

Solubility Determination of Raw Energetic Materials in Molten 2,4-Dinitroanisole

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Abstract: 2,4-Dinitroanisole (DNAN) is an ingredient used in several insensitive munition formulations that have recently been qualified by the US Army. A phenomenon known as irreversible growth is found to occur during conditioning cycles of insensitive munitions (IM) that contain DNAN. A possible cause of the irreversible growth may be the potential solubility of energetic components formulated with

melted DNAN. This report documents methods development and procedures used to determine the solubility of energetic constituents in molten DNAN at 100 °C. High performance liquid chromatography and ion chromatography were used for quantitation. Solubilities (given as g energetic per 100 g DNAN) of RDX, HMX, NTO, NQ, and AP were found as 13.7, 3.02, 0.222, 0.448, and 0.088, respectively.

Keywords: Energetic materials • DNAN • NTO • RDX • HMX • Ammonium perchlorate (AP) • Nitroguanidine (NQ) • Chromatography • Solubility

1 Introduction

2,4-Dinitroanisole (DNAN) is a key insensitive munition (IM) melt-phase ingredient that is currently featured in several IM melt-pour formulations developed by the U.S. Army. Explosive formulations that contain DNAN are tailored to have TNT or Composition-B performance while exhibiting decreased sensitivity to external stimuli.

The recent development and performance characterization of insensitive explosives based on DNAN formulations has led to the possible replacement of TNT and Composition-B in fielded munitions. DNAN offers lower toxicity and sensitivity than TNT. DNAN-based explosives have been demonstrated to have greatly improved insensitive munition (IM) characteristics, while maintaining explosive performance requirements. The use of lower shock sensitive ingredients in the IM development is a key driving force behind modern explosives formulations. A number of successful strategies to include polymer bonded explosives are employed to reduce some of the response of ordnance to planned and unplanned aggressive stimuli; however not until the use of DNAN in formulations did the US government significantly improve IM test results. DNAN is currently produced by BAE Systems in Kingsport, TN [1].

Recent use of DNAN includes insensitive munitions (IM) developed by the U.S. Army. DNAN-based IM formulations are high performance melt-cast explosives that contain DNAN in various combinations with energetic materials including 3-Nitro-1,2,4-triazol-5-one (NTO), nitroguanidine (NQ), RDX, HMX, and ammonium perchlorate (AP).

Samples of DNAN-based IM formulations experience irreversible growth during condition cycling. This has raised concerns with the military regarding safety, reliability, and performance of rounds that contain DNAN. As a result of

concerns with irreversible growth of DNAN based formulations, scientists have investigated its causes. One potential cause may be the solubility of crystalline energetic materials formulated with DNAN during melt casting processes. Workers hypothesized that energetics dissolved in DNAN during melt casting may be crystallizing out during thermal cycling.

This paper describes the methods development and the procedures used to determine the solubility of energetic materials commonly formulated with DNAN. The energetic materials analyzed in this study are NTO, RDX, HMX, and AP.

Initial methods development was performed taking aliquots of stirred RDX in molten DNAN at 100 °C. Previous solubility studies based on differential scanning calorimeter (DSC) methodology estimated RDX solubility in DNAN with minimal percent error [1]. For this reason RDX was the material of choice for the initial trials. High performance liquid chromatography (HPLC) and ion chromatography (IC) were used to determine the percentage of solid energetic materials in molten DNAN.

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2 Results and Discussion

For the purpose of collecting accurate aliquot samples, the length of heating required to melt the DNAN must be minimized to reduce evaporation. The melting point of DNAN is approximately 94–96 °C [2].

Initial determinations of the solubility range of each energetic material in DNAN were made using a 1:1 weight ratio mixture of each energetic and DNAN. Once a rough solubility range was determined, the preparation ratio of each energetic to DNAN was changed to envelop the expected solubility.

