Effects of Component Interactions on the Aqueous Solubilities and Dissolution Rates of the Explosive Formulations Octol, Composition B, and LX-14

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The effects of component interactions on aqueous solubilities and dissolution rates were determined for the explosive formulations octol, composition B, and LX-14 and for mixtures of three separate explosive compounds that make up these formulations. Experiments were performed over the temperature range of (10−30)°C at a constant mixing rate of 2.5 revolutions per second (rps), and data were measured using high-pressure liquid chromatography with UV detection. Formulation results are compared to results of nonbound mixtures of individual explosive compounds and to results of explosive compounds studied separately. The solubilities determined for the formulations and the various mixtures were comparable to the solubilities of the explosive compounds studied independently. The dissolution rates of the explosive compounds in various nonbound mixtures were also comparable to the rates determined independently. However, the dissolution rates for explosive compounds in the formulations were generally lower than those determined independently. Correlation expressions are proposed to describe the initial dissolution rates of explosive compounds in the formulations as a function of temperature and solid surface area. Previous solubility correlations are refined by inclusion of the single-component data from this study.

Introduction

Exposure to certain explosive compounds has the potential of causing detrimental human health effects. The U.S. Environmental Protection Agency (EPA) has established lifetime exposure drinking water health advisory limits for 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) at 2, 2, and 400 μg/L, respectively.[1] A key word search of active Superfund sites on the EPA web page for TNT, RDX, and/or HMX identified 22 National Priority List (NPL) locations.[2] Other potential sources of explosive compound contamination are places where explosives have been manufactured, stored, disposed, or used.[3] Of recent interest are explosive compounds in unexploded ordnance (UXO) found on formerly used defense sites that are raising both safety and environmental concerns.[4] There are between 1500 and 7500 possible sites that could contain UXO. Dissolution is the primary method by which solid explosive compounds are made available for transport in the environment, yet information on dissolution kinetics has been limited.[5] Characterizing an explosive compound source with respect to its aqueous dissolution rate and solubility will contribute to environmental models useful for predicting source persistence, conducting risk assessments, and comparing remediation alternatives.

The limited number of correlations describing the aqueous dissolution rates of explosives have, to date, focused on individual compounds without any explosive-to-explosive interactions. Gilcrease et al.,[6] for example, reported the effects of surface area and mixing rate on TNT dissolution rates. We have reported on the effects of surface area, temperature, mixing rate, and pH on the separate aqueous dissolution rates of TNT, RDX, and HMX.[7,8] Using the Lynch, Brannon, and Delfino[7] data and a mixing rate of 2.5 rps, correlations predicting dissolution rates for TNT, RDX, and HMX as a function of temperature were developed as follows:

$$\text{TNT} \qquad \frac{1}{a}\left(\frac{\mathrm{d}m}{\mathrm{d}t}\right) = 7 \times 10^{-5}\mathrm{e}^{(0.0779\theta)} \tag{1}$$

$$\text{RDX} \qquad \frac{1}{a}\left(\frac{\mathrm{d}m}{\mathrm{d}t}\right) = 1 \times 10^{-5}\mathrm{e}^{(0.0779\theta)} \tag{2}$$

$$\text{HMX} \qquad \frac{1}{a}\left(\frac{\mathrm{d}m}{\mathrm{d}t}\right) = 6 \times 10^{-5}\mathrm{e}^{(0.0568\theta)} \tag{3}$$

where the left sides of the equations represent the mass (m) in milligrams of solid explosive dissolved per second (t) per square centimeter of solid surface area (a) and where θ is the temperature in degrees Celsius.

With the exception of a column test performed by Spanggord et al.[9] including both TNT and RDX, explosive compound aqueous solubilities have been studied separately without consideration of explosive-to-explosive interactions. Examples of recently proposed correlations for independently determined explosive compound solubilities as a function of temperature include those of Ro et al.[10] for TNT and Lynch et al.[8] for TNT, RDX, and HMX. The Lynch et al.[8] temperature-based solubility (S) correlations for TNT, RDX, and HMX are

$$\text{TNT} \qquad \ln(S/\mathrm{mg{\cdot}L^{-1}}) = 16.981 - \frac{3607.5\ \mathrm{K}}{T} \tag{4}$$

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$$\text{RDX} \qquad \ln(S/\text{mg}\cdot\text{L}^{-1}) = 19.52 - \frac{4670.9\ \text{K}}{T} \qquad (5)$$

$$\text{HMX} \qquad \ln(S/\text{mg}\cdot\text{L}^{-1}) = 22.835 - \frac{6358.2\ \text{K}}{T} \qquad (6)$$

Independent explosive compounds, however, are generally not expected in a field environment. Of the 22 NPL sites previously mentioned, at least 10 sites contain two or more of the three explosive compounds. In addition, high explosives are not often used in their pure form but rather in explosive formulations. Multiple types of ordnance, containing differing formulations, have been used on training ranges. Explosive formulations are varying blends of explosive compounds with additives such as binders and desensitizers tailored for specific applications. The processes by which formulations are made and/or the presence of more than one explosive compound in the formulation might result in dissolution rates or solubilities different from those predicted by studies using separate explosive compounds. In this paper, we determine the dissolution rates and solubilities of the primary explosive compounds in the formulations known as octol, composition B, and LX-14 and evaluate the applicability of explosive compound dissolution rate and solubility correlations (eqs 1−6) to these formulations. Also evaluated are the dissolution rates and solubilities of military-grade RDX and HMX crystals and TNT flakes in seven different nonbound mixture combinations.

