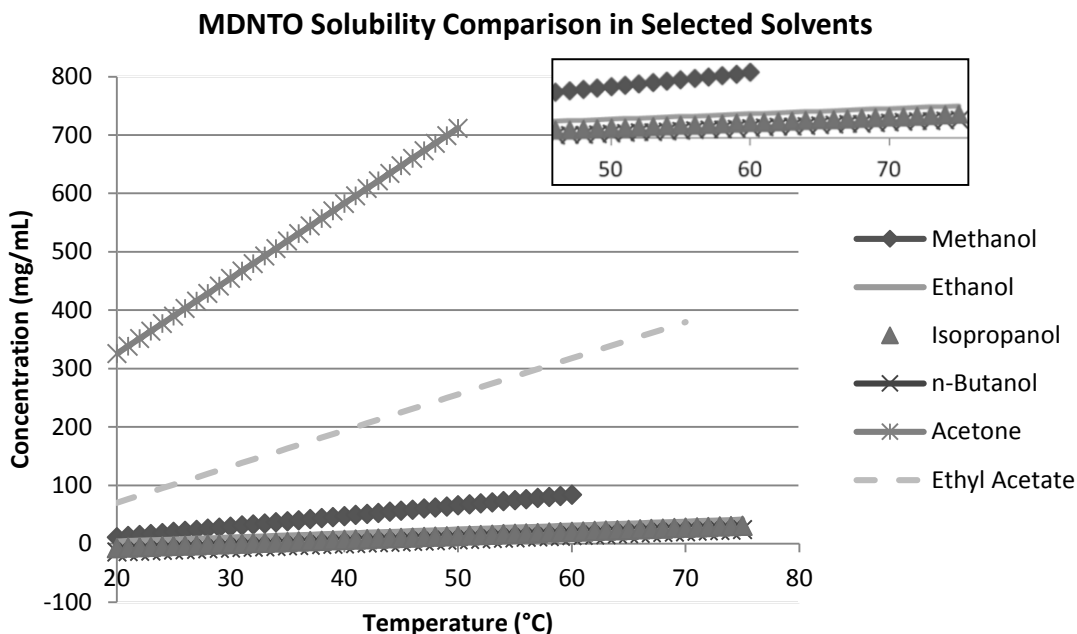
Figure 8

The solubility curves of MDNT represented by trendline equations in the temperature range examined for each selected solvent

Table 1

Predicted solubility of MDNT (mg/mL) from trendline equations in selected solvents at 30°C and the highest temperature evaluated in the Crystal16

| Solvent | Solubility of MDNT (mg/mL) | |
|---------------|----------------------------|---------------------------|
| | 30°C | Maximum temperature (X°C) |
| n-Butanol | 0 | 74.174 (75) |
| Isopropanol | 0 | 84.06 (75) |
| Ethanol | 26.817 | 183.9885 (75) |
| Methanol | 48.219 | 503.1467 (60) |
| Ethyl acetate | 308.06 | 1609.06 (70) |
| Acetone | 1321.06 | 2219.76 (50) |



The solubility curves of MDNTO represented by trendline equations in the temperature range examined for each selected solvent

Table 2

Predicted solubility of MDMT (mg/mL) from trendline equations in selected solvents at 30°C and the highest temperature evaluated in the Crystal16

| Solvent | Solubility of MDNTO (mg/mL) | |
|---------------|-----------------------------|---------------------------|
| | 30°C | Maximum temperature (X°C) |
| n-Butanol | 0 | 24.0775 (75) |
| Isopropanol | 0 | 27.4745 (75) |
| Ethanol | 10.62 | 41.2698 (75) |
| Methanol | 29.327 | 83.768 (60) |
| Ethyl acetate | 132.066 | 379.494 (70) |
| Acetone | 454.21 | 711.73 (50) |

The experimental solubility curves for MDNT and MDNTO in each of the investigated solvents are shown in figures 2 through 7 with associated predictive trend equations and R^2 values. Saturation temperatures or clear points of the co-formers in selected solvent were easily discernible by sharp transitions to near 0% turbidity. As the method developed to include three temperature cycles, multiple data points are associated with each clear point for each concentration of solute examined. The median standard deviation of clear point temperature with this technique is 0.46°C with a maximum of 4.88°C and minimum of 0.06°C. Data points were excluded if the clear point was not definitive. This is typically associated with a significant amount of noise due to the ripening of large solute crystals upon cooling that disrupt turbidity measurements. In some cases, fewer data points are available at lower temperatures for those concentrations at which the solute did not crystallize from solution upon cooling to the lower temperature limit of 20°C. Under these circumstances, only one clear point from the three data points associated with the temperature cycles is available as the solute remained in solution for the duration of the experiment. All of the solubility curves are represented by the van't Hoff equation for better extrapolation.

