

Effects of pH and Temperature on the Aqueous Solubility and Dissolution Rate of 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)

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Aqueous solubilities and dissolution rates are reported and examined 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) over the pH range of (4.2–6.2) and the temperature range of (3.1–33.3) °C. Measurements were performed using high-pressure liquid chromatography with ultraviolet detection. Solubilities and dissolution rates were not statistically affected by pH within the experimental design limits. Correlations are proposed to estimate the aqueous solubility of these high explosives as a function of temperature.

Introduction

High-explosive compounds such as 2,4,6-trinitrotoluene (TNT), cyclotrimethylenetrinitramine (RDX), and cyclotetramethylenetetranitramine (HMX) have entered the environment from sites where they were manufactured, stored, disposed, or used in military training.¹ TNT has been associated with liver and blood damage, anorexia, and anemia. RDX and HMX have been associated with systemic poisoning usually affecting bone marrow and the liver. Both TNT and RDX have been classified as possible human carcinogens, whereas HMX is not yet classified as to its human carcinogenicity.^{2–4} Understanding the factors that affect the environmental fate of these compounds and the possible routes for human exposure is important.^{5,6}

Environmental factors such as temperature and pH can affect solubility and therefore chemical fate and toxicity.⁷ If ideal conditions are assumed, solubility can be estimated using the equation⁸

$$\ln x_B = -\left(\frac{\Delta_{\text{fus}}H}{R}\right)\left(\frac{1}{T} - \frac{1}{T^*}\right) \quad (1)$$

where x_B = mole fraction of solute, $\Delta_{\text{fus}}H$ = enthalpy of fusion of solute, R = ideal gas constant, T = absolute temperature, and T^* = solute melting temperature. Aqueous solutions of explosive compounds are not ideal, but the general equation remains similar following the form

$$\ln S = A - \frac{B}{T} \quad \text{or} \quad S = A^* \exp\left(\frac{-B}{T}\right) \quad (2)$$

where S = solubility and A and B = arbitrary constants.

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Taylor and Rinckenbach⁹ conducted one of the earliest studies on the aqueous solubility of TNT over the temperature range (0–100) °C but did not evaluate the effect of pH. Spanggard et al.¹⁰ reported expressions for TNT and RDX solubility based on measurements at (10, 20, and 30) °C but also did not investigate pH. Ro et al.¹¹ reported aqueous solubilities for TNT at differing pH and temperatures. In their report, Ro et al.¹¹ proposed a solubility correlation and found that temperature had the greater impact on solubility and that solubility varied widely at higher pH. Phelan and Barnett¹² reported TNT pH-independent aqueous solubility values that agree with those reported by Spanggard et al.¹⁰ None of the predictive solubility correlations are similar to the others (Figure 1). Townsend and Myers¹³ and Gibbs and Popolato¹⁴ list solubilities from the literature for TNT, RDX, and HMX as a function of temperature and independent of pH. In this paper we re-evaluate TNT solubility correlations as a function of temperature and pH and add evaluations of RDX and HMX solubility as a function of these same variables.

Dissolution is the primary mechanism allowing for transformation and transport of nonvolatile explosive compounds. An explosive's dissolution rate and solubility control the persistence of the contamination at the source and the degree of contamination some distance away from this source. Fick's law can be used to predict the concentration of compounds dissolved in water as well as the time required to reach solubility limits:

$$\frac{dc}{dt} = K_L a (c_s - c_b) \quad (3)$$

In eq 3 dc/dt = dissolution rate, $K_L a$ = overall mass transfer coefficient, c_s = solubility, and c_b = concentration in bulk liquid. If the dissolution rate is known, eq 1 can be integrated to give the concentration, c_b at any time t .¹⁵