Experimental Section

Chemicals. The Holston Army Ammunition Plant, Kingsport, Tennessee, provided experimental quantities of TNT and the explosive formulations octol and composition B. Picatinny Arsenal, Picatinny, New Jersey, provided experimental quantities of LX-14. Three samples of TNT and eight samples each of composition B and octol were melt-cast into 5.5-cm-diameter disk-shaped molds with an average thickness of (0.88 ± 0.08) cm at the Holston plant. Octol is the formulation name given to a bound mixture of HMX and TNT.[11] The octol used here consisted of 70% by mass HMX and 30% by mass TNT. Composition B is a bound mixture of TNT and RDX that might also include a wax desensitizer.[11] Composition B consisted of 59.5% by mass RDX, 39.5% by mass TNT, and 1% by mass wax. Both octol and composition B are prepared by stirring into melted TNT the other components of the formulation and, after mixing, allowing the resulting formulation to solidify. LX-14 is a plastic-bonded explosive consisting of 95.5% by mass HMX and 4.5% by mass polyurethane that is trademarked as Estane. LX-14 is prepared by mixing the polyurethane (dissolved in a solvent) with a slurry of HMX and water, removing the water and solvent, and allowing the polyurethane to lacquer coat the HMX in granule shapes.

Experimental quantities of weapons-grade RDX and HMX crystals and TNT flakes were provided by the Environmental Processes and Engineering Division of the Engineer Research and Development Center, U.S. Army Corps of Engineers Waterways Experiment Station, Vicksburg, Mississippi. These explosive compounds were used separately and in the preparation of the nonbound explosive mixtures to compare with the explosive compounds in the formulations. Even though the quantities of explosive compounds used in this study were small, health precautions to protect against inhalation and electrical grounding to protect from detonation by electrostatic charge were used. Demineralized water (reverse osmosis) served as the experimental solvent.

Procedure. *Solubility.* The experimental procedure for solubility is outlined in Lynch et al.[8] A nonbound mixture of individual explosive compounds was prepared by adding together excess (quantities greater than the expected solubility) amounts of RDX and HMX crystals and TNT flakes. Solubility tests for each formulation were run separately using sufficient amounts of formulation to ensure excesses each explosive component. The solvent used for all experiments was 200 mL of demineralized water in a 250-mL Erlenmeyer flask. The first experiment, conducted at a temperature of (29.0 ± 2.2) °C, compared the solubility of each explosive compound in a formulation to that of each explosive compound independently. A second experiment, conducted at a temperature of (26.3 ± 0.2) °C, compared the solubilities of the three explosive compounds in the mixture to those of each explosive compound independently. Formulation and mixture experiments were performed in triplicate.

Dissolution Rate. The procedure for the dissolution rate experiments is outlined in Lynch et al.,[8] with one modification. The width of the formulation disks required that the mold be added first to the beaker and that the 500 mL of water be added subsequently at time zero while the stirring propellers were turning. For the runs involving mixtures, sufficient masses of RDX, HMX, and TNT to provide 6 cm^2 of surface area each were added together according to the particular mixture requirements of the experimental run. A binder, either Indramic wax or polyurethane Estane (1.5 cm^2 each) was also added to selected mixtures to mimic the components of composition B and LX-14. In addition, both Indramic wax and polyurethane Estane were added to one mixture containing all three explosive compounds. Each experimental run was performed in triplicate.

Equipment. Samples (1 mL each) were immediately passed through a 0.45-μm Millipore filter and combined with an equal amount of 0.45-μm-filtered acetonitrile in preparation for HPLC analysis. Vials containing the sample and acetonitrile were sealed with a Teflon-faced silicone rubber cap, and their contents were mixed using a vortex mixer for 5 s and then stored quiescently in the dark for at least 25 min before analysis. Analyses were performed using a Waters HPLC running a Millennium Software package with a model 486 tunable detector ($\lambda = 245$ nm) and auto sampler, in accordance with Method 8330.[12] A reverse-phase eluent (50:50 methanol and water) was used in the HPLC system. The analytical column was a 25 cm × 4.6 mm, 5-μm Supelco LC-18 reverse-phase HPLC column. The HPLC was calibrated using a seven-point calibration curve. A sample replicate, blank, and check standard were included in each analytical run. Percent recoveries were 99.1%, 99.5%, and 99.0% for TNT, RDX, and HMX, respectively. The average percent differences between replicate analyses for TNT, RDX, and HMX were 5.1% (standard deviation of 3.7, 92 samples), 7.0% (standard deviation of 5.3, 71 samples), and 3.8% (standard deviation of 3.1, 89 samples), respectively.

