Solubility of 2,4-Dinitrotoluene and 2,4,6-Trinitrotoluene in Seawater

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The solubility of 2,4-dinitrotoluene (2,4-DNT) and 2,4,6-trinitrotoluene (2,4,6-TNT) in seawater with ionic strength = (0.3352, 0.5071, and 0.6820) mol·L^{-1} and pure water was measured at 4 °C, 20 °C, 30 °C, and 40 °C. The pure water solubility values compare well with values reported previously. The solubility in seawater was lower than that in pure water. The average salting-out coefficients for 2,4-DNT and 2,4,6-TNT were (0.11 and 0.12) L·mol^{-1}, respectively, which are consistent with measurements for other nitroaromatic compounds. The salting-out coefficients did not show any significant variation with temperature over the range examined.

Introduction

Nitrogenous energetic compounds can enter and pollute the aquatic environment through the fallout of unexploded ordnance (UXO) at shooting ranges and the corrosion of UXO casings. The impact of this pollution source on aquatic systems depends on the capacity of the aquatic system to transform (chemically or biologically) these pollutants into less harmful species. Most research into the transformation of explosives has focused on terrestrial and freshwater systems,[1−4] and very little research has addressed marine systems.[5] One component to modeling pollutant transformation in marine systems is knowledge of the solubility of these compounds in seawater systems under various temperature and salinity conditions.

The presence of salt has been found to reduce the solubility of many organic compounds (see review in Xie et al.[6]), and this process is commonly called the "salting-out" or "salt" effect. The salting-out effect has been applied to transferring low-level concentrations of nitroaromatic compounds from the aqueous phase to an organic phase for analysis,[7,8] but very little research has been done on measuring the actual solubility of nitroaromatic compounds in salt solutions.[9] For the organic compounds whose solubilities in salt solutions have been measured (see review by Ni and Yalkowsky[10]), the Setschenow equation is commonly used to relate organic compound solubility measurements to salt concentration (C_{salt}):

$$\log(S_{\mathrm{w}}/S) = K_{\mathrm{s}}C_{\mathrm{salt}} \qquad (1)$$

where S_{w} is the solute solubility in pure water, S is the solute solubility in the salt solution, and K_{s} is the salting-out parameter, which is often referred to as the Setschenow coefficient. A modified version of this equation relates organic compound solubility to ionic strength, I:[9,11]

$$\log(S_{\mathrm{w}}/S) = K_{\mathrm{s}}'I \qquad (2)$$

where K_{s}' is a modified salting-out parameter. The latter equation was used in this study because seawater is a complex mixture of salts. Hashimoto et al.[9] reported K_{s}' values ranging from 0.136 L·mol^{-1} to 0.163 L·mol^{-1} for monosubstituted nitrophenols and nitrotoluene in sodium chloride solutions. The goal of this research was to measure the solubility of 2,4-dinitrotoluene (2,4-DNT) and 2,4,6-trinitrotoluene (2,4,6-TNT) in seawater over a range of salinity encompassing most coastal waters and at various temperatures.

Table 1. Ionic Strength and Molarity of Individual Ions in Seawater of Varying Composition (Salinity)

	c/(mol·L^{-1})		
ion	50 % seawater (16.6 g of salt/kg of seawater)	75 % seawater (24.8 g of salt/kg of seawater)	100 % seawater (33.1 g of salt/kg of seawater)
Cl^-	0.2625	0.3971	0.5340
SO_4^{2-}	0.0136	0.0205	0.0276
HCO_3^-	0.0012	0.0018	0.0024
Br^-	0.0004	0.0006	0.0008
H_3BO_3	0.0002	0.0003	0.0004
F^-	0.0000	0.0000	0.0001
Na^+	0.2256	0.3412	0.4589
Mg^{2+}	0.0254	0.0384	0.0517
Ca^{2+}	0.0049	0.0075	0.0101
K^+	0.0049	0.0074	0.0100
Sr^{2+}	0.0000	0.0001	0.0001
ionic strength	0.3352	0.5071	0.6820

