Solubility of 2,6-Dinitrotoluene, 2,3-Dinitrotoluene, and 1,3,5-Trinitrobenzene in Pure Water and Seawater

Dianne J. Luning Prak* and Daniel W. O'Sullivan

Chemistry Department, United States Naval Academy, 572M Holloway Road, Annapolis, Maryland 21402

The solubility of 2,6-dinitrotoluene (2,6-DNT), 2,3-dinitrotoluene (2,3-DNT), 4-nitrotoluene (NT), and 1,3,5-trinitrobenzene (TNB) was measured in seawater with ionic strength \( = (0.1662, 0.3352, 0.5071, and 0.6820) \) mol\( \cdot \)L\(^{-1} \) and pure water at temperatures between (277 and 314) K. 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 NT, 2,6-DNT, 2,3-DNT, and TNB were (0.15, 0.12, 0.13, and 0.09) L\( \cdot \)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

Nitroaromatic compounds can enter and pollute the aquatic environment through the improper use and disposal of feedstocks from chemical production (explosives, urethane, dyes) and through the corrosion of unexploded ordnance casings at shooting ranges or battlefield sites. Once in the environment, chemical and biological processes can transform these compounds into other pollutants or less harmful species. Compared to freshwater systems,\(^1\)\(^-\)\(^4\) there has been a dearth of research on the transformation of nitroaromatic compounds in marine systems.\(^5\) To develop accurate mathematical models of pollutant transformation in marine systems, the solubility of these compounds under various temperature and salinity conditions needs to be determined.

The aqueous solubility of neutral organic compounds has been found to decrease in the presence of inorganic salts (see Xie et al\(^6\)), and this process is commonly called “salting-out” or the “salt” effect. Salting-out has been used to enhance the analysis of low-level concentrations of nitroaromatic compounds,\(^7\)\(^-\)\(^8\) but very little research has been done on measuring the solubility of nitroaromatic compounds in salt solutions.\(^9\)\(^-\)\(^10\) For those compounds whose solubility in salt solutions has been measured (see Ni and Yalkowsky\(^11\)), the compound solubility measurement can be related to the salt concentration (\( C_{\text{salt}} \)) through the Sertchenow equation

\[
\log(S_o/S) = K_s C_{\text{salt}}
\]

(1)

where \( S_o \) is the solute solubility in pure water, \( S \) is the solute solubility in the salt solution, and \( K_s \) is the Sertchenow coefficient or salting-out parameter. For solutions such as seawater that are a complex mixture of salts, a modified version of this equation relates organic compound solubility to ionic strength, \( I \), \(^9\)\(^-\)\(^10\)\(^12\):

\[
\log(S_o/S) = K_s' I
\]

(2)

where \( K_s' \) is a modified salting-out parameter. Hashimoto et al.\(^9\) reported \( K_s' \) values ranging from 0.136 L\( \cdot \)mol\(^{-1} \) to 0.163 L\( \cdot \)mol\(^{-1} \) for monosubstituted nitrophenols and nitrotoluene in sodium chloride solutions, while Luning Prak and O’Sullivan\(^10\) reported average \( K_s' \) values of 0.011 L\( \cdot \)mol\(^{-1} \) and 0.12 L\( \cdot \)mol\(^{-1} \) for 2,4-dinitrotoluene (2,4-DNT) and 2,4,6-trinitrotoluene (TNT), respectively, in seawater. The goal of this research was to measure the solubility of 2,6-dinitrotoluene (2,6-DNT), 2,3-dinitrotoluene (2,3-DNT), 4-nitrotoluene (NT), and 1,3,5-trinitrobenzene (TNB) in seawater over a range of salinity encompassing most coastal waters and at various temperatures. These compounds represent substances produced during explosive manufacturing or the chemical or biological degradation of TNT.\(^13\)\(^14\)

