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HNS Crystallization Studies

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DEVELOPMENT DIVISION

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ABSTRACT

High purity HNS, on a laboratory scale, has been repeatedly recrystallized from a dual solvent system consisting of acetonitrile and dimethylformamide. The crystalline crop has been subjected to preliminary evaluation of specification requirements.

INTRODUCTION

While investigating the crystallization of HNS from its DMF solution, it was observed that introduction of acetonitrile into an HNS/DMF solution accelerated the crystallization process. Furthermore, the ensuing crystalline product displayed exceptional characteristics. On addition of acetonitrile, CH_3CN, into a hot solution of 2,2', 4,4', 6,6'-hexanitrostilbene (HNS) in N,N-dimethyl formamide (DMF), a crystalline crop of well-defined HNS particles, with a bulk density approaching 0.4 g/cc is produced.

This study was initiated to establish the acetonitrile-DMF volume ratios involved, along with any other physical factors, which influence the crystallization of HNS from this solvent pair.

EXPERIMENTAL

Apparatus:

Reaction Flask	- 500 mℓ, round bottom; 3-neck
Blender	- Waring blender - 2 speed (8000, 15000 rpm)
Stirrer	- Cole Parmer, 4555-20, Dual shaft laboratory stirrer
Stirrer Rod	- Glass (Teflon blade)
Thermometer	- Mercury

Reagents:

HNS	- Chemtronics, HNS-1, Lot 66-48
DMF	- Fisher, D-119; Fisher Certified ACS
Acetonitrile	- Burdick and Jackson, 3867 (Glass distilled)
Other	- All other reagents were best grade available from Fisher Scientific Co.

All processing was promoted with utmost care to preclude material contamination. Clean glassware was employed throughout. Where ground joints were involved, Teflon sleeves were employed, eliminating the use of grease.

Acetonitrile and DMF are completely miscible. HNS is moderately soluble in DMF but its solubility in acetonitrile is negligible; thus, it was of interest to establish solubility values of HNS in compositions of the two solvents. Four solutions (5, 10, 20 and 30% by volume of acetonitrile in DMF) were prepared and cursory solubility values of HNS in this solution were determined at 25, 50 and 70 C. These values are plotted in Fig. 1