$$c_t = c_s (1 - e^{-K_L a t}) \quad (4)$$

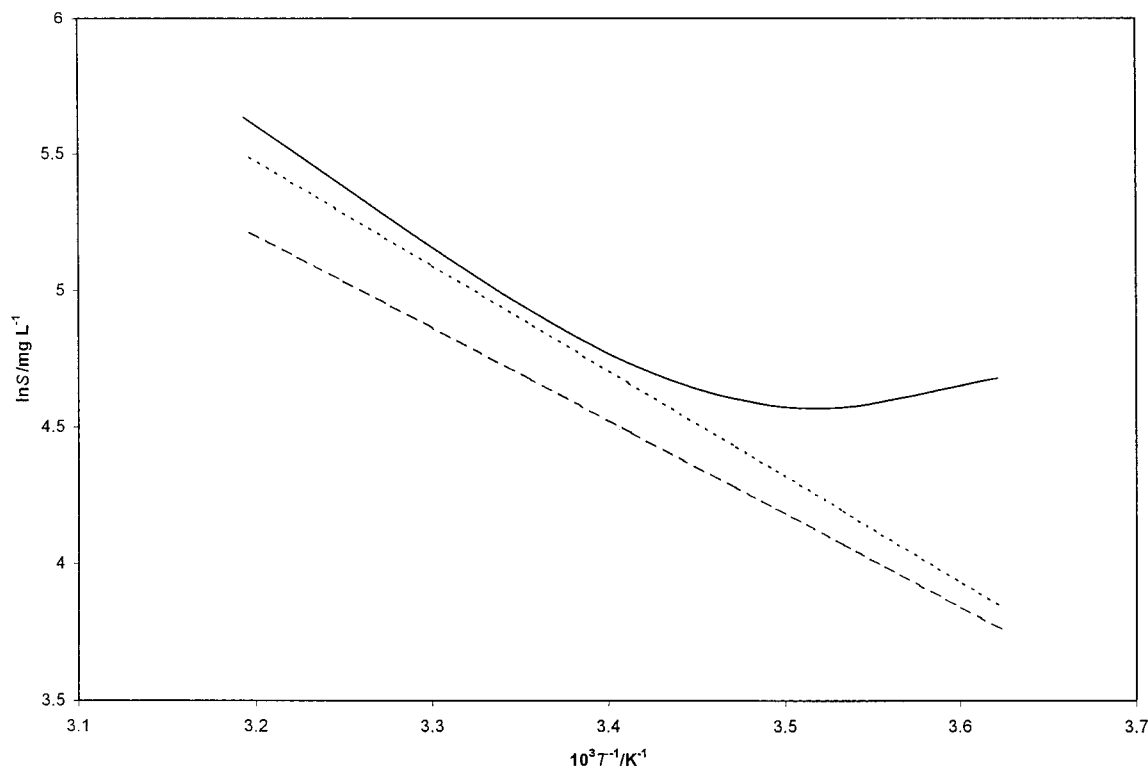


Figure 1. Reported TNT solubility prediction curves in the literature: —, Taylor and Rinckenbach (1923); ···, Spanggard et al. (1983); ---, Ro et al. (1996).

Information on high-explosive dissolution rates is sparse. Gilcrease et al.¹⁶ reported surface area and mixing rate effects on TNT dissolution rate. Lynch, Brannon, and Delfino¹⁷ reported surface area, temperature, and mixing rate effects on the dissolution rate of TNT, RDX, and HMX. Neither of these papers addressed pH. A general zero-order, multivariable, dissolution rate (dc/dt) equation proposed by Lynch, Brannon, and Delfino¹⁷ is

$$\frac{dc}{dt} = (R \hat{T} - I) ar \quad (5)$$

where R = correlation factor with units of $\text{mg s}^{-1} \text{ } ^\circ\text{C}^{-1} \text{ cm}^{-2} \text{ rps}^{-1}$ (for TNT, $R = 2.75 \times 10^{-9}$, for RDX, $R = 4.15 \times 10^{-10}$, and for HMX, $R = 1.19 \times 10^{-9}$), I = correlation factor with units of $\text{mg s}^{-1} \text{ cm}^{-2} \text{ rps}^{-1}$ (for TNT, $I = 1.3 \times 10^{-8}$, for RDX, $I = 1.7 \times 10^{-9}$, and for HMX, $I = 2.0 \times 10^{-10}$), a = nominal surface area in cm^2 , \hat{T} = temperature in $^\circ\text{C}$, and r = revolutions per second.

Price et al.¹⁸ presented the effects of redox potential and pH on TNT transformation in soil-water slurries. Price et al.¹⁹ studied the effects of redox potential and pH on RDX and HMX transformation in soils but did not directly address their effects on dissolution rate. In this work, we examine pH effects on the dissolution rates of TNT, RDX, and HMX at 30°C and at a mixing rate of 2.5 revolutions per second (rps). Surface area effects on dissolution rate were normalized by dividing the dissolution rate by the nominal explosive surface area used in a given experiment, resulting in a dissolution rate with units of $\text{mg cm}^{-2} \text{ s}^{-1}$.

Experimental Section

Chemicals. Experimental quantities of weapons grade TNT, RDX, and HMX were provided by the Environmental Processes and Engineering Division of the Engineer Re-

search and Development Center, U.S. Army Corps of Engineers Waterways Experiment Station, Vicksburg, MS. Demineralized water (reverse osmosis with a pH of ~ 5.7) was used with the pH adjusted lower by addition of H_2SO_4 and HNO_3 or higher by addition of Na_2CO_3 and NaOH . These chemicals were selected to approximate acidic rain conditions expected in the natural environment.

Procedure. Solubility. Aqueous solutions with pH values of 4.2, 5.7, and 6.2 were used as the solvent for the solid explosive dissolution experiments. An excess amount of solid explosive was added to 200 mL of pH-adjusted water in a 250 mL Erlenmeyer flask wrapped in aluminum foil to minimize photolysis.¹³

A magnetic stir bar was added to the flask, which was then sealed with Parafilm, and the solution was stirred on a magnetic stirrer at a rate sufficient to maintain a deep vortex. Experiments were performed in duplicate and at temperatures of $(3.1 \pm 0.8)^\circ\text{C}$, $(21.1 \pm 1.4)^\circ\text{C}$, and $(33.3 \pm 3.0)^\circ\text{C}$. Replicate sample aliquots were taken 7 and 14 days after agitation began. Samples were immediately passed through a $0.45 \mu\text{m}$ pore size membrane filter and combined with an equal volume of $0.45 \mu\text{m}$ filtered acetonitrile in preparation for high-performance liquid chromatographic (HPLC) analysis.