HPLC was used to determine the composition of the aliquot retrieved from the initial sample. HPLC is a known effective means of obtaining solubility data for low to mid molecular weight organic compounds [3]. Chromatograms displayed in Figure 1 contain peaks whose retention times are specific to each analyte, e.g. the retention time of DNAN is approximately 6 min in the analysis for HMX and RDX, and 8 min in the analysis of NTO and NQ. The energetic analytes ran with DNAN all have retention times shorter than DNAN. Components were identified based on their UV spectra and retention times when compared to reference materials [4,5]. A photodiode array (PDA) is the detector used for this procedure to detect and quantify the organic materials. Chromatograms were extracted on wavelengths that produced optimum signal for each component. Solubility of ammonium perchlorate (AP) was determined using ion chromatography. This is because AP is an inorganic compound and is more conveniently analyzed as the perchlorate anion using a conductivity detector.

The ion chromatogram for AP is shown in Figure 2. Perchlorate is a negative ion and is quantified as the key constituent. The percentage of perchlorate is then back calculated with the molecular weight of AP to compensate for the ammonium ion in AP. Since DNAN does not ionize under the test conditions it does not appear in the ion chromatogram.

For each combination of organic energetic material and DNAN, HPLC standards were prepared in acetonitrile from known amounts of reference materials. For each energetic material, calibration curves were obtained by linear regression. The ratio of peak area of energetic (e.g. RDX) to that of DNAN served as the abscissa, while concentration ratio of the same in the standard solution served as the ordinate. The solubility of the given energetic material in a sample was then back-calculated from the peak area ratios and the calibration curve.

DNAN quantification by HPLC was attempted when prepared with AP, however due to the low solubility of AP in DNAN, the resulting DNAN values were 99.5 to 100.5 % of the sample weight, and ultimately DNAN was determined by difference without significant error in the solubility results.

Table 1–5 show the weights of energetic materials (1st column) and DNAN (2nd column) used to prepare the