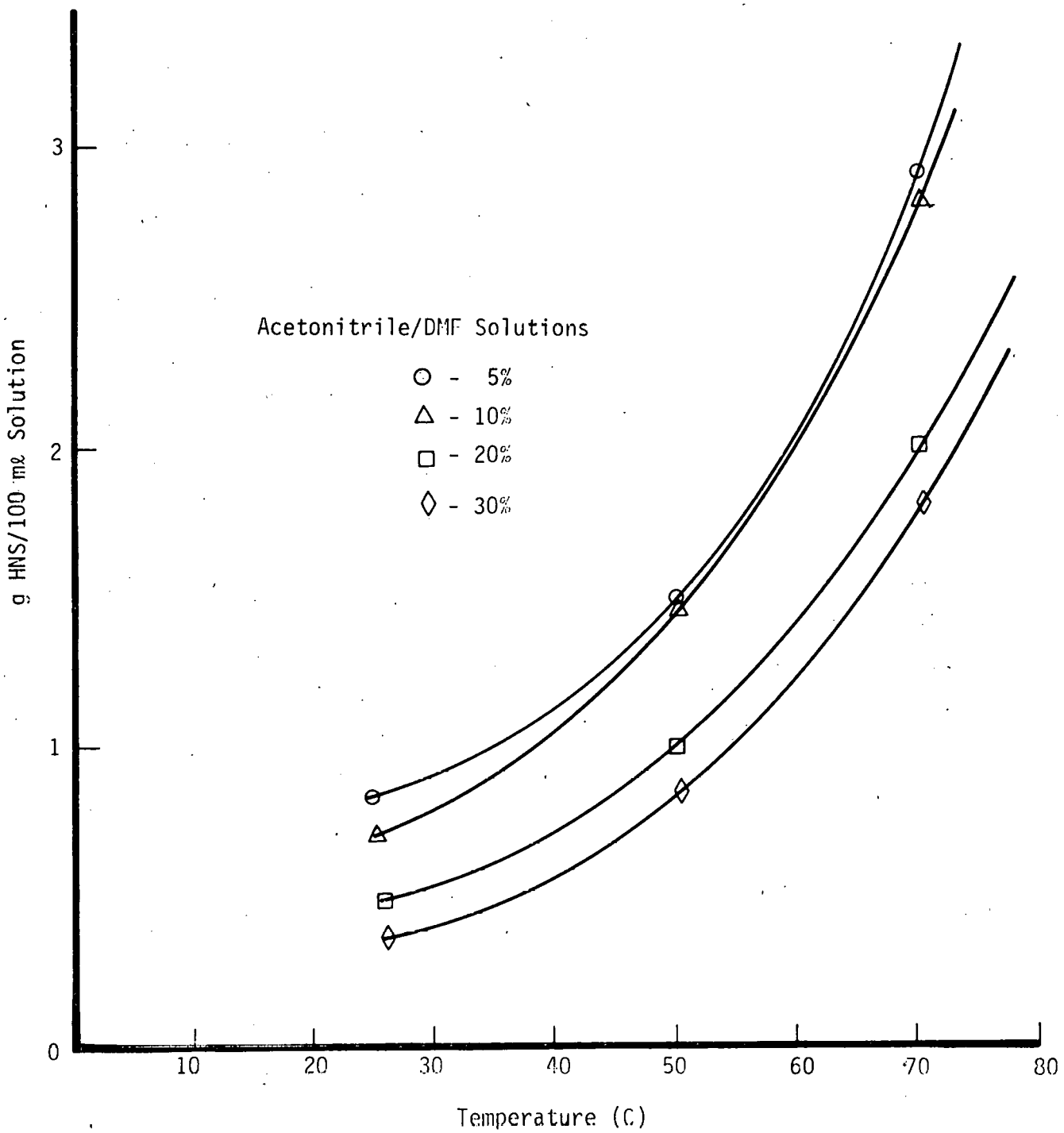

Fig. 1. Solubility of HNS in Acetonitrile/DMF as a Function of Temperature and concentration

which confirms that the HNS solubility rate in an acetonitrile/DMF solution decreases as the acetonitrile content increases.

During this study all of the HNS/DMF solutions (8 g solute/100 mℓ solvent) were treated similarly, except for the quantity of acetonitrile employed. This consisted of volume ratios of 10, 20 and 30 parts of acetonitrile/100 parts of HNS/DMF solution. The acetonitrile was poured in one operation, into the hot solution (105 C). Throughout the process the reaction flask contents were stirred at 325 rpm. Following introduction of the acetonitrile the oil bath was removed and the flask contents were allowed to cool slowly to 40 C, before the ensuing crystalline crop was collected by filtration. The crop (∿ 13 g/effort) was rinsed twice with 75 mℓ acetone (half portion/rinse) and subsequently dried under plant vacuum at 100 C for one hour.

All tests were run in duplicate and in all endeavors, except Sample 10/21/75, the HNS/DMF mixtures were heated over an oil bath until dissolution of the HNS was affected. The ensuing solutions, while hot, were transferred into the reaction flask by suction filtration through a fritted, coarse-porosity, sintered glass funnel.

The HNS involved in test 10/21/75 was also dissolved in DMF at 105 C, but instead of being filtered the solution was allowed to cool to ambient temperature. The precipitated HNS from the cold solvent was collected, rinsed twice with acetone (∿ 40 mℓ/rinse) and dried. This HNS (Sample No. 10/20/75-R) was introduced into the reaction flask and covered with DMF (7 g HNS/100 mℓ DMF). The solution from this mixture, at 105 C, was subsequently treated with acetonitrile.

Following the drying of the crystalline crops, bulk density determinations were made before the HNS particles were transferred into a Waring blender and covered with water (∿ 20 mℓ H_2O/g HNS). Activation of the unit at a fast speed for 5 seconds promoted longitudinal-fracturing of the crystals.

This treatment enhanced the length to width ratio and increased the bulk density to above 0.6 g/cc.

Table I provides a summary of the test conditions involved in this study along with the melting point (DTA) and bulk density determinations of the test samples before and following treatment in the blender.

One sample from each experimental set was selected for preliminary evaluation and each was subjected to analysis by liquid chromatography (Table II), vacuum stability testing (Table III) and particle characterization (Table IV).

Along with the test samples, compositional analyses by liquid chromatography were also determined for Sample No. 10/20/75-R, from which HNS Sample No. 10/21/75 was produced, and for Chemtronics HNS I (66-48) and II (66-47). These analyses are also listed in Table II. Comparison of the compositions of the test samples with that of HNS I (66-48) reveals the degree of purity promoted through utilization of acetonitrile in the crystallization process.