Dissolution Rate. The experimental design is based on the dissolution test described in the United States Pharmacopeia.²⁰ Five hundred milliliters of pH-regulated demineralized water was maintained overnight at 30°C using a Fisher Scientific Isotemp Refrigerated Circulator combined with a LabLine Aquabath in duplicate 600 mL beakers. A three-blade propeller rotated by an overhead Yamato Scientific StedFast Digital Lab Stirrer set at 2.5 rps was centered and lowered into the beaker and raised to a height of 2.5 cm above the beaker bottom. Dry explosive was then added to these beakers, and 1 mL samples were periodically pipetted from a zone midway between the surface of the solution and the top of the

Table 1. Solubilities of High-Explosive Compounds as a Function of pH and Temperature

TNT			RDX			HMX											
pH 4.2		pH 5.7		pH 6.2		pH 4.2		pH 5.7		pH 6.2		pH 4.2		pH 5.7		pH 6.2	
T/°C	S/mg L ⁻¹	T/°C	S/mg L ⁻¹	T/°C	S/mg L ⁻¹	T/°C	S/mg L ⁻¹	T/°C	S/mg L ⁻¹	T/°C	S/mg L ⁻¹	T/°C	S/mg L ⁻¹	T/°C	S/mg L ⁻¹	T/°C	S/mg L ⁻¹
2.3	49.5	2.3	54.5	2.4	55.9	2.7	13.5	2.5	12.6	2.1	13.1	2.7	0.81	2.5	0.77	2.1	0.77
2.3	50.5	2.3	54.2	2.4	56.4	2.7	13.0	2.5	12.8	2.1	13.5	2.7	0.80	2.5	0.77	2.1	0.77
2.6	54.9	2.3	47.5	2.4	54.9	2.7	13.3	2.6	13.8	2.6	12.9	2.7	0.76	2.7	0.77	2.6	0.60
2.6	55.7	2.3	47.3	2.4	55.4	2.7	13.2	2.6	13.7	2.6	13.3	2.7	0.78	2.7	0.78	2.6	0.65
4.2	57.6	4.1	47.9	4.7	56.7	2.8	13.5	2.7	13.2	2.9	13.7	3.6	0.92	3.6	1.01	3.6	0.98
4.2	57.7	4.1	48.2	4.7	57.4	2.8	12.9	2.7	13.2	2.9	13.9	3.6	0.91	3.6	0.95	3.6	0.93
4.2	45.7	4.6	58.1	5.2	56.7	3.2	13.9	3.5	13.6	3.9	14.1	3.6	0.89	3.7	0.90	3.6	0.93
4.2	48.4	4.6	59.1	5.2	56.1	3.2	14.0	3.5	13.9	3.9	13.5	3.6	0.91	3.7	0.99	3.6	0.94
20	100.7	20	96.7	20	99.6	20.1	38.9	20	37.7	20	37.5	22.6	3.82	22.7	3.84	22.5	3.88
20	99.0	20	98.7	20	100.2	20.1	36.8	20	37.8	20	37.6	22.6	3.84	22.7	3.82	22.5	3.88
20	99.2	20.1	98.9	20.1	99.5	20.1	38.6	20.2	38.0	20	38.2	22.8	3.68	22.8	3.88	22.7	3.80
20	101.7	20.1	100.6	20.1	96.3	20.1	38.3	20.2	38.0	20	38.8	22.8	3.68	22.8	3.89	22.7	3.79
20.1	96.3	20.2	98.8	20.1	99.5	20.2	35.8	20.4	35.4	20.4	35.5	23.1	3.87	23	3.94	23.4	3.93
20.1	95.9	20.2	99.8	20.1	99.8	20.2	35.7	20.4	35.6	20.4	35.3	23.1	3.85	23	3.95	23.4	3.72
20.1	96.0	20.2	97.5	20.2	94.6	20.2	36.0	20.4	35.1	20.4	36	23.7	3.94	23.5	3.90	23.7	3.75
20.1	97.8	20.2	100.4	20.2	97.2	20.2	36.3	20.4	35.6	20.4	36.1	23.7	3.97	23.5	3.94	23.7	3.89
36	211.7	35.7	208.5	35.9	216.5	31.6	65.1	31.7	62.5	31.7	67.6	28.5	5.35	28.5	5.40	28.5	6.21
36	213.1	35.7	213.5	35.9	213.9	31.6	65.4	31.7	62.2	31.7	68.1	28.5	5.55	28.5	5.43	28.5	6.10
36	208.5	36	215.2	36	212.2	31.9	46.5	32	60.6	32	58.7	28.6	5.74	28.6	5.96	28.6	6.13
36	211.6	36	214.3	36	215.3	31.9	48.5	32	61.8	32	59.8	31.2	7.58	28.6	6.02	28.6	6.66
37.7	219.6	37.7	229.7	37.6	229.4	32.1	65.9	34	73.4	34.1	85.2	31.2	7.74	31.7	7.25	32.3	7.67
37.7	219.4	37.7	230.6	37.6	231.4	32.1	66.3	34	87.8	34.1	86.5	32	7.41	31.7	7.19	32.3	7.75
37.8	218.2	37.7	226.2	38	234.4	32.1	65.6	34.1	86.8	34.2	85.7	32	7.47	32.2	7.39	32.3	7.60
37.8	214.8	37.7	228.3	38	235	32.1	64.1	34.1	85.7	34.2	81.8			32.2	7.39	32.3	7.63
						34.9	92.5										
						34.9	89.95										