Results and Discussion

Dissolution Rates of High Explosive Compounds. The dissolution rates for all analytical runs were recorded in units of milligrams per second per square centimeter of solid surface area to normalize for the variations in solid surface area. TNT, RDX, and HMX were run independently, in addition to being run in the formulations and mixtures, to serve as a basis for comparison of the dissolu-

Table 1. Dissolution Rates, *r*, of Explosive Compounds Measured Separately and in Mixtures (mg s^{-1} cm^{-2}) Stirred at 2.5 rps and Measured at Temperatures Indicated

	10^5 r/(mg s^{-1} cm^{-2})								
	θ = 10 °C			θ = 20 °C			θ = 30 °C		
constituent[a]	TNT	RDX	HMX	TNT	RDX	HMX	TNT	RDX	HMX
pure	15			27			60		
pure	16			25			52		
pure	14			18			60		
pure		2.8			5.3			10	
pure		2.4			5.6			11	
pure		2.4			5.2			10	
pure			5.6			14			37
pure			8.0			14			32
pure			6.6			18			38
mix	14	2.4		28	5.0		69	9.6	
mix	13	2.3		33	5.0		57	11	
mix	14	2.6		21	5.6		57	10	
mix		2.4	7.0		4.9	17		11	51
mix		2.6	8.2		5.3	15		10	33
mix		2.4	7.6		5.3	12		11	37
mix	16		7.6	31		18	57		45
mix	16		7.2	29		16	58		34
mix	15		7.7	31		14	61		36
mix	16	2.4	8.4	31	5.3	24	73	9.1	50
mix	16	2.4	8.3	31	5.4	16	62	8.1	37
mix	14	2.3	8.3	33	4.8	19	63	9.6	38
mix + W	18	2.5		32	5.5		63	9.4	
mix + W	15	2.7		31	5.6		67	11	
mix + W	16	2.4		34	6.3		65	11	
pure + P			10			20			33
pure + P			8.3			14			32
pure + P			9.1			17			49
mix + W + P	16	2.2	12	32	4.4	20	67	9.8	37
mix + W + P	15	2.2	9.3	29	5.4	17	67	9.2	46
mix + W + P	17	2.2	11	34	4.7	19	68	9.8	50

[a] W and P indicate addition of wax and polyurethane, respectively, to the explosive compounds.

Table 2. Dissolution Rates, *r*, of Explosive Compounds Found in Formulations and TNT Mold Measured at Temperature Indicated and Mixed at 2.5 rps

10^5 r/(mg s^{-1} cm^{-2})								
θ = 10 °C			θ = 20 °C			θ = 30 °C		
TNT	RDX	HMX	TNT	RDX	HMX	TNT	RDX	HMX
			TNT mold					
7.4		0.092	19		0.47	36		0.24
7.6		0.093	21		0.52	43		0.35
8.5		0.071	23		0.50	43		0.19
			LX-14 mold					
		0.48			0.91			2.8
		0.46			0.94			2.8
		0.41			0.93			2.7
			octol mold					
6.4		0.22	16		0.48	30		0.81
7.2		0.22	16		0.48	34		1.0
7.4		0.24	15		0.48	34		1.1
			composition B mold					
5.1	1.1	0.19	9.9	2.1	0.37	18	2.8	0.40
5.3	1.3	0.21	13	2.6	0.48	20	4.3	0.75
4.9	1.3	0.20	12	2.7	0.49	23	4.6	0.82

tion rate. The dissolution rates for the various mixtures and separate compounds at 2.5 rps and three temperatures are summarized in Table 1. The dissolution rates for the formulations in the form of molds at 2.5 rps and three temperatures are summarized in Table 2.

The dissolution rate for each explosive compound in a specific mixture compared well with the dissolution rate of that particular explosive compound alone. Overall, RDX showed the smallest variance in dissolution rate between the highest and lowest values of the three runs, with a difference averaging less than 0.000017 mg s^{-1} cm^{-2}. It was followed by HMX, with an average difference of less than 0.000083 mg s^{-1} cm^{-2}, and TNT, with an average difference of less than 0.00017 mg s^{-1} cm^{-2}. TNT consistently exhibited the highest dissolution rates at each temperature, followed sequentially by HMX and RDX. The dissolution rates of the various explosive compounds determined at one temperature did not overlap, regardless of the mixing conditions.

The dissolution rates for a specific explosive compound across the different mixtures were similar. Although still relatively small, the greatest difference in dissolution rates existed between runs of an explosive compound alone and in the two mixtures containing all three explosive compounds. Of the three explosive compounds, TNT exhibited the largest variations in dissolution rate among the various runs (Figure 1). In general, the dissolution rates for TNT and HMX in the two mixtures containing all three explosive compounds were somewhat higher than the rates for the respective compounds run separately, whereas for RDX, the dissolution rates in the mixtures were somewhat lower than those measured for RDX run separately.

The difference between the dissolution rate of an explosive compound determined in a three explosive compound mixture and the rate of this compound determined individually might be partially explained by the physical interactions taking place in the reaction beaker. The increased mass of explosive compounds in a fixed volume of water results in increased solid-to-solid frictional contact. This friction might increase the dissolution rates for TNT and HMX by exposing more surface area. RDX crystal dissolution rates, however, are slightly suppressed in these mixtures (Table 1). This suppression might be partially explained by the observation that RDX crystals routinely