Table I. Test Conditions Involved in Crystallization Endeavor

Sample No.	Solution Concentration (g/100 mℓ HNS/DMF)	CH_3CN/Solution (mℓ/100 mℓ)	Recovery (g)	Yield (%)	Bulk Density (g/cc)	Melting Point (DTA)	Adjusted Bulk Density* (g/cc)
10-15-75-1	6.86	20	10.8	81	0.38	318.0	0.70
10-16-75-1	7.96	20	12.4	79	0.30	317.0	0.64
10-16-75-2	7.93	20	13.0	83	0.39	317.5	0.73
10-16-75-3	7.16	20	10.5	77	0.32	317.5	0.70
10-17-75-1	8.00	10	12.1	77	0.33	319.0	0.68
10-17-75-2	8.00	10	12.1	77	0.36	318.0	0.72
10-20-75-1	7.96	30	13.2	84	0.23	318.0	0.62
10-20-75-2	7.97	30	13.0	83	0.29	317.5	0.57
10-21-75-1	7.00	20	11.6	82	0.43	318.0	0.75
10-21-75-2	7.00	20	11.4	81	0.46	318.0	0.76

**Blender Treated*

Table II. HNS Composition (Liquid Chromatographic)

Sample No.	% Composition		
	Trinitrobenzene	HNS	Dipicrylethane
10-16-75-2	<0.1	99.55 ± 0.01	0.45 ± 0.01
10-16-75-3	<0.1	99.61 ± 0.02	0.39 ± 0.02
10-17-75-2	<0.1	99.51 ± 0.02	0.49 ± 0.02
10-20-75-1	<0.1	99.52 ± 0.04	0.48 ± 0.04
10-20-75-R	<0.1	99.41 ± 0.12	0.59 ± 0.12
10-21-75-1	<0.1	99.90	<0.1
HNS II (66-47)	<0.1	99.67 ± 0.01	0.33 ± 0.01
HNS I (66-48)	<0.1	97.37 ± 0.07	2.63 ± 0.07

Table III. Vacuum Stability at 260 ± 0.5 C*

Sample No.	HNS (g)	Hot Zone Volume (cc)	Temperature Initial (C)	Temperature Final (C)	Pressure Bartherm Initial (mm)	Pressure Bartherm Final (mm)	Volume STP (mℓ/g/20 min)	Volume STP (mℓ/g/hr)
10-16-75-2	0.1999	25.59	23.5	260 ± 0.5	668.3	668.3	0.30	0.22
	0.1991	25.65	23.5		668.3	668.3	0.31	0.22
10-21-75-1	0.1996	25.59	25.0		676.5	677.9	0.04	0.15
	0.1998	25.65	25.0		676.5	677.9	0.04	0.15
10-16-75-3	0.2005	25.59	26.0		678.2	678.2	0.21	0.19
	0.2007	25.65	26.0		678.2	678.2	0.13	0.19
10-17-75-2	0.2005	25.59	24.8		671.9	670.7	0.09	0.19
	0.1999	25.65	24.8		671.9	670.7	0.09	0.16
10-20-75-1	0.1994	25.59	25.0		669.7	667.8	0.26	0.17
	0.2013	25.65	25.0		669.7	667.8	0.17	0.17
10-20-75-R	0.2018	25.59	26.0		675.3	675.3	0.68	0.24
	0.2011	25.65	26.0		675.3	675.3	0.69	0.24
HNS I (66-48)	0.2018	25.59	23.5		675.3	675.3	1.41	0.64
	0.2009	25.65	23.5		675.3	675.3	1.41	0.64

NOTE: Spec Values - Code Ident 1001 (NORL):

(a) mℓ/g/20 min - HNS I, 3.0, Max.; HNS II, 0.6, Max.
(b) mℓ/g/hr - HNS I, 1.1, Max.; HNS II, 0.6, Max.

Table IV. Particle Characterization - Zeiss Analysis

Sample No.	Fisher Sub-Sieve Surface Area (cm^2/g)	Gas Adsorption Surface Area (cm^2/g)	Microscopy Surface Area (cm^2/g)	Length (μm)	Width (μm)	L/W	Cross-Sectional Area (μm^2)	Surface Area (μm^2)	Volume (μm^3)
10-16-75-2	1465	5200	1600	107	48	2.79	5900	15400	87040
10-16-75-3	1435	5415	1320	135	60	2.24	10025	27310	218909
10-17-75-2	1500	5010	1640	118	46	2.69	6045	16845	101825
10-20-75-1	1725	6090	1905	130	43	3.02	6755	18125	98840
10-21-75-1*	1150	3700	1930	135	46	2.77	7625	20165	110725

**Prepared from Sample No. 10-20-75-R.*

The vacuum stability test values for the samples were determined through procedures outlined in Para. 4.5.1.2, Code Ident 10001, WS 5003 F, Naval Ordnance Command (Rev. 5/6/74). These values, listed in Table IV, are the gas volumes, at STP, produced at 260 ± 0.5 C.