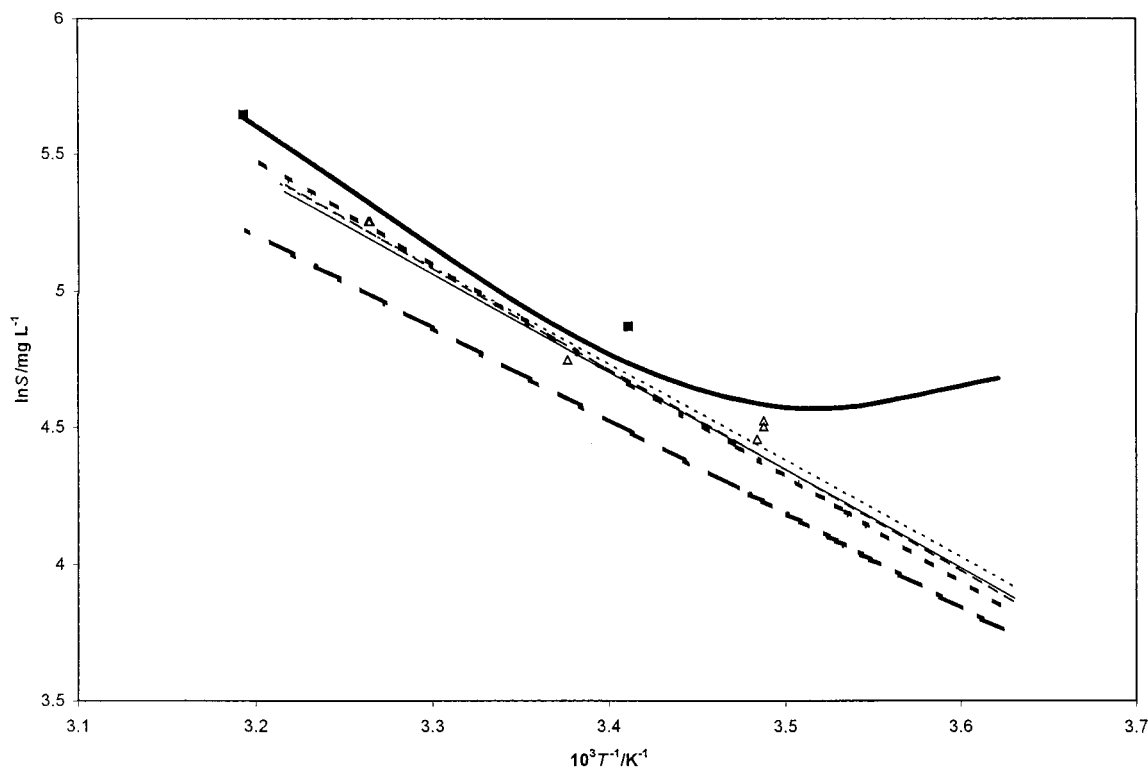


Figure 2. Comparison of literature TNT solubility to results from this study: —, Taylor and Rinckenbach (1923); - - -, Spanggord et al. (1983); - · - ·, Ro et al. (1996); ■, Gibbs and Popolato (1980); △, Phelan and Barnett (2001); —, this study, pH 4.2 [$\ln(S/\text{mg}\cdot\text{L}^{-1}) = 16.895 - 3586.4K/T$, $R^2 = 0.9822$]; - - -, this study, pH 5.7 [$\ln(S/\text{mg}\cdot\text{L}^{-1}) = 17.263 - 3691.3K/T$, $R^2 = 0.9837$]; - · - ·, this study, pH 6.2 [$\ln(S/\text{mg}\cdot\text{L}^{-1}) = 16.777 - 3542.5K/T$, $R^2 = 0.9785$].

stirring propeller and midway between the beaker wall and the propeller shaft while the solution continued to be stirred. Five samples were taken during each experimental run and immediately passed through a 0.45 μm Millipore filter and combined with equal amount of 0.45 μm -filtered acetonitrile in preparation for HPLC analysis.

Equipment. Vials containing the sample and acetonitrile were sealed with a Teflon-faced silicone rubber cap, 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 ($\lambda = 245 \text{ nm}$) and autosampler following Method 8330.²¹ A reversed phase eluent (50:50 methanol and water) was used in the HPLC system. The analytical column was a 25 cm \times 4.6 mm, 5 μm Supelco LC-18 reversed phase