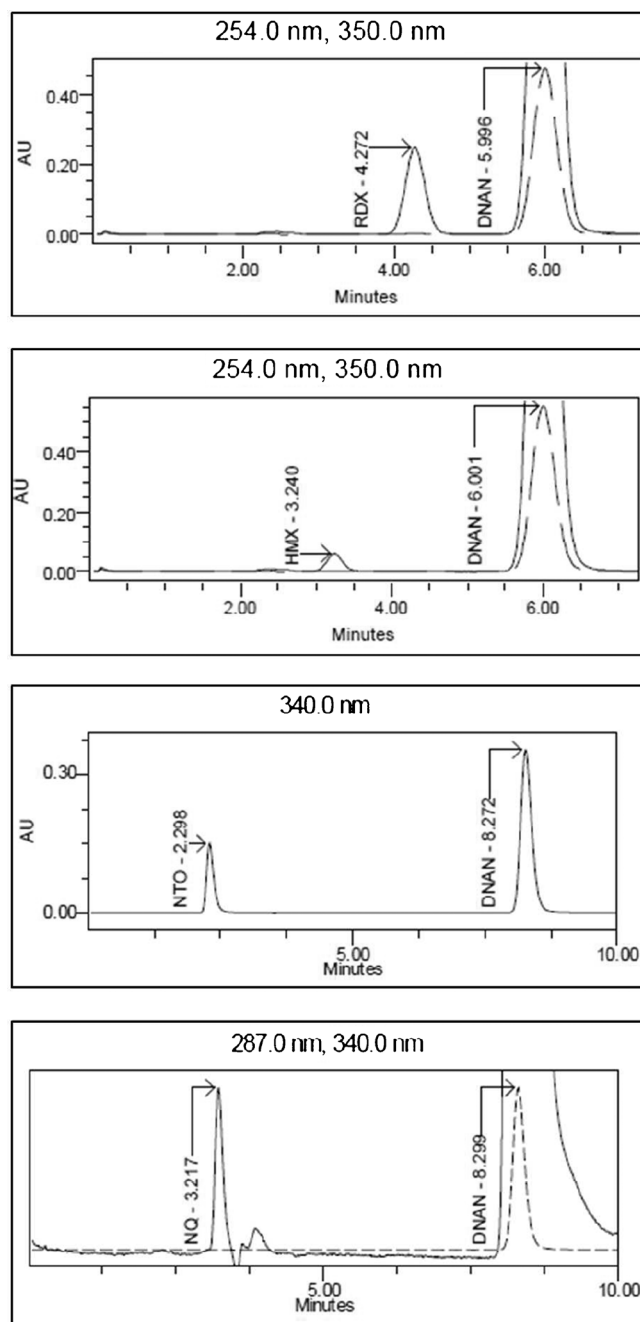


Figure 1. HPLC chromatograms extracted from the PDA detector. From top: Chromatograms of RDX and HMX extracted at 254 nm with DNAN extracted at 350 nm. NTO and DNAN extracted at 340 nm. NQ extracted at 287 nm when analyzed with DNAN extracted at 340 nm; NQ/DNAN chromatograms were normalized to show NQ.

melts, their ratio normalized to a 100 g DNAN basis (3rd column) and the apparent solubility normalized to a 100 g DNAN basis as obtained by chromatography (4th column).

Before average solubilities could be obtained, the apparent solubilities (4th columns in Table 1–5) were compared to the starting ratios (3rd columns) to verify the absence of

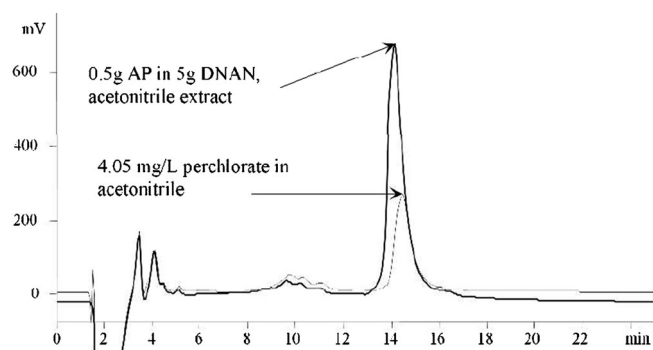


Figure 2. Ion chromatogram of AP in DNAN.

trends between the two. If a true solution was formed in the melt, then there should be no trend beyond the maximum solubility, meaning the solution reaches saturation and no matter how much more solute was put in, the maximum solubility will not change. If however, the solution was actually a suspension, a significant positive trend was expected and additional testing was conducted. Once the absence of trends was verified, an average was determined from the trendless region of solubilities. Chauvenet's criterion was used to handle outliers [6]. Table 6 shows the final solubility results taken as an average of non-rejected data for each energetic constituent stirred in molten DNAN. The

Table 1. Data for the solubility of RDX in molten DNAN.

RDX used in prep [mg]	DNAN used in prep [mg]	Prep RDX/DNAN [g per 100 g]	Solubility RDX/DNAN [g per 100 g]
119	1098	10.8	11.2
119	1098	10.8	11.1
232	1174	19.8	13.6
232	1174	19.8	13.6
249	1077	23.1	13.1
249	1077	23.1	13.2
202	1070	18.9	14.6
202	1070	18.9	14.3
299	1045	28.6	13.8
299	1045	28.6	13.7

Table 2. Data for the solubility of HMX in DNAN.

HMX used in prep [mg]	DNAN used in prep [mg]	Prep HMX/DNAN [g per 100 g]	Solubility HMX/DNAN [g per 100 g]
52	1110	4.7	3.27
52	1110	4.7	3.27
68	1062	6.4	2.95
68	1062	6.4	2.96
83	998	8.3	2.94
83	998	8.3	2.96
109	1013	10.8	2.93
109	1013	10.8	2.91

Table 3. Data for the solubility of NQ in DNAN.

NQ used in prep [mg]	DNAN used in prep [mg]	Prep NQ/DNAN [g per 100 g]	Solubility NQ/DNAN [g per 100 g]
45.0	1093	4.12	0.430
45.0	1093	4.12	0.422
54.0	1117	4.83	0.442
54.0	1117	4.83	0.432
63.0	998	6.31	0.455
63.0	998	6.31	0.465
68.0	1000	6.80	0.442
68.0	1000	6.80	0.469
70.0	1032	6.78	0.458
70.0	1032	6.78	0.449

Table 4. Data for the solubility of NTO in molten DNAN. Trials 3, 4 from Figure 3.