Through procedures described herein, HNS quantities of approximately 0.5 kg have been obtained. Some of the test conditions along with some test results of a typical crystallization are tabulated in Table V.

In the crystallization effort, summarized in Table V, the HNS (Chemtronics 66-48) destined for treatment with acetonitrile, was recrystallized once from DMF before it was used. It was introduced into a 10 ℓ reactor and covered with the prescribed DMF (7 g/HNS/100 mℓ DMF). Dissolution of the HNS was effected by heating the mixture to 105 C. The hot solution was emptied into a 40 ℓ stainless steel vessel lined with a double layered Nylon (15° mesh) filter sock, which on removal from the container retained all insoluble foreign matter.

The solution was allowed to cool to ambient and left undisturbed for 16 hours. The recovered crystalline crop, representing 76% of the starting material, was readied for subsequent treatment.

The HNS recovered in the above effort (662 g) and 9.4 ℓ of DMF were introduced into the 10 ℓ reactor, and the mixture (7 g HNS/100 mℓ DMF) was heated to the dissolution temperature (102 C). The steam through the reactor coils was shut off and immediately 1.9 ℓ of acetonitrile was added to the reactor contents. A short lived temperature rise to 106° resulted, but within 30 seconds the temperature had dropped to 99°. Cooling of the reactor contents to 30 C was aided by circulation of tap water through the reactor coils. The resulting cooling rate history, over a 78 minute period is given in Table VI.

The crystallization crop was collected by filtration, washed twice with acetone (1 ℓ/wash) and dried under vacuum at 100 C. A total of 553 g of HNS, with a bulk density of 0.4 g/cc, was obtained. The length to width ratio (2:1) was rather disproportionate; consequently the HNS was transferred to the Cowles Dissolver and covered with ∿ 15 ℓ of distilled water, then the unit was activated for 6 minutes at 2000 rpm. The recovered crop was washed with 3 ℓ of methanol (1 ℓ/wash) and then dried under vacuum at 100 C for 16 hours.

Treatment of the HNS in the Cowles Dissolver improved the crystal length to width ratio. Furthermore, it also increased the bulk density to a value of 0.55 g/cc.

In these endeavors, dissolution of HNS in DMF (7 g solute/100 mℓ solvent) was affected at 105 C and the ensuing solutions were filtered hot to extract fibers and other insolubles from the HNS. The hot solutions were either filtered directly into the crystallization flask or the filtrates were cooled and the resulting precipitates, upon drying, were employed as the starting HNS.

Table V. HNS Recrystallization (Scale-Up)

HNS (g)	DMF (mℓ)	CH_3CN (mℓ)	Recovery (g)	Yield (%)	Bulk Density (g/cc)	Adjusted Bulk Density (g/cc)	Comments
871	12400	-	622	76	0.66	-	Solution* filtered hot through Nylon, 15 μm mesh; left undisturbed 16 hours.
622	9457	1890	553	84	0.40	0.55	Solution cooled to ambient over 78 minutes. Recovered crop treated 6 minutes in Cowles Dissolver.

*Note: *Reactor capacity necessitated 2 dissolution efforts. Solutions combined. (661 g HNS/9400 mℓ DMF; 210 g HNS/3000 mℓ DMF)*

Table VI. Cooling Rate (10 Litre Reactor Contents)

Time (min)	Temperature (C)
0	102
0.25	106
0.50	99
8.0	80
10.0	82
15.0	78
17.0	71
20.0	68
25.0	63
30.0	57
35.0	52
40.0	49
45.0	45
55.0	39
60.0	37
70.0	32
78.0	30

From the compositional analyses listed in Table II it is noted that Sample 10/20/75-R, recrystallized from HNS I (66-48) was not only freed of insoluble contaminants but the solvent (DMF) also retained most of the dipicrylethane. It thus appears that a higher degree of purity, of the recrystallized HNS, is obtained when the starting HNS is subjected to an earlier precipitation from its DMF solution.

From Table IV note that Sample 10/21/75-1, recrystallized from Sample 10/20/75-R has the lowest specific surface area. The same sample exhibits the greatest degree of purity (Table II) and manifests the highest bulk density (Table I). At this time it is uncertain whether there is a relationship between surface area and sample purity.

COMMENTS, CONCLUSIONS

Testing of the HNS recrystallized from the solvent system, as detailed in this report, was abbreviated due to time and funding limitations; however, the data from the preliminary analyses indicate the product is at high quality. All values on the test performed, as reported herein, are within the specification limits as established in Code Ident 1001, WS 5003 F, Naval Ordnance Command (Rev. 5/6/74).