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The MDNT in methanol produced the only solubility curve that did not correlate well to any one trendline. The solubility of MDNT in methanol increased steadily in a linear fashion until approximately 42°C where it began to increase at an exponential rate. It was initially postulated that the difference could be due to small amounts of residual water in the solvent. This theory was negated when anhydrous methanol was used and data produced with stock and anhydrous solvent showed identical results within experimental error. This anomaly is also expressed in the van't Hoff plot where two linear ranges are apparent. The NMR studies were then performed to determine the presence of possible chemical or solvate changes with increased temperature.

Proton data collected at variable temperatures were examined for changes in the methyl group of the MDNT molecule. The singlet methyl group peak remained unchanged at ~4.36 ppm throughout the range of the experiment from 25° to 60°C indicating no change with respect to the formation of tautomers or solvates. The deuterated alcohol methanol signal shifted down with temperature from 4.80 ppm at 25°C to 4.42 ppm at 60°C while the signal from the methyl group remained unchanged at 3.31 ppm. Solvent signal movement was confirmed with repeated measurements of a blank solvent sample.

Carbon-13 NMR performed at room temperature was complicated by the dilute nature of the sample; although MDNT was saturated in the solvent, the concentration of the sample was low. Due to the low concentration, 10240 scans were required to give ample signal to noise for detection of the MDNT ring carbons that were located at 158.69 and 152.52 ppm. The methyl carbon and deuterated methanol solvent peak were located at 42.23 and 49.04 ppm respectively. Elevated temperature carbon was run at 50°C which allowed for the concentration of the MDNT to dramatically increase, allowing 1024 scans to be enough for needed resolution of the ring carbons. Ring carbons were located at 156.87 and 150.55 ppm, while the methyl carbon and deuterated methanol solvent peak were located at 40.15 and 47.25 ppm respectively. Minor changes to the chemical shift between samples were concluded to be a temperature effect as the deuterated methanol peaks shifted an equal amount to the ring and methyl MDNT carbons. Unfortunately, variable temperature studies, both ¹H and ¹³C, of MDNT in deuterated methanol yielded no evidence of a change in structure at elevated temperatures. Further research is required to determine the cause of the distinct change in MDNT solubility in methanol.

CONCLUSIONS

Solubility curves of 1-Methyl-3,5-Dinitro-1*H*-1,2,4-Triazole (MDNT) and 2-methyl-4,5-dinitro-2*H*-1,2,3-triazole 1-oxide (MDNTO) have been provided in multiple organic solvents using the Avantium Crystal16™. This technique showed good precision of measurement yielding median standard deviation of clear point temperature of 0.46°C. Most model fits were linear and exhibited a predicted single smooth trend line. The MDNT in methanol exhibits a different behavior in which two distinct regions of solubility were observed. Effort was made to determine the cause of the change using ¹H and ¹³C variable temperature studies of MDNT in deuterated methanol. Unfortunately, the nuclear magnetic resonance data produced no explanation for the solubility change; research is ongoing for this matter. Solubility data collected was converted using the van't Hoff equation for better extrapolation of solubility values. This work will be the basis for additional work with MDNT and MDNTO including co-crystal screening for the potential formation of MDNT/MDNTO energetic co-crystals.

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Steven M. Nicolich

Division Chief

2/25/15
(Date)

- d. This draft copy of this report has been reviewed for sensitive material and approved by the Intelligence and Technology Protection Office, Bldg 83, 1st Floor, Room 120 (Vault).

Andrew Pskowski

RDAR-CIS

1/24/15
(Date)

PART 2. To be signed either when draft report is submitted or after review of reproduction copy.

This report is approved for publication.

Steven M. Nicolich

Division Chief

11/16/2015
(Date)