Solubilities of Explosives—Dimethylformamide as General Solvent for Explosives

Michael E. Sitzmann[1] **and Stephen C. Foti**
Naval Ordnance Laboratory, White Oak, Silver Spring, Md. 20910

Solubilities of representative explosives (RDX, HMX, HNS, and DATB) in various solvents are determined in a search for a general solvent for explosives. Dimethylformamide, although it forms a solvate with HMX, appears to be the best choice. Dimethylsulfoxide, butyrolactone, or butyrolactone–dimethylsulfoxide mixtures can be used for HMX. Solubilities of both organic and inorganic explosives (inorganic components of explosives) in dimethylformamide are given.

In recent years, new high-melting explosives have been developed for special applications. For example, 2,2′,4,4′,6,6′-hexanitrostilbene (HNS) was developed for its ability to withstand high thermal environments and has been very useful in the space program. These newly developed explosives often cannot be removed and/or recovered from explosive devices by conventional methods such as steaming, high-pressure water jetting, and machining. A possible alternative for removal of these explosives is by chemical dissolution of the explosive.

Indeed, the chemical dissolution method can, under certain circumstances, be advantageous for explosives in general. For example, many explosives are sensitive especially after degradation resulting from extended storage. Solutions of these explosives would be much less sensitive and could be removed more safely. A general solvent for explosives, i.e., a solvent which would dissolve most or all of the commonly used explosives, would be useful if the chemical dissolution method were to have a wide range of applicability. To find such a solvent, a systematic study of the solubilities of representative explosives in various solvents was undertaken.

Experimental

The procedure used to determine the solubilities is described in the section Solubility Determinations. We estimate that the solubility values obtained by this procedure have uncertainties of ±5%. The solubility values are reproducible within that range at all the temperatures. The temperature control was to ±0.5°C by conventional methods. In view of the fact that our procedure gives only approximate solubility values, temperature precision greater than ±0.5°C was not deemed necessary.

All solvents were used as received from the manufacturer. *N*-methylpyrrolidone (J. T. Baker Chemical Co.) was practical-grade solvent. The other solvents were of reagent-grade quality (Fisher Scientific Co.). The solvents DMSO, DMF, and butyrolactone are quite toxic, and care should be taken not to allow contact of these chemicals with the skin. Special caution should be observed in handling solutions of explosives in DMSO. DMSO has a translocation property which allows material dissolved in DMSO to be rapidly transferred through the skin into the blood stream.

The explosives used in this study were standard military-grade explosives that passed military specifications for purity. The HMX used is the β polymorph of HMX. HMX forms molecular addition compounds (solvates) with NMP and DMF (2). The solvates are less soluble than the original HMX and begin to precipitate soon after the HMX is dissolved. However, precipitation of the solvate is not complete at the end of the 5-min period that is used as a standard in our procedure. Consistent results for the solubility of HMX in NMP and DMF after a 5-min period could not be obtained because of variance in the rate of precipitation of the solvate.

Approach

The solubilities of representative explosives in various solvents at temperatures ranging from 25° to 98°C were determined. The representative explosives included standard military explosives such as cyclotetramethylenetetranitramine (HMX), cyclotrimethylenetrinitramine (RDX), and 2,4,6-trinitrotoluene (TNT), in addition to some of the new high-melting explosives such as 2,2′,4,4′,6,6′-hexanitrostilbene (HNS) and 2,4-diamino-1,3,5-trinitrobenzene (DATB). RDX and HMX are two of the least soluble of the standard explosives, and the new high-melting explosives are much less soluble than either RDX or HMX. If a good solvent were found for RDX, HMX, and the new high-melting explosives, it would probably also be a good solvent for explosives in general. Thus, our search for a general solvent for explosives was conducted with emphasis on the solubilities of RDX, HMX, HNS, and DATB.