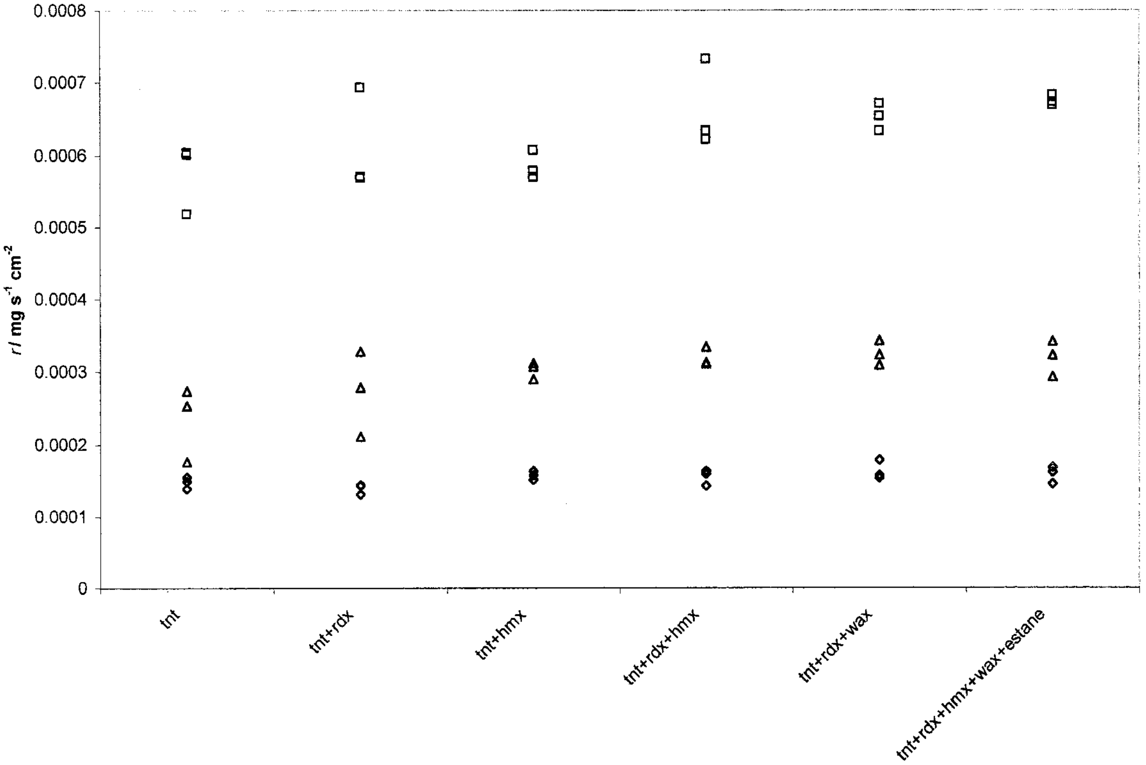

Figure 1. Comparison of TNT dissolution rates individually and in various nonbound mixtures at various temperatures: □, 30 °C; △, 20 °C; and ◇, 10 °C.

converge to the beaker's bottom center and are shielded by the TNT flakes.

Taking the physical interactions among explosives into account, experimental results indicate that the presence of more than one independent explosive compound in a single solution does not significantly affect individual compound dissolution rates. Dissolution rate data from the experiments where the explosive compounds were run independently were combined with earlier data[7] to update the accuracy of the correlations presented in eqs 1−3 as follows:

$$\text{TNT} \qquad \frac{1}{a}\left(\frac{\mathrm{d}m}{\mathrm{d}t}\right) = 7 \times 10^{-5} \mathrm{e}^{(0.0755\theta)} \qquad (7)$$

$$\text{RDX} \qquad \frac{1}{a}\left(\frac{\mathrm{d}m}{\mathrm{d}t}\right) = 1 \times 10^{-5} \mathrm{e}^{(0.0762\theta)} \qquad (8)$$

$$\text{HMX} \qquad \frac{1}{a}\left(\frac{\mathrm{d}m}{\mathrm{d}t}\right) = 5 \times 10^{-5} \mathrm{e}^{(0.0635\theta)} \qquad (9)$$

To determine whether the formulations had any effect on the dissolution rates, surface areas were back-calculated from the multivariable dissolution rate equations presented in Lynch et al.[8] and compared to the actual formulation surface areas available. The three TNT molds served as a second standard for comparison because the surface areas for the military-grade flakes and crystals are estimated values.[7] HPLC analysis of the TNT molds, however, revealed that they were contaminated with small amounts of HMX, most likely occurring during the melt-pour process. This contamination was considered in the overall surface area analysis.

Judging from the dissolution rate results for the prepared molds, the formulation constituents appear to be relatively well mixed. Using the results from the three molds analyzed at each temperature for octol and LX-14, the average percent difference between the high and low dissolution rates was mostly below 20%, whereas for composition B, the average percent difference was 30% (Table 2). The use of an average of the three dissolution rates for each formulation in these experiments should yield representative dissolution rates applicable to other samples containing these formulations.

Table 3. Formulation Dissolution Rate (mg s^{-1} cm^{-2}) Correlations and r^2 Values for Explosive Compounds Mixed at 2.5 rps as a Function of Temperature over the Range (10−30) °C

compound	formulation/correlation	r^2
	octol	
TNT	$3 \times 10^{-5}\mathrm{e}^{(0.0769\theta)}$	0.99
HMX	$1 \times 10^{-6}\mathrm{e}^{(0.0728\theta)}$	0.98
	composition B	
TNT	$3 \times 10^{-5}\mathrm{e}^{(0.069\theta)}$	0.97
RDX	$7 \times 10^{-6}\mathrm{e}^{(0.0574\theta)}$	0.90
	LX-14	
HMX	$2 \times 10^{-6}\mathrm{e}^{(0.0903\theta)}$	0.98