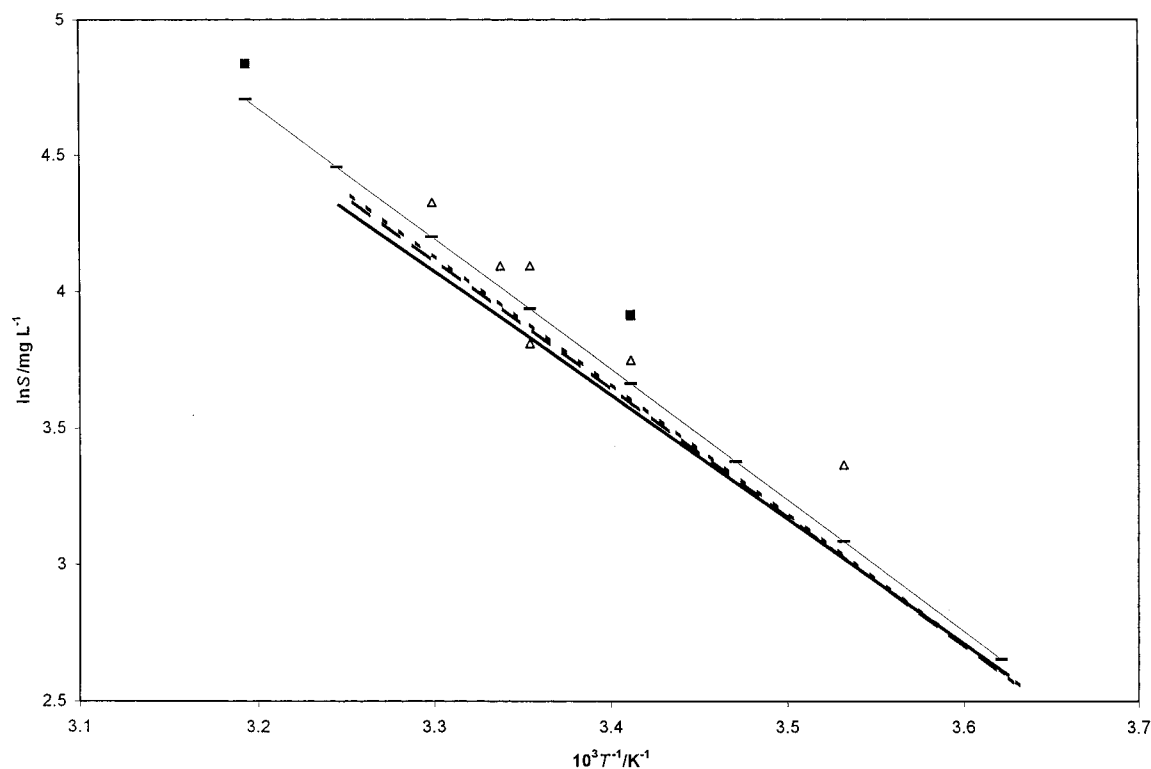


Figure 3. Comparison of literature RDX solubility to this study: + + +, Spanggard et al. (1983); ■, Gibbs and Popolato (1980); △, Townsend and Meyers (1996); —, this study, pH 4.2 [$\ln(S/\text{mg}\cdot\text{L}^{-1}) = 19.087 - 4549.1K/T$, $R^2 = 0.987$]; --, this study, pH 5.7 [$\ln(S/\text{mg}\cdot\text{L}^{-1}) = 19.718 - 4727.8K/T$, $R^2 = 0.995$]; ---, this study, pH 6.2 [$\ln(S/\text{mg}\cdot\text{L}^{-1}) = 19.818 - 4753.2K/T$, $R^2 = 0.995$].