Materials and Methods

Batch mixing experiments were conducted in 15 mL borosilicate glass vials (Pierce, Rockford, IL) sealed with Teflon screw caps. Acetone (Fisher Scientific) solutions containing either 2,4-DNT (Aldrich, 97 % purity) or 2,4,6-TNT (Eastman Chemical, >95 % purity) were added to each vial, and the acetone was evaporated, resulting in approximately 2.0 mg of 2,4,6-TNT and 2.5 mg of 2,4-DNT. These masses are greater than required to reach equilibrium. Furthermore, the presence of excess solid 2,4,6-TNT and 2,4-DNT was visually confirmed at the end of each experiment. Five milliliters of either 18 M Ω Milli-Q (deionized water purified by a Millipore Milli-Q Plus water system) or seawater diluted with various amounts of Milli-Q water were added to each vial (see Table 1). The uncertainty in the concentrations and ionic strength is less than 1 % of the tabulated value. The seawater was originally taken from the surface of the Middle Atlantic Bight and has a salinity of 33.1 g of salt/kg of seawater. After collection, it was filtered through 0.2 μm polysulfide filters (Gelman, Pall). Triplicate vials were run for most experimental conditions. The vials were

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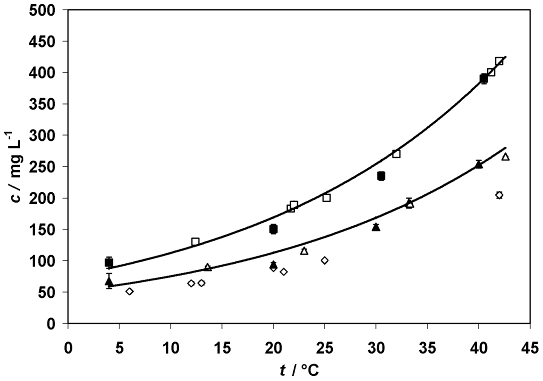

Figure 1. Solubility in pure water: □, 2,4-DNT, Phelan and Barnett;[12] ■, 2,4-DNT, this study; △, 2,4,6-TNT, Phelan and Barnett;[12] ◇, 2,4,6-TNT, Ro et al.[13] at pH = 6.8; ▲, 2,4,6-TNT, this study. Error bars show the standard deviation of the concentration of replicate vials. Error bars for temperature are not included.

Table 2. Solubility of 2,4-DNT and 2,4,6-TNT in Aqueous Samples

% seawater	t / °C	no. of samples	c(DNT) / mg·L^{-1}	SD	no. of samples	c(TNT) / mg·L^{-1}	SD
0	4	3	97	8.9	3	68	12.1
50	4	3	87	1.4	3	64	6.6
75	4	3	84	0.8	3	58	3.7
100	4	3	78	0.6	3	56	4.6
0	20	3	150	7.5	3	94	2.7
50	20	3	138	1.7	3	87	2.7
75	20	3	136	3.5	3	81	3.0
100	20	3	127	1.7	3	86	0.5
0	30	3	235	1.5	2	154	3.9
50	30	3	222	0.6	3	143	6.7
75	30	3	212	1.9	3	127	2.2
100	30	3	197	0.8	3	121	2.0
0	40	3	390	7.8	3	253	5.1
50	40	3	354	0.3	3	231	7.0
75	40	3	339	2.6	3	211	3.0
100	40	3	321	0.9	3	207	2.2

shaken at 45 rpm on a reciprocal shaker (Precision, Inc.) that was placed in either a Thermax temperature-controlled room (4 °C, 30 °C, and 40 °C) or in a Precision 818 low-temperature incubator (20 °C), which maintained the temperature within 0.5 °C. A rate study at 20 °C for both compounds revealed that equilibrium was achieved within 3 h. For all subsequent experiments, a 24 h period was allowed to establish equilibrium prior to sampling.

Aqueous samples were analyzed using a high-performance liquid chromatograph (Agilent 1100 series HPLC) equipped with a C-18 column (platinum, 100 A, 5 μm, 150 mm by 4.6 mm, Alltech) and a variable wavelength detector set to 254 nm. Samples (10 μL) were injected into an eluent (methanol volume fraction of 50 % in water) for an isocratic separation with a flow rate of 0.5 mL·min^{-1}. To eliminate precipitation, all samples were maintained at or above their equilibration temperature prior to injection into the instrument.

Results and Discussion

Table 2 shows the solubility data for 2,4-DNT and 2,4,6-TNT. The results for aqueous solubility in pure water are slightly lower than data reported by Phelan and Barnett[12] and are higher than the data reported by Ro et al.[13] for pH 6.8 (Figure 1). The pH 6.8 values are used for comparison because the pH of the Milli-Q samples was around pH 7.0. Using the data presented herein and from Phelan and Barnett,[12] exponential fits of 2,4-DNT and 2,4,6-TNT pure water concentration as a function of temperature were generated and are shown in Figure 1. The solubility of 2,4-DNT, c(DNT), as a function of temperature (t) with an $R^2 = 0.992$ is

$$c(\text{DNT})/\text{mg}\cdot\text{L}^{-1} = 74.8 \exp(0.0408\ t/°\text{C}) \qquad (3)$$

The 95 % confidence interval for the temperature coefficient is (0.0408 ± 0.0024) °C^{-1}. The solubility of 2,4,6-TNT, c(TNT), as a function of temperature (t) with an $R^2 = 0.984$ is

$$c(\text{TNT})/\text{mg}\cdot\text{L}^{-1} = 50.3 \exp(0.0403\ t/°\text{C}) \qquad (4)$$

The 95 % confidence interval for the temperature coefficient is (0.0403 ± 0.0034) °C^{-1}.