The processes used in the preparation of octol, composition B, and LX-14 appear to have affected the dissolution rates of certain explosive compounds. A comparison of TNT dissolution rates is presented in Figure 2. The separately determined TNT dissolution rates (TNT flakes) proceeded the fastest, followed sequentially by TNT in the TNT molds, TNT in the octol molds, and TNT in the composition B molds. The comparison of HMX dissolution rates is presented in Figure 3. The separately determined crystalline HMX dissolution rates greatly exceeded those in the formulations (e.g., at 30 °C, HMX has a mean dissolution rate of 0.000354 mg s^{-1} cm^{-2}, which is more than an order of magnitude higher than the highest HMX rate reported for the formulations) and are above the range presented in Figure 3. The HMX crystalline dissolution rates are sequentially followed by HMX in the LX-14 granules, HMX

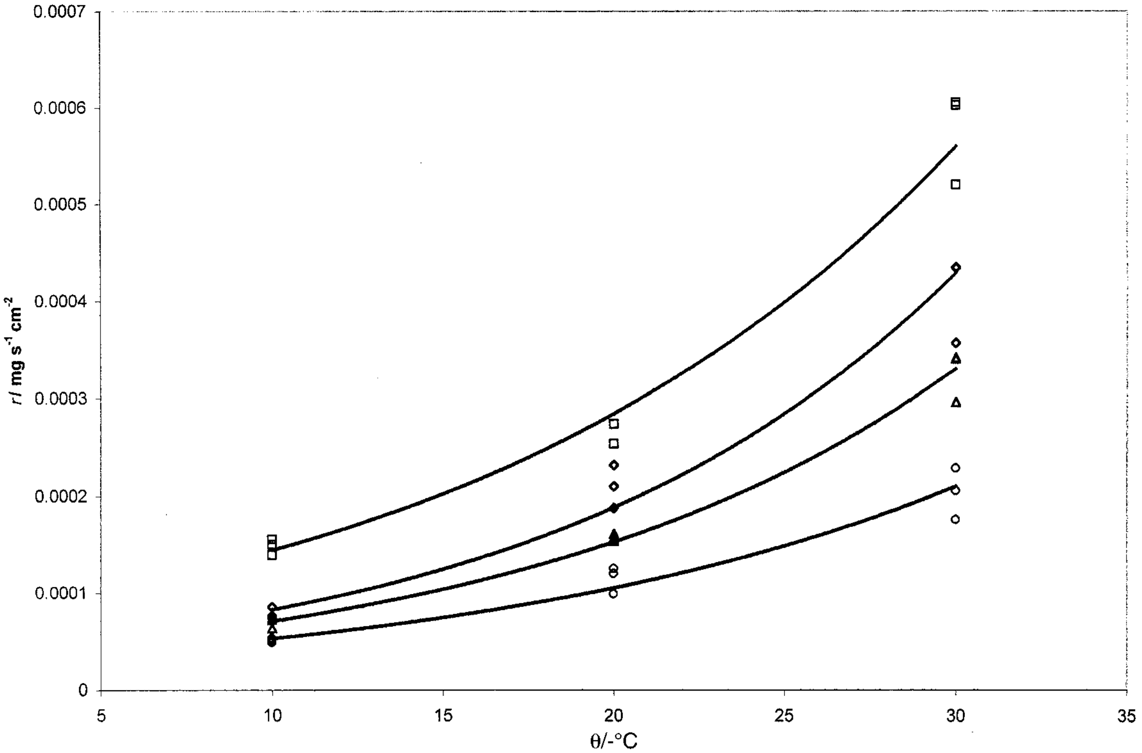

Figure 2. Comparison of TNT dissolution rates among the various experimental runs at 2.5 rps: □, TNT flakes; ◇, TNT in TNT mold; △, TNT in octol; ○, TNT in composition B.