NTO used in prep [mg]	DNAN used in prep [mg]	Prep NTO/DNAN [g per 100 g]	Solubility NTO/DNAN [g per 100 g]
5.2	507.9	1.02	0.198
5.2	507.9	1.02	0.187
15.2	508.2	2.99	0.382
15.2	508.2	2.99	0.226
15.2	507.3	3.00	0.722
15.2	507.3	3.00	0.237
49.8	505.7	9.85	0.262
49.8	505.7	9.85	0.278
49.9	500.5	9.97	0.317
49.9	500.5	9.97	0.417
50.2	501.8	10.0	0.200
50.2	501.8	10.0	0.218
100.4	508.1	19.8	0.208
100.4	508.1	19.8	0.210

Table 5. Data for the solubility of AP in molten DNAN.

AP used in prep [mg]	DNAN used in prep [mg]	Prep AP/DNAN [g per 100 g]	Solubility AP/DNAN [g per 100 g]
15.2	509.7	2.98	0.104
15.2	509.7	2.98	0.106
25.1	504.2	4.98	0.094
25.1	504.2	4.98	0.094
49.8	501.9	9.92	0.080
49.8	501.9	9.92	0.076
50.0	505.4	0.989	0.086
50.0	505.4	0.989	0.102
99.0	499.5	20.0	0.064
99.0	499.5	20.0	0.070

"±" values refer to the standard deviation of each average solubility.

For RDX (Table 1) the preparation ratios ranged from 10.8 to 28.6 g RDX in 100 g DNAN. The first two Table entries are solutions approaching saturation [1], so the preparation ratio and apparent solubility are the same within approx. 3%. The other preparations seem to form saturated solutions, whose RDX concentration is largely invariant with the

Table 6. Estimated solubility results.

Energetic Compound	SOLUBILITY [g per 100 g DNAN, 100 °C]
RDX	13.7 ± 0.2
HMX	3.02 ± 0.05
NTO	0.222 ± 0.009
NQ	0.448 ± 0.005
AP	0.088 ± 0.005

preparation ratio. Therefore, it's reasonable to simply average the eight latter entries.

The preparation and apparent solubility of HMX in DNAN is described in Table 2. The first two solubility entries are different from the rest, which may indicate a small amount of suspended HMX in the sampled aliquot; however they are not different enough to be excluded. HMX appears to be sparingly soluble in DNAN.

Data in Table 3 show the amounts of NQ used for the solubility preparation in DNAN. The data is clustered around 0.45 g per 100 g, but shows a slight positive trend in the apparent solubility of NQ. Because the solubility is low and varies only slightly with the preparation ratio, it's not unacceptable for the purpose of this study to arrive at an average without running additional trials. However, one can estimate the lower solubility bound, without further testing, as the point where the trendline crosses the "preparation ratio equals the apparent solubility" line. This places the lower solubility bound at 0.39 g per 100 g DNAN.

Solubility determinations of NTO in DNAN were particularly problematic. NTO often remained suspended in DNAN, making sampling difficult. Apparent solubility ranged from 0.2 to 6 g per 100 g DNAN (Figure 3) with large variation in the first two trials. In the latter two trials, however, smaller samples were obtained from areas of DNAN clear of suspended matter. The results thus obtained showed much less variation (Table 4). Some obvious outliers, 0.722 and 0.417 g per 100 g DNAN, were omitted from the average. Some statistically less obvious results (0.382 and 0.317 g per 100 g DNAN) were omitted as well, since they likely

represent suspensions. The solubility of NTO is then estimated at 0.2 g per 100 g DNAN.

AP (Table 5) is only slightly soluble in DNAN. The data shows more variation than for the other compounds; a negative trend whose significance is unclear is also present. Since apparent solubility is so low, the results are very sensitive to even the smallest amounts of suspended AP crystals.

3 Experimental Section

3.1 Materials

Energetic materials used in the procedure were synthesized by BAE Systems at Holston Army ammunition plant. The same materials used in the solubility sample preparation were used to make the analytical standards for the chromatography quantification methods. All solvents used were HPLC grade.