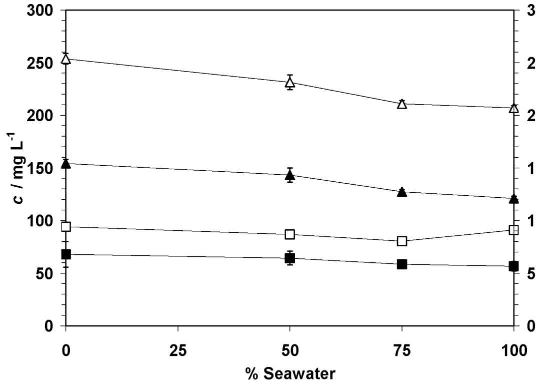

Figure 2. Solubility of 2,4,6-TNT as a function of percentage of seawater: △, 40 °C; ▲, 30 °C; □, 20 °C; ■, 4 °C. Error bars show the standard deviation of replicate vials.

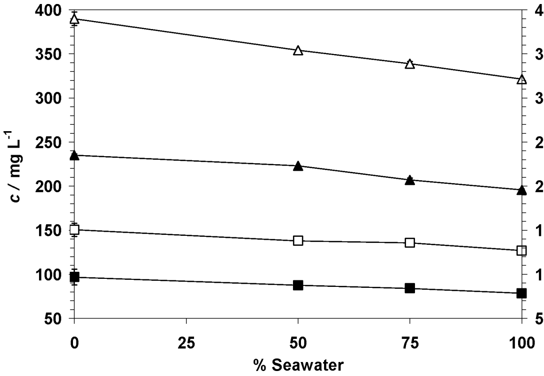

Figure 3. Solubility of 2,4-DNT as a function of percentage of seawater: △, 40 °C; ▲, 30 °C; □, 20 °C; ■, 4 °C. Error bars show the standard deviation of replicate vials.

Table 3. Salting-Out Coefficients for 2,4-DNT and 2,4,6-TNT at Various Temperatures

	2,4-DNT		2,4,6-TNT	
t/°C	K_s'/L·mol^{-1}	SE	K_s'/L·mol^{-1}	SE
4	0.13	0.004	0.11	0.01
20	0.10	0.01	0.09	0.02
30	0.10	0.01	0.15	0.02
40	0.12	0.001	0.14	0.01

The presence of salt lowers the solubility of 2,4-DNT and 2,4,6-TNT for all the temperatures examined as shown in Figures 2 and 3, respectively. Values of the salting-out parameter for 2,4-DNT (0.11 ± 0.01) L·mol^{-1} and for 2,4,6-TNT (0.12 ± 0.02) L·mol^{-1} based on eq 2 do not vary significantly with temperature, assuming a 95 % confidence interval (Table 3). These parameters compare well with the values given for paranitrotoluene (0.163 L·mol^{-1}), *o*-nitrophenol (0.136 L·mol^{-1}), *m*-nitrophenol (0.147 L·mol^{-1}), and *p*-nitrophenol (0.165 L·mol^{-1}) reported by Hashimoto et al.[9] for sodium chloride solutions. In their work, they found that, for selected compounds, the solubility in sodium chloride solutions was similar to that in seawater.

As with the pure water systems, the solubility of 2,4-DNT and 2,4,6-TNT in saline solutions increased with increasing temperature. Using the data for the seawater solutions, exponential fits of 2,4-DNT and 2,4,6-TNT concentration as a function of temperature were generated. For 100 % seawater, the solubility of 2,4-DNT, c(DNT), as a function of temperature (t) with an $R^2 = 0.986$ is

$$c(\mathrm{DNT})/\mathrm{mg{\cdot}L^{-1}} = 63.2 \exp(0.0391\ t/°\mathrm{C}) \qquad (5)$$