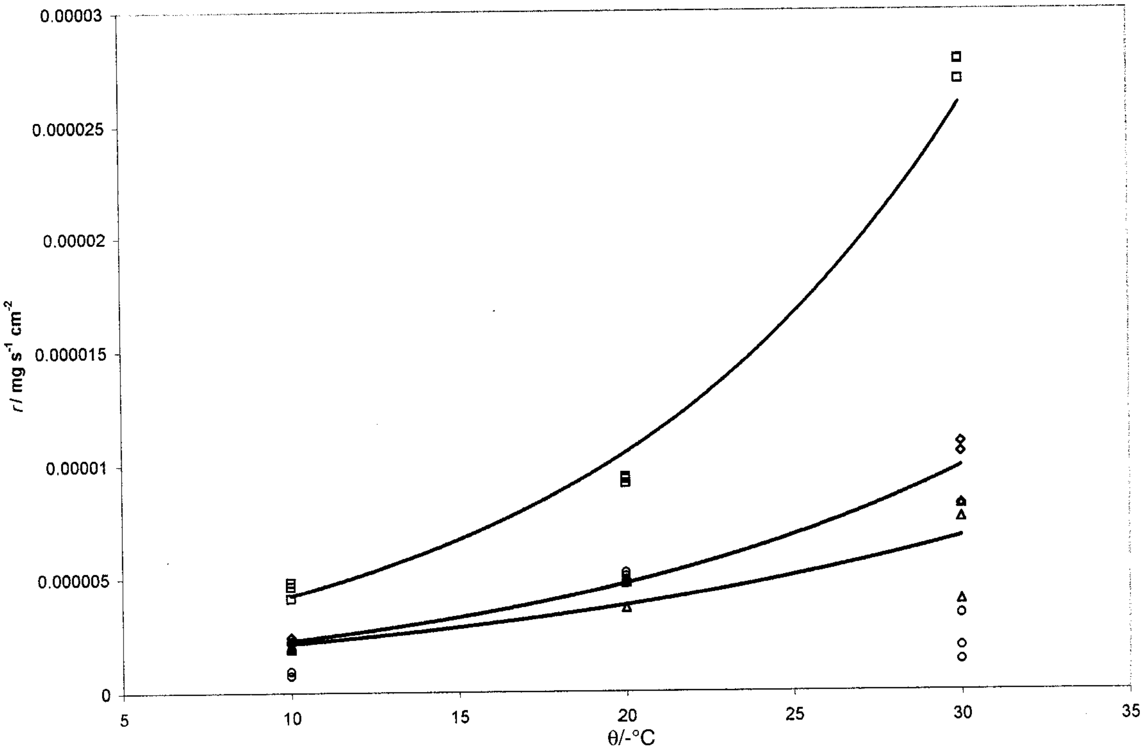

Figure 3. Comparison of HMX dissolution rates among the various experimental runs at 2.5 rps: □, HMX in LX-14; ◇, HMX in octol; △, HMX in composition B; ○, HMX in the TNT molds. Note: The HMX crystal dissolution rate exceeds the range shown on this graph.

in the octol molds, and HMX in the composition B molds. It should be noted that the TNT molds were reused to determine dissolution rates at each temperature starting with the 20 °C experiment. HMX dissolution rates from these molds at 30 °C are lower than those seen at 20 °C, indicating that the HMX availability decreased as the experimentation progressed. A comparison of RDX dissolution rates is presented in Figure 4. The separately determined crystalline RDX dissolution rates were greater than those of RDX in the composition B molds. Initial dissolution rate correlations for the explosive compounds in the formulations are presented in Table 3.

Using surface area comparisons, both the TNT and HMX dissolution rates in octol were suppressed, with calculated

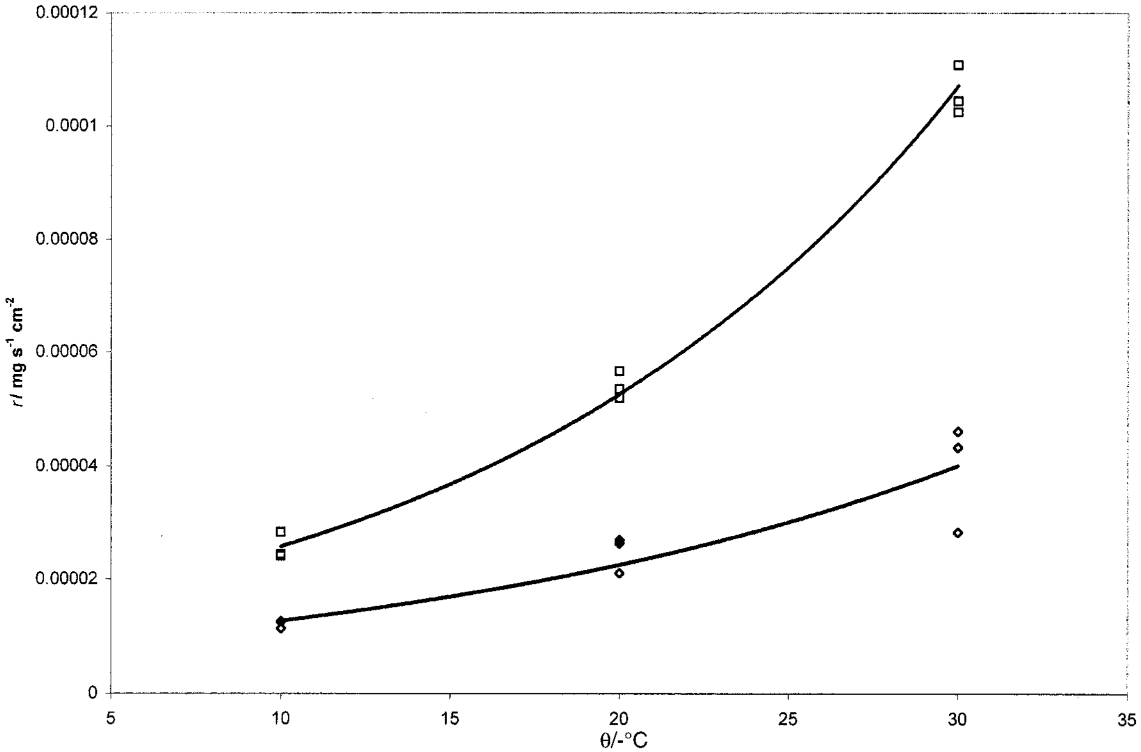

Figure 4. Comparison of RDX dissolution rates between RDX crystals and RDX in composition B at 2.5 rps: □, RDX crystals; ◇, RDX in composition B.