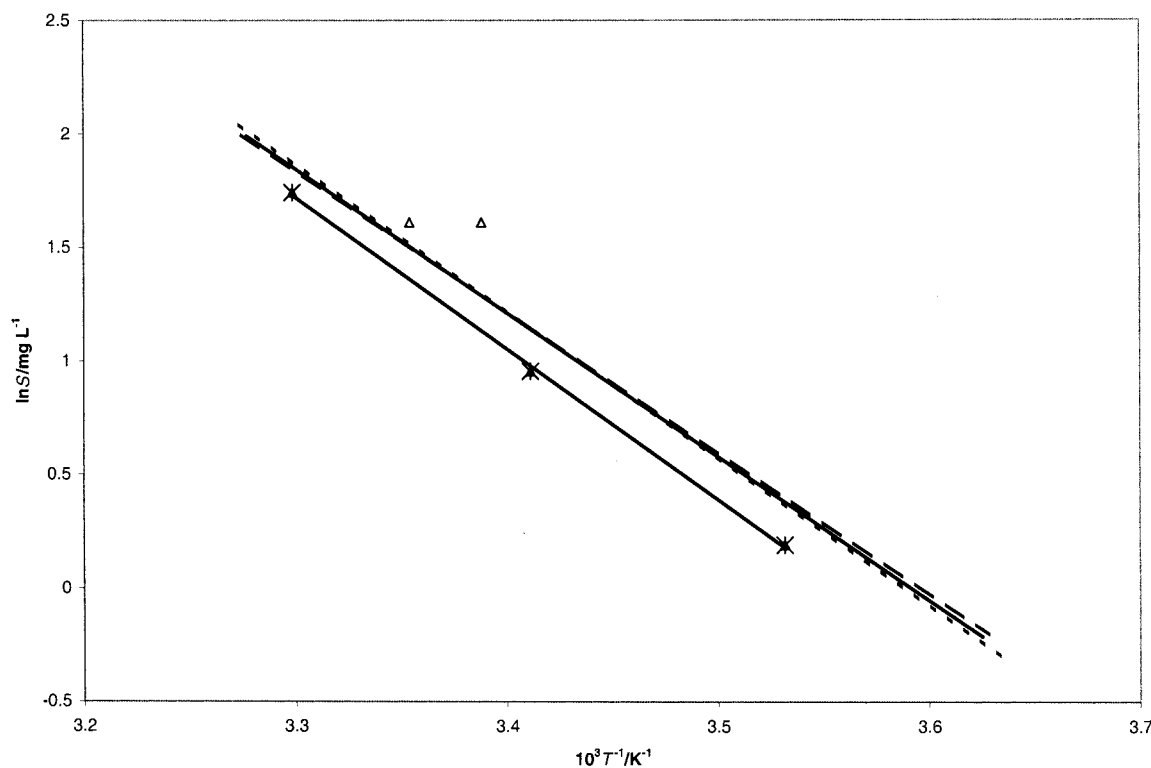


Figure 4. Comparison of literature HMX solubility to this study: - * -, Spanggard et al. (from Townsend and Meyers, 1996); △, Townsend and Meyers (1996); —, this study, pH 4.2 [$\ln(S/\text{mg}\cdot\text{L}^{-1}) = 22.741 - 6332K/T$, $R^2 = 0.9974$]; --, this study, pH 5.7 [$\ln(S/\text{mg}\cdot\text{L}^{-1}) = 22.399 - 6230K/T$, $R^2 = 0.9968$]; ---, this study, pH 6.2 [$\ln(S/\text{mg}\cdot\text{L}^{-1}) = 23.344 - 6506.8K/T$, $R^2 = 0.9901$].

HPLC column. The HPLC was calibrated using a seven-point calibration curve. A sample replicate, a blank, and a check standard were included in each analytical run. An Accumet model 50 combination pH/ion/conductivity meter was used to measure the pH of the solutions.

Results and Discussion

Solubility of High-Explosive Compounds as a Function of pH and Temperature. The temperature range studied, (3.1–33.3) °C, is representative of ambient condi-

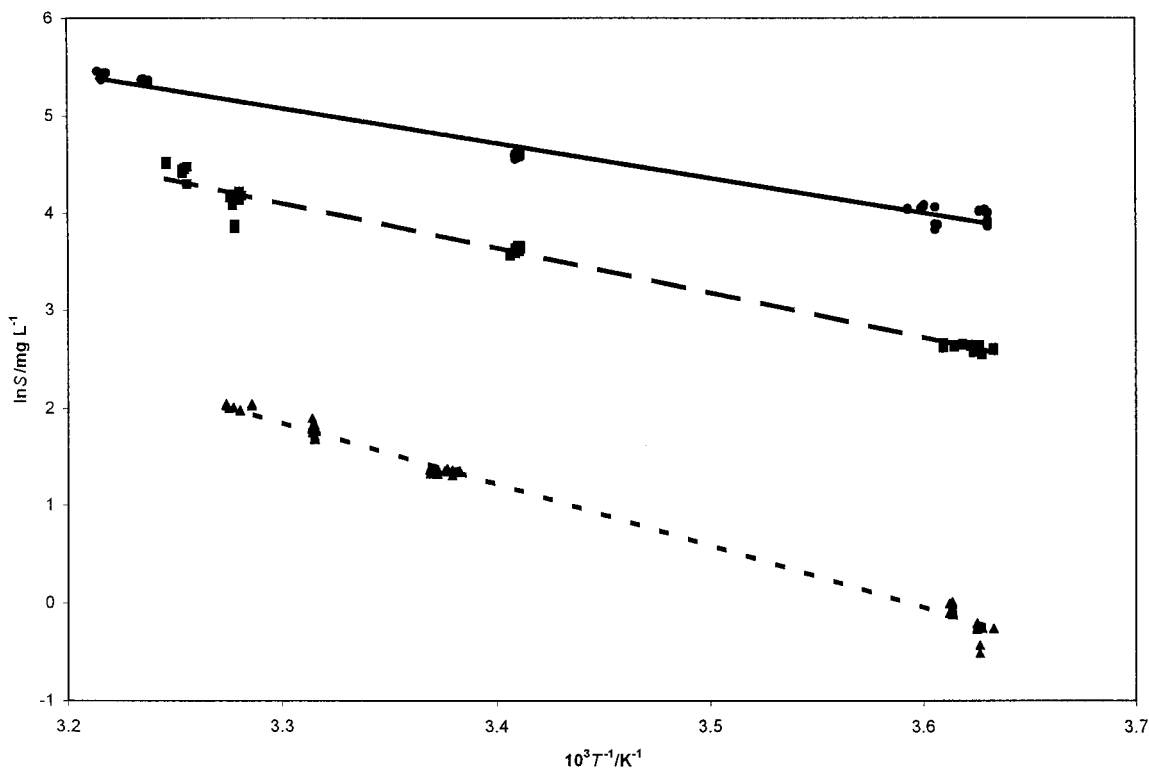


Figure 5. Composite explosive solubility prediction correlations: —, ●, TNT [$\ln(S/\text{mg}\cdot\text{L}^{-1}) = 16.981 - 3607.5K/T$, $R^2 = 0.990$]; ···, ▲, HMX [$\ln(S/\text{mg}\cdot\text{L}^{-1}) = 22.835 - 6358.2K/T$, $R^2 = 0.997$]; - -, ■, RDX [$\ln(S/\text{mg}\cdot\text{L}^{-1}) = 19.52 - 4670.9K/T$, $R^2 = 0.992$].