The solvents used were from many classes of compounds (acids, amides, amines, esters, ketones, nitriles, nitro compounds, etc.). The better solvents were dimethylsulfoxide (DMSO), dimethylformamide (DMF), *N*-methylpyrrolidone (NMP), and butyrolactone. Solubilities of the representative explosives in these solvents are given in Tables I–IV. The representative explosives are essentially insoluble (<0.5 gram/100 grams at 25°C) in most of the more common solvents such as benzene, chloroform, ethanol, and diethyl ether. Of the more common solvents, acetone is by far the best for these explosives. Solubilities of the representative explosives in acetone are included in Tables I–IV for comparison. Binary solvent mixtures (DMSO–DMF, DMSO–NMP, and DMSO–butyrolactone) were also investigated for the representative explosives. Only for HMX does a binary mixture offer any advantage over the single solvent systems (see Results and Discussion section).

Solubility Determinations

A volume of 10, 20, or 50 ml of solvent was used, depending on the solubility of the explosive, the larger volumes being used for the less soluble explosives. A volume of solvent (measured by pipet) was weighed and stirred at the desired temperature in a water bath. An excess of explosive was added, and the mixture was stirred for a 5-min period. The mixture was filtered rapidly (a heated filter funnel was used for filtration of mixtures above 25°C), and the undissolved explosive was sucked dry on the funnel and then washed with water (the explosives with an appreciable water solubility were insoluble

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[1] To whom correspondence should be addressed.

in either carbon tetrachloride or chloroform and were washed with one of these solvents). The undissolved explosive was dried at 50°C for 16 hr and then weighed. The weight of explosive dissolved in the solvent was taken as the difference between the amount of explosive added to the solvent and the amount of undissolved explosive. The solubilities were calculated as grams of explosive per 100 grams of solvent.

Solubilities over a 30-min period were also determined for a number of the explosives and solvents. These 30-min values were generally the same as those for the 5-min period (Table V). This would indicate that any additional explosive dissolved after the 5-min period is very small, and the 5-min value is an accurate measure of the solubility of the explosive in the solvent.

Taylor and Rinkenbach describe procedures for measuring the solubility of TNT in a number of common organic solvents (*1*). For solvents in which TNT is not very soluble, accurate solubility values were obtained by a wagon-pipet method. For solvents in which TNT is quite soluble, the wagon-pipet method could not be used, and a cooling-curve method was used instead. However, the cooling-curve method gives only approximate solubility values. The solubility of TNT in carbon tetrachloride at 25°C by the wagon-pipet method is 0.82 gram/100 grams. Our method as described above gives 0.8 gram/100 grams. The solubility of TNT in acetone at 25°C is 132 grams/100 grams by the cooling-curve method. Our method yields a value of 130 grams/100 grams. Although the results by our method are admittedly only approximate, they are sufficiently accurate to be of practical value. *It must be emphasized, however, that we do not represent these as true equilibrium solubilities.*

Results and Discussion

Choice of general solvent for explosives. Based on the ability to dissolve the representative explosives, the candidates as a general solvent for explosives should include dimethylsulfoxide (DMSO), dimethylformamide (DMF), and *N*-methylpyrrolidone (NMP). These three solvents dissolve nearly equal amounts of RDX at 25°C, but at higher temperatures DMSO appears to be a slightly better solvent. NMP dissolves more HNS and DATB at 25°C than DMF or DMSO, but at 98°C DMSO dissolves the greatest amounts of these explosives. A disadvantage for NMP and DMF is that they form solvates with HMX. Shortly after HMX is dissolved in NMP or DMF, precipitation of the solvate crystals occurs. Although DMSO (mp 18°C, 65°F) is a good solvent for HMX, a practical disadvantage in certain important situations is that DMSO cannot conveniently be used or stored in cold environments. Attempts to circumvent these disadvantages by using mixtures of DMSO with NMP and DMF were unsuccessful. Although the melting point of DMSO can be depressed by the addition of NMP or DMF, precipitation of the HMX solvate occurs from the mixtures.