Table 4. Solubilities of Explosive Compounds Determined Independently and in a Nonbound Mixture with Correlation Predictions and the Average Percent Difference (APD) between Measurements and Predictions

	TNT			RDX			HMX		
θ/°C	predicted S/(mg L^{-1})	actual S/(mg L^{-1})	APD %	predicted S/(mg L^{-1})	actual S/(mg L^{-1})	APD %	predicted S/(mg L^{-1})	actual S/(mg L^{-1})	APD %
explosive compounds run independently									
26.3	136.07	128.87	5.44						
26.3	136.07	127.06	6.85						
26.3	136.07	126.34	7.42						
26.3	136.07	127.02	6.88						
26.5				50.32	52.74	−4.69	4.99	4.52	9.94
26.6				50.60	52.52	−3.73	5.03	4.50	11.06
26.6				50.60	51.68	−2.10	5.03	4.46	12.03
26.3				49.77	53.47	−7.18	4.92	4.56	7.63
26.2							4.88	4.54	7.31
26.3							4.92	4.48	9.31
26.3							4.92	4.46	9.67
25.9							4.77	4.64	2.76
explosive compounds run in a nonbound mixture									
26.0	134.36	125.82	6.57	48.95	51.61	−5.29	4.81	4.53	5.96
26.2	135.50	127.51	6.07	49.49	51.86	−4.67	4.88	4.57	6.52
26.2	135.50	129.91	4.21	49.49	53.08	−7.00	4.88	4.63	5.22
26.0	134.36	129.18	3.93	48.95	52.20	−6.43	4.81	4.51	6.32

surface areas totaling less than the areas actually available on the molds. Even though it comprised only 30% of the total mass of octol, TNT accounted for more mold surface area than did HMX. In the composition B molds, RDX accounted for most of the predicted total formulation surface area, followed by TNT and then HMX. The sample of 5 cm^2 of LX-14 yielded a dissolution rate similar to that of 0.3 cm^2 of HMX crystals under similar conditions.

Estimations of the activation energies for dissolution based on the Arrhenius equation were made for each explosive compound (as a formulation component and separately). The calculated activation energies are lower for all explosive compounds in composition B (49 kJ mol^{-1} for TNT, 41 kJ mol^{-1}for RDX, and 41 kJ mol^{-1} for HMX) than for the compounds independently (51 kJ mol^{-1} for TNT, 53 kJ mol^{-1} for RDX, and 52 kJ mol^{-1} for HMX). Calculated activation energies for HMX in LX-14 (64 kJ mol^{-1}) and TNT in octol (55 kJ mol^{-1}) are higher than those determined independently.

Solubility of High Explosive Compounds. A mixture of the three explosive compounds was prepared to investigate explosive-to-explosive interactions, if any, when more than one independent compound was present in a solution. The solubility data for the explosive compounds studied independently and in the mixture are summarized in Table 4. As described in the Chemicals section, the formulations provided unique opportunities to explore (a) the formulation processes, (b) explosive-to-explosive binding, and (c)

Table 5. Solubilities of Explosive Compounds in Formulations Compared to Correlation Predictions with Average Percent Difference[a]

	TNT			RDX			HMX		
θ/°C	predicted S/(mg L^{-1})	actual S/(mg L^{-1})	APD %	predicted S/(mg L^{-1})	actual S/(mg L^{-1})	APD %	predicted S/(mg L^{-1})	actual S/(mg L^{-1})	APD %
				octol					
30.2	160.41	145.95	9.44	61.77	0.42	197.32	6.62	5.90	11.56
30.2	160.41	146.54	9.04	61.77	0.38	197.55	6.62	5.76	13.88
30.2	160.41	156.26	2.62	61.77	0.41	197.35	6.62	6.14	7.57
30.4	161.77	156.65	3.22	62.46	0.67	195.77	6.72	5.94	12.33
31.4	168.75	144.87	15.23	66.01	0.43	197.42	7.25	6.38	12.87
31.5	169.46	156.86	7.72	66.38	0.43	197.41	7.31	6.48	12.02
31.2	167.33	169.10	−1.06	65.29	0.72	195.66	7.14	6.56	8.51
				composition B					
26.5	137.23	141.19	−2.85	50.32	57.23	−12.85	4.99	5.00	−0.06
26.3	136.07	137.83	−1.29	49.77	54.68	−9.41	4.92	5.04	−2.46
26.3	136.07	142.21	−4.41	49.77	56.48	−12.64	4.92	5.14	−4.50
26.1	134.93	134.38	0.40	49.22	53.50	−8.35	4.84	4.69	3.25
27.5	143.14	137.81	3.80	53.19	54.94	−3.24	5.39	5.07	6.05
27.5	143.14	136.75	4.57	53.19	54.34	−2.14	5.39	5.08	5.81
27.1	140.74	140.46	0.20	52.02	55.68	−6.80	5.23	4.99	4.67
				LX-14					
30.6				63.15	0.36	197.71	6.82	6.08	11.53
30.2				61.77	0.39	197.48	6.62	6.18	6.86
30.2				61.77	0.39	197.48	6.62	6.14	7.51
30.3				62.11	0.37	197.64	6.67	5.83	13.40
31.5				66.38	0.37	197.79	7.31	6.79	7.32
31.2				65.29	0.36	197.81	7.14	6.20	14.20
31.9				67.87	0.38	197.77	7.53	6.79	10.37

[a] Deviations in predicted solubility and actual concentration (i.e., APD > 100%) indicate that insufficient explosive compound was present in the beaker to reach solubility.