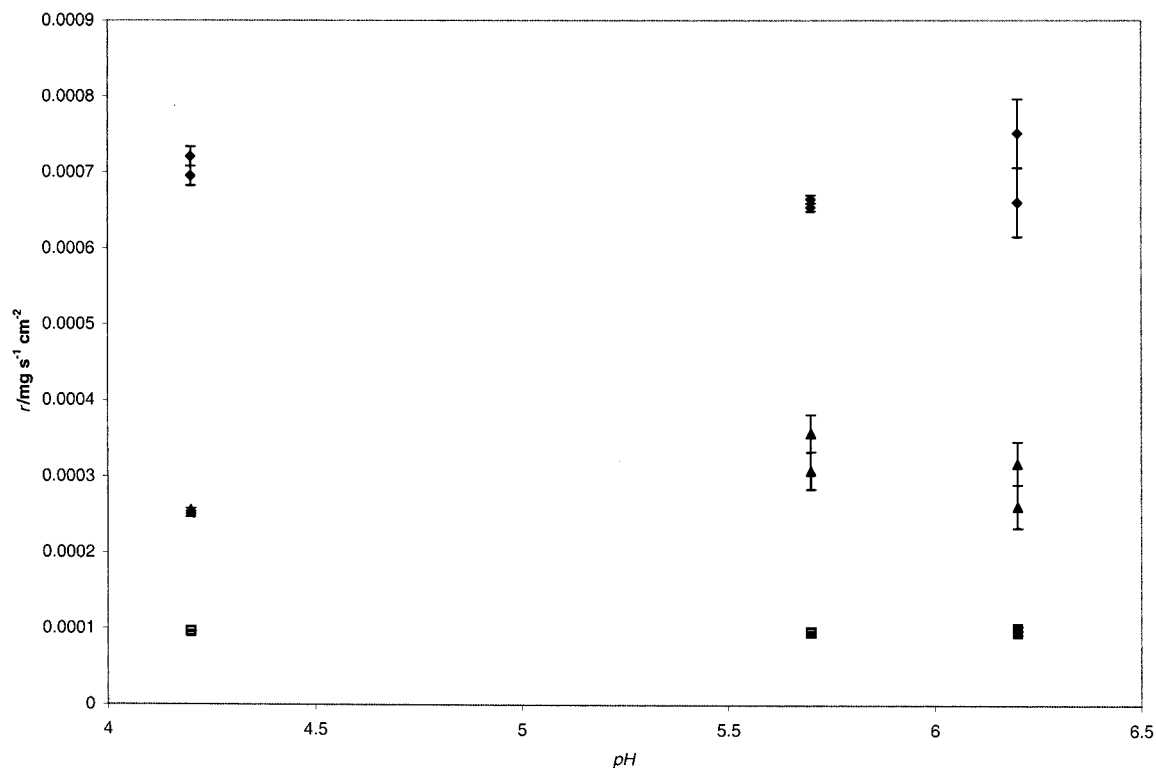


Figure 6. Comparison of explosive dissolution rates at three pH values: ◆, TNT; ▲, HMX; ■, RDX.

tions at which explosives residues are typically found, whereas the pH range was selected on the basis of maximum and minimum pH values reported for rainfall in the continental United States.²² The experimental solubility data for the three high explosives at three pH values and temperature are summarized in Table 1. To

conform to the format in eq 2, data were plotted as $\ln[S]$ versus $1/K$ and linearly regressed.

Evaluation based on the mean solubility values at each pH suggested a trend that solubilities increase as pH and temperature increase. This trend is much less apparent when viewed on the basis of the solubility range of plus or

Table 2. Summary of Mass of High Explosives Dissolved at Specified Sampling Times and pH Normalized for Solid Explosive Surface Area (Experiments Performed Twice at Each pH) and Resulting Dissolution Rate, r ($T = 30\text{ }^{\circ}\text{C}$ and $rps = 2.5$)