Considering all the factors in the choice of a solvent (solubility values, physical properties, cost, availability,

Table I. Solubility of RDX[a]

Solvent	25°C	40°C	60°C	80°C	98°C
Dimethylsulfoxide	41	51	66	87	113
Dimethylformamide	37	45	58	76	96
N-Methylpyrrolidone	40	47	58	72	84
Butyrolactone	14		28	41	61
Acetone	8.2	12	17[b]		

[a] Grams of RDX per 100 grams of solvent after 5 min of stirring. [b] At the boiling point.

Table II. Solubility of HMX[a]

Solvent	25°C	60°C	98°C
Dimethylsulfoxide	57	68	89
Dimethylformamide	Solvate[b]	Solvate	Solvate
N-Methylpyrrolidone	Solvate	Solvate	Solvate
Butyrolactone	12	20	35
Acetone	2.8	4.2[c]	
Butyrolactone (73%), dimethylsulfoxide (27%)	26	33	49

[a] Grams of HMX per 100 grams of solvent after 5 min of stirring. [b] Shortly after the HMX dissolves, precipitation of the solvate crystals occurs. [c] At the boiling point.

Table III. Solubility of HNS[a]

Solvent	25°C	60°C	80°C	98°C
Dimethylsulfoxide	1.4	2.4	3.6	9.1
Dimethylformamide	1.5	3.2	4.6	7.0
N-Methylpyrrolidone	2.4	4.6	6.4	8.4
Butyrolactone	0.4			3.2
Acetone	<0.1	0.4[b]		

[a] Grams of HNS per 100 grams of solvent after 5 min of stirring. [b] At the boiling point.

Table IV. Solubility of DATB[a]

Solvent	25°C	60°C	80°C	98°C
Dimethylsulfoxide	2.2	8.8	14	19
Dimethylformamide	2.5	5.1	9.7	14
N-Methylpyrrolidone	4.5	7.8	11	17
Butyrolactone	0.8			4.8
Acetone	0.4	1.4[b]		

[a] Grams of DATB per 100 grams of solvent after 5 min of stirring. [b] At the boiling point.

Table V. Comparison of Solubilities[a] after 5 and 30 Min of Stirring at 25°C

Explosive	Solvent	5 Min	30 Min
DATB	Dimethylsulfoxide	2.2	2.3
HNS	Dimethylsulfoxide	1.4	1.4
RDX	Dimethylsulfoxide	41	41
RDX	Dimethylformamide	37	36
HMX	Dimethylsulfoxide	57	58
HMX	Butyrolactone	12	13

[a] Grams of explosive per 100 grams of solvent.

Table VI. Solubilities of Explosives in Dimethylformamide[a]

Explosive	0°C	25°C	60°C	80°C	98°C
RDX	27	37	58	76	96
TNT	90	142			
Tetryl[b]	91	114			
HNS		1.5	3.2	4.6	7.0
DATB		2.5	5.1	9.7	14
Ammonium picrate	84	90			
Nitroguanidine		15	20		28
Ammonium nitrate	47	54			
Ammonium perchlorate	46	47			

[a] Grams of explosive per 100 grams of DMF. [b] Tetryl = 2,4,6-trinitrophenylmethylnitramine.

convenience, and toxicity), dimethylformamide appears to be the best choice as a general solvent for explosives. DMSO, butyrolactone, or DMSO–butyrolactone mixtures can be used for HMX. The solubility of HMX in a DMSO–butyrolactone mixture (27% DMSO by weight) is given in Table II. The mixture has mp −30°C (−22°F) and could conveniently be used or stored in cold environments. The mixture is a better solvent for HMX than butyrolactone.

Solubilities of explosives in dimethylformamide are given in Table VI. Solubility values at temperatures above 25°C are listed for explosives which are less soluble than 40 grams/100 grams at 25°C. Solubility values at 0°C are listed for the more soluble explosives. It should be noted that DMF is a good solvent for both organic and inorganic explosives (inorganic components of explosives).