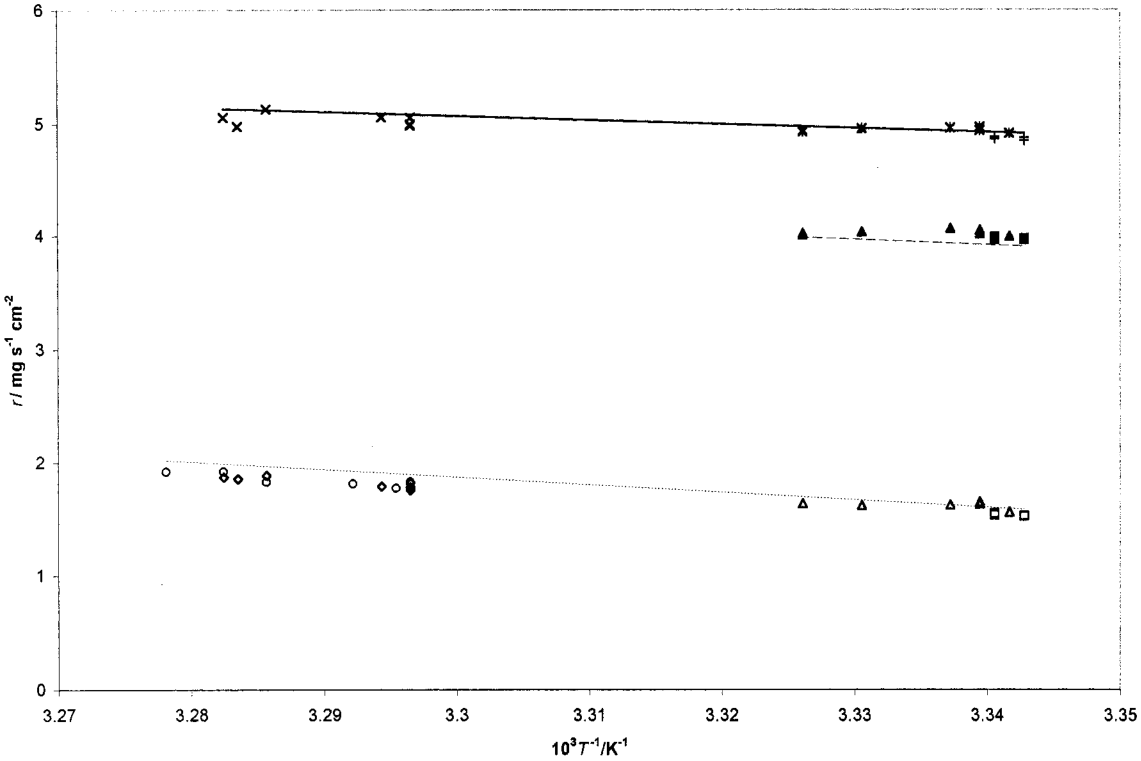

Figure 5. Comparison of measured explosive compound solubility to that predicted by eqs 4−6 at 2.5 rps: —, eq 4; +, TNT in mixture; ×, TNT in octol; *, TNT in composition B; — —, eq 5; ■, RDX in mixture; ▲, RDX in composition B; · · ·, eq 6; □, HMX in mixture; ◇, HMX in octol; ○, HMX in LX-14; △, HMX in composition B.

explosive-to-binder binding effects on solubility. The solubility data for each explosive compound in each formulation are summarized in Table 5.

None of the combinations studied, either in the formulations or as a mixture, resulted in significant changes in explosive compound solubility compared with those of the separate explosive compounds. In addition, the experimental solubility values compared well with those predicted by eqs 4−6 (Tables 4 and 5 and Figure 5). Independently run solubility results from the current study were combined with the original correlation data[7] to produce new correlations based on a larger data set. The revised solubility correlations as a function of temperature for TNT, RDX, and HMX are presented below:

$$\text{TNT} \qquad \ln(S/\text{mg}\cdot\text{L}^{-1}) = 16.793 - \frac{3556.3\ \text{K}}{T} \tag{10}$$

$$\text{RDX} \qquad \ln(S/\text{mg}\cdot\text{L}^{-1}) = 19.683 - \frac{4715.4\ \text{K}}{T} \tag{11}$$

$$\text{HMX} \qquad \ln(S/\text{mg}\cdot\text{L}^{-1}) = 22.399 - \frac{6236.7\ \text{K}}{T} \tag{12}$$

The results of this study will aid in the modeling of fate and transport of these explosive compounds and have been included in the analysis of three models designed to predict persistence and flux.[13] HPLC measurements identified more compounds than expected in the formulations and military-grade explosives. The military-grade RDX used in this study contained sufficient HMX to allow the HMX, itself, to reach its solubility in solution. TNT contained detectable quantities of its photodegradation byproduct, trinitrobenzene. LX-14 samples contained detectable quantities of RDX. Composition B contained sufficient quantities of HMX to allow the latter to reach saturation in solution and also contained detectable amounts of trinitrobenzene, dinitrobenzene, and 2,4-dinitrotoluene. Octol contained detectable quantities of RDX and trinitrobenzene. These findings are important considerations in studies of source characterization at field sites containing these explosive compounds and formulations.

Conclusions

Solubilities and dissolution rates of TNT, RDX, and HMX were not significantly affected by the presence of more than one of these separate explosive compounds in the same solution. TNT, RDX, and HMX solubilities were not significantly affected when these explosive compounds were components in explosive formulations. The formulation production process affects dissolution rates of the explosive compounds in the formulations. Dissolution rates are suppressed in LX-14 and octol and are mostly unaffected in composition B.

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