t/s	pH 4.2		pH 5.7		pH 6.2	
	$c/\text{mg cm}^{-2}$	$c/\text{mg cm}^{-2}$	$c/\text{mg cm}^{-2}$	$c/\text{mg cm}^{-2}$	$c/\text{mg cm}^{-2}$	$c/\text{mg cm}^{-2}$
	TNT					
240	0.19	0.20	0.18	0.18	0.18	0.20
600	0.45	0.48	0.44	0.44	0.45	0.46
1200	0.89	0.89	0.81	0.84	0.84	0.96
1800	1.25	1.28	1.20	1.14	1.18	1.43
2400	1.63	1.71	1.52	1.60	1.56	1.72
$r/\text{mg cm}^{-2}\text{ s}^{-1}$	0.00070	0.00072	0.00065	0.00066	0.00066	0.00075
	RDX					
240	0.03	0.03	0.03	0.03	0.03	0.03
600	0.06	0.06	0.06	0.07	0.07	0.06
1200	0.12	0.12	0.12	0.12	0.12	0.12
1800	0.16	0.18	0.17	0.17	0.17	0.18
2400	0.23	0.23	0.22	0.23	0.22	0.24
$r/\text{mg cm}^{-2}\text{ s}^{-1}$	0.000095	0.000098	0.000094	0.000097	0.000095	0.0001
	HMX					
60	0.023	0.023	0.033	0.030	0.030	0.023
110	0.035	0.035	0.050	0.044	0.043	0.035
160	0.043	0.044	0.063	0.055	0.057	0.046
210	0.053	0.055	0.073	0.062	0.066	0.054
260	0.059	0.059	0.083	0.072	0.074	0.061
$r/\text{mg cm}^{-2}\text{ s}^{-1}$	0.00025	0.00026	0.00036	0.00031	0.00032	0.00026

minus one standard deviation around the mean. From this perspective the pH-specific solubility range bars tend to overlap one another. The average percent difference found between replicate samples at one pH and temperature was comparable with those between the low-end value at pH 4.2 and the high-end value at pH 6.2 evaluated at the same temperature. No statistically significant difference in solubility for TNT, RDX, or HMX based on different pH values can be drawn within the range of conditions employed in this study.

Solubilities for TNT compare favorably with those reported by Spanggard et al.¹⁰ and Phelan and Barnett¹² (Figure 2). Solubilities for TNT were found to be less than those reported by Taylor and Rinkenbach⁹ but higher than those reported by Ro et al.¹¹ Solubilities for RDX (Figure 3) again compare favorably with those of Spanggard et al.,¹⁰ although they are generally less than values reported in the literature. Solubilities for HMX agree well with those values reported by Townsend and Meyers¹³ (Figure 4). A correlation was made for solubilities reported by Spanggard as cited by Townsend and Meyers¹³ and plotted in Figure 4 for comparative purposes. Composite correlations that utilize all TNT, RDX, and HMX data from this study to predict solubility are presented in Figure 5 together with the experimental data upon which they are based.

High-Explosives Dissolution Rate as a Function of pH and Temperature. Evaluation of pH effects on dissolution rate was conducted at 30 °C because of the higher solubility values for each explosive. Samples were taken at a frequency and over a time period so that sample concentrations would be well below solubility maxima, hence keeping the solution dilute. The effects of pH on dissolution rates for TNT, RDX, and HMX were not statistically different (Figure 6), falling within each other's one standard deviation confidence bars. In general, TNT has the fastest dissolution rate, followed by HMX and RDX. Composite dissolution rates incorporating all pH data from this study for TNT, HMX, and RDX (Table 3) compared well with those predicted by eq 5.¹⁷

The effect of pH on dissolution rate was found to be minimal within the range of this study. Nevertheless, pH does appear to play a role in explosive compound trans-

Table 3. Zero-Order pH-Related Explosive Dissolution Rates Measured at 30 °C, 2.5 rps, and Normalized Solid Explosive Surface Area

method	dissolution rate/ $\text{mg cm}^{-2}\text{ s}^{-1}$	R^2	av % diff ^a
	TNT		
eq 5	= 0.00063	n/a ^b	9.1
composite	= 0.00069	0.984	
	HMX		
eq 5	= 0.00032	n/a	9.8
composite	= 0.00029	0.628	
	RDX		
eq 5	= 0.00097	n/a	1.0
composite	= 0.00096	0.991	

^a Average percent difference for equations from data is 10% for TNT and RDX and 15% for HMX (Lynch, Brannon, and Delfino).¹⁷

^b R^2 not applicable (n/a) for equation-based dissolution rate.

formations. For example, Brannon et al.²³ found that the abiotic reduction of TNT was pH sensitive, with rates increasing as pH increased under anaerobic conditions.

The ability to predict both solubility and dissolution rate at a given temperature permits the prediction of solution concentration at any given time using eq 4. This equation was used in this paper to confirm that solubility had been reached prior to the seventh day of stirring. Using a conservative mixing rate of 3.5 rps and 30 °C, HMX attained saturation in <0.5 day, RDX had attained saturation in <5 days, and TNT reached 99.996% of saturation in 7 days.

Conclusions. Solubilities and dissolution rates of TNT, RDX, and HMX were not significantly affected by pH over the range 4.2–6.2 but were significantly affected by temperature over the temperature range (3.1–33.3) °C. TNT was the most soluble and had the highest dissolution rate, whereas RDX had the second highest solubility but exhibited the slowest dissolution rate. Composite correlations incorporating all pH data are presented in Figure 5 to predict explosive solubility as a function of temperature and in eq 5 to predict dissolution rates using specified variables. These equations can be used in predicting the solubilities of TNT, RDX, and HMX, their dissolution rates, and, with eq 4, solution concentrations over time.

Note Added after ASAP Posting

This article was posted ASAP on 9/15/2001 with incorrect mixing speeds. The correct mixing speeds are included in this version, posted on 10/19/2001.

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