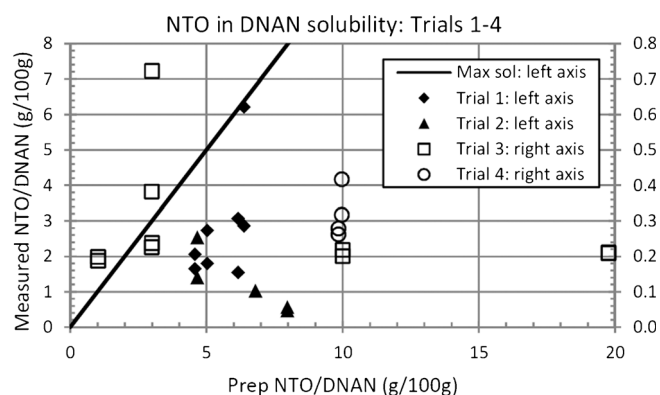
3.2 Procedures and Equipment

The methodology for solubility determination consisted of weighing a known amount of each material using a Mettler Toledo AX205 Delta Range digital balance and distributing the materials into a 16×10 mm Fisher brand disposable test tube. The test tube was suspended in a 400 mL Pyrex beaker containing a water bath at 100 °C and held in place on a Corning hot/stir plate in order to melt the DNAN. When the DNAN was melted, a 1 cm mono-mold stir bar was added to the sample and the stir rate was adjusted to maintain a steady vortex. The sample was stirred for approximately 15 min to allow full dissolution of energetic material into DNAN. Next, the stirring was stopped and the solution allowed to settle for 15 min. A magnifying glass was used to locate a clear portion of the solution. A Kontes Company 14.075 cm thin glass disposable pipette was used to collect the sample in its molten state. (It was observed that after stirring, the remaining unsolubilized material would settle on the bottom of the test tube). The sample was then allowed to cool and solidify. The glass pipette containing the solidified aliquot of material was carefully broken into pieces in order to collect the specimen for analyses.

3.2.1 Chromatography Procedures

NTO and NQ samples in DNAN were analyzed by HPLC with a Waters 2995 with a 2996 PDAD. Duplicate samples (15 mg) were dissolved in 1:1 acetonitrile-DI water (25 mL, v:v), filtered, and 3 µL injections run on a Restek C18 250×2.1 mm 5 µm column at 40 °C with 15:45:40 acetonitrile: water: methanol at 0.2 mL min⁻¹. Detection of NTO and DNAN was at 340 nm, and of NQ at 287 nm.

HMX and RDX samples in DNAN were analyzed by HPLC. Duplicate samples (40 mg) were dissolved in acetonitrile

**Figure 3.** NTO solubility in DNAN results of Trials 1–4.

(25 mL), filtered, and 3 μ L injections run on a Restek PFP 150 \times 2.1 mm 3 μ m column at 40 °C with 45 : 55 water : methanol at 0.2 mL min⁻¹. Detection of HMX and RDX was at 254 nm and of DNAN at 350 nm.

AP samples in DNAN were analyzed by ion chromatography on a Metrohm IC system with 788/818/819/820/830/833 modules. Duplicate samples (100 mg) were dissolved in acetonitrile (25 mL), filtered, and 350 μ L injections made onto a Metrohm Metrosep A Supp 5 150 \times 4 mm column at 35 °C with 1 mL min⁻¹ aqueous 5 mM LiOH/12 mM *p*-cyanophenol. The eluent stream was suppressed before being analyzed by the conductivity detector module; the suppressor was regenerated by 50 mM H₂SO₄. DNAN was determined by difference.

4 Conclusion

A method has been developed to determine solubility limits in molten DNAN. HPLC methods were developed to analyze common organic energetic materials in DNAN. Ion chromatography methodology was employed to determine the solubility of ammonium perchlorate in DNAN. Final results indicate that RDX is considerably soluble in DNAN showing an average solubility of 14 g RDX per 100 g DNAN. HMX was shown to be sparingly soluble with an average of 3 g dissolved per 100 g DNAN. NQ, NTO, and AP demonstrate very low solubility limits in DNAN with AP being the lowest with an average of 0.08 g per 100 g DNAN.

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