The 95 % confidence interval for the temperature coefficient is $(0.0391 \pm 0.0144)\ °\mathrm{C}^{-1}$. Similar temperature coefficients were found for 50 % seawater, $(0.0390 \pm 0.0156)\ °\mathrm{C}^{-1}$, and 75 % seawater, $(0.0387 \pm 0.0136)\ °\mathrm{C}^{-1}$. For 100 % seawater, the solubility of 2,4,6-TNT, c(TNT), as a function of temperature (t) with an $R^2 = 0.970$ is

$$c(\mathrm{TNT})/\mathrm{mg{\cdot}L^{-1}} = 45.9 \exp(0.0352\ t/°\mathrm{C}) \qquad (6)$$

The 95 % confidence interval for the temperature coefficient is $(0.0352 \pm 0.0190)\ °\mathrm{C}^{-1}$. Similar temperature coefficients were found for 50 % seawater, $(0.0358 \pm 0.0250)\ °\mathrm{C}^{-1}$, and 75 % seawater $(0.0355 \pm 0.0237)\ °\mathrm{C}^{-1}$. Comparison of the temperature coefficients for pure water systems with seawater systems shows that the dependence of concentration on temperature is the same within the 95 % confidence interval.

Conclusions

The solubility of 2,4-DNT and 2,4,6-TNT has been determined in pure water and seawater. The pure water solubility for the compounds determined in this work fall between values observed in earlier studies.[12,13] Equations describing the aqueous solubility as a function of temperature have been derived (eqs 3 to 6). Equations describing the solubility of 2,4-DNT and 2,4,6-TNT as a function of ionic strength for seawater have been derived in the form of eq 2. The average values of the salting out coefficient for 2,4-DNT and 2,4,6-TNT were $(0.11 \pm 0.01)\ \mathrm{L{\cdot}mol^{-1}}$ and $(0.12 \pm 0.02)\ \mathrm{L{\cdot}mol^{-1}}$, respectively, and did not vary significantly with temperature.

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Literature Cited

(1) Alnaizy, R.; Akgerman, A. Oxidative treatment of high explosives contaminated wastewater. *Water Res.* **1999**, *33*, 2021−203.

(2) Garcia Einschlag, F. S.; Lopez, J.; Carlos, L.; Capparelli, A. L. Evaluation of the efficiency of photodegradation of niroaromatics applying the UV/H_2O_2 technique. *Environ. Sci. Technol.* **2002**, *36*, 3936−3944.

(3) Rodgers, J. D.; Bunce, N. J. Treatment methods for the remediation of nitroaromatic explosives. *Water Res.* **2001**, *35*, 2101−2111.

(4) Spain, J. C., Hughes, J. B., Knackmuss, H. J., Eds. *Biodegradation of Nitroaromatic Compounds and Explosives*; Lewis Publishers: New York, 2000.

(5) Zhao, J.-S.; Greer, C. W.; Thiboutot, S.; Ampleman, G.; Hawari, J. Biodegradation of the nitramine explosives hexahydro-1,3,5-trinitro-1,3,5-triazine and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine in cold marine sediment under anaerobic and oligotrophic conditions. *Can. J. Microbiol.* **2004**, *50*, 91−96.

(6) Xi, W.-H.; Shiu, W.-Y.; Mackay, D. A review of the effect of salts on the solubility of organic compounds in seawater. *Mar. Environ. Res.* **1997**, *44*, 429−444.

(7) Leggett, D. C.; Jenkins, T. F.; Miyares, R. H. Salting-out solvent extraction for preconcentration of neutral polar organic solutes from water. *Anal. Chem.* **1990**, *62*, 1355−1356.

(8) Nitroaromatics and nitramines by high performance liquid chromatography (HPLC). EPA Method 8330A, January 1998.

(9) Hashimoto, Y.; Tokura, K.; Kishi, H.; Strachan, W. M. J. Prediction of seawater solubility of aromatic compounds. *Chemosphere* **1984**, *13*, 881−888.

(10) Ni, N.; Yalkowky, S. H. Prediction of Setschenow constants. *Int. J. Pharm.* **2003**, *254*, 167−172.

(11) Sada, E.; Kito, S.; Ito, Y. Solubility of toluene in aqueous salt solutions. *J. Chem. Eng. Data* **1975**, *20*, 373−375.

(12) Phelan, J. M.; Barnett, J. L. Solubility of 2,4-dinitrotoluene and 2,4,6-dinitrotoluene in water. *J. Chem. Eng. Data* **2001**, *46*, 375−376.

(13) Ro, K. S.; Venugopal, A.; Adrian, D. D.; Constant, D.; Qaisi, K.; Valsaraj, K. T.; Thibodeaux, L. J.; Roy, D. Solubility of 2,4,6-trinitrotoluene in water. *J. Chem. Eng. Data* **1996**, *41*, 758−761.

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