Literature Cited

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Solubility of Silver Sulfate in Acidified Ferric Sulfate Solutions

John E. Dutrizac,[1] **Raymond J. C. MacDonald, and Robert E. Lamarche**
Extraction Metallurgy Division, Mines Branch, Department of Energy, Mines and Resources,
Ottawa, Ont., Canada K1A 0G1

The solubility of silver sulfate in acidified ferric sulfate solutions was investigated over the temperature interval 0–100°C. At constant acid concentration, the solubility increased slightly with increasing ferric ion strengths in the range 0–0.3*M* Fe^{3+}. At a constant ferric ion concentration of 0.1*M* Fe^{3+}, the solubility increased with increasing concentrations of sulfuric acid in the range 0–1.0*M* H_2SO_4. Under conditions of high temperature, low acidity, and high ferric ion concentration, silver precipitated as insoluble silver jarosite ($AgFe_3(SO_4)_2(OH)_6$).

High silver values are frequently encountered in copper sulfide ore deposits, and this silver represents a valuable by-product of copper mining operations. During the dump or heap leaching of low-grade ores (*6*), silver recovery can lag substantially behind that of copper, and the reason for this is not fully understood (*5*). One explanation is that silver sulfate is not very soluble in the acidified ferric sulfate medium generally used for leaching. The solubility of Ag_2SO_4 in water is about 0.03*M* (~10 g Ag_2SO_4/l.) over the temperature interval 0–240°C (*3*). The addition of sulfuric acid substantially increases the solubility of Ag_2SO_4 at all temperatures (*2*).

This observation was shown (*2*) to be consistent with the known temperature dependence of the $HSO_4^- \rightleftarrows H^+ + SO_4^{2-}$ equilibrium constant (*4*) and with the assumption that the solubility of Ag_2SO_4 varied with ionic strength according to a Debye-Hückel type relationship. The solubility of silver sulfate in acidic solutions containing dissolved ferric sulfate is, however, not known. To determine if the poor silver recoveries obtained during the dump leaching of copper ores were caused by inherently low silver solubilities in the leaching medium, the solubility of Ag_2SO_4 in acidified ferric sulfate solutions was determined over the range of temperatures and concentrations likely to be encountered during commercial copper percolation leaching operations.

Experimental

Reagents. Baker reagent-grade silver sulfate was used without further treatment; this material was white and dissolved completely in an excess of water. Test solutions were prepared with distilled water, reagent-grade sulfuric acid, and hydrated ferric sulfate. The ferric sulfate was dissolved in water and filtered before use to remove any insoluble iron residues. The actual acid and ferric ion concentrations of the solutions were determined by standard titration procedures and agreed with the prepared compositions.

Apparatus. Measurements were made with a three-neck flask, closed to the atmosphere except when the solution was being sampled. The contents of the flask were stirred magnetically except during the sampling period. The flask was heated in a temperature-controlled oil bath that was held to within ±0.1°C, and the actual temperature of the solution was measured by an immersed thermometer.

Procedure. One liter of solution of known composition was placed in the three-neck flask, together with an excess of silver sulfate. Depending on the temperature, the contents were then stirred for 8–24 hr to permit the solution to attain saturation equilibrium. After this period, the stirrer was stopped, and the solids were allowed to settle. The solution was then sampled with a calibrated pipet, the end of which was fitted with a filter paper sleeve to minimize the transfer of suspended solids. The contents of the pipet were discharged directly into a weighing bottle which was immediately sealed, brought to room temperature, and then weighed. The pipet was calibrated at each temperature with pure water and the same experimental technique that was employed when sampling the silver saturated solutions.

Ten milliliters of solution were withdrawn for each sample, and the silver content was determined by the standard Volhard titration method. The solution density was calculated from the weight of the aliquot and the volume of the pipet as determined by the water calibration at that temperature. The flask was inspected at each temperature to determine if any iron-bearing compounds had formed by hydrolysis.

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[1] To whom correspondence should be addressed.