Materials and Methods

Batch-mixing experiments were conducted in Pierce 15 mL borosilicate glass vials (Rockford, IL) sealed with Teflon screw caps. Acetone (Fisher Scientific) solutions containing 2,6-DNT (Aldrich, 98 % purity), 2,3-DNT (Aldrich, 99 % purity), NT (Aldrich, 99 % purity), or TNB (Aldrich, 99.9 % purity) were added to each vial, and the acetone was evaporated, resulting in masses ranging from 3.8 mg to 8.5 mg. These masses are greater than required to reach equilibrium, therefore some solid remained in each vial at the end of each experiment. Five milliliters of either 18 M\( \Omega \)cm\(^{-1} \) MilliQ (deionized water purified by a Millipore MilliQ 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 consisted of water taken from the surface of the Middle Atlantic Bight (salinity of 33.1 g of salt/kg of seawater) that was filtered through 0.2 \( \mu \)m polysulfide filters (Gelman, Pall). Triplicate vials were run for most experimental conditions. The vials were shaken at 45 rpm on a reciprocal shaker (Precision, Inc.) or Labquake tube shaker (Barnstead International) that was placed in either a Thermax temperature-controlled room or a Precision 818 low-temperature incubator, which maintained the temperature within 0.5 K, or on the bench top (room-temperature samples) where the temperature varied within 0.6 K. A rate study at 303.2 K for NT revealed that equilibrium was achieved within 3.5 h; this is an amount of time similar to that found for TNT.

* Corresponding author. Phone: (410) 293-6339. Fax: (410) 293-2218. Email: prak@usna.edu.
# Solubility of 4-Nitroluene, 2,6-Dinitrotoluene, 2,3-Dinitrotoluene, and 1,3,5-Trinitrobenzene in Pure Water and Seawater

**United States Naval Academy, Chemistry Department, 572M Holloman Road, Annapolis, MD, 21402**

**Approved for public release; distribution unlimited**

**Report Documentation Page**

<table>
<thead>
<tr>
<th>1. REPORT DATE</th>
<th>2. REPORT TYPE</th>
<th>3. DATES COVERED</th>
</tr>
</thead>
<tbody>
<tr>
<td>2007</td>
<td></td>
<td>00-00-2007 to 00-00-2007</td>
</tr>
</tbody>
</table>

**4. TITLE AND SUBTITLE**

**Solubility of 4-Nitroluene, 2,6-Dinitrotoluene, 2,3-Dinitrotoluene, and 1,3,5-Trinitrobenzene in Pure Water and Seawater**

**5a. CONTRACT NUMBER**

**5b. GRANT NUMBER**

**5c. PROGRAM ELEMENT NUMBER**

**5d. PROJECT NUMBER**

**5e. TASK NUMBER**

**5f. WORK UNIT NUMBER**

**7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)**

**United States Naval Academy, Chemistry Department, 572M Holloman Road, Annapolis, MD, 21402**

**8. PERFORMING ORGANIZATION REPORT NUMBER**

**9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)**

**10. SPONSOR/MONITOR’S ACRONYM(S)**

**11. SPONSOR/MONITOR’S REPORT NUMBER(S)**

**12. DISTRIBUTION/AVAILABILITY STATEMENT**

Approved for public release; distribution unlimited

**13. SUPPLEMENTARY NOTES**

**14. ABSTRACT**

**15. SUBJECT TERMS**

**16. SECURITY CLASSIFICATION OF:**

<table>
<thead>
<tr>
<th>a. REPORT</th>
<th>b. ABSTRACT</th>
<th>c. THIS PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>unclassified</td>
<td>unclassified</td>
<td>unclassified</td>
</tr>
</tbody>
</table>

**17. LIMITATION OF ABSTRACT**

Same as Report (SAR)

**18. NUMBER OF PAGES**

5

**19a. NAME OF RESPONSIBLE PERSON**
Table 1. Ionic Strength and Molarity, $c$, of Individual Ions in Seawater of Varying Composition (Salinity)

<table>
<thead>
<tr>
<th>Ion</th>
<th>$c$(mole\cdot L$^{-1}$)</th>
<th>25 % seawater (8.8 g of salt/kg of seawater)</th>
<th>50 % seawater (16.6 g of salt/kg of seawater)</th>
<th>75 % seawater (24.8 g of salt/kg of seawater)</th>
<th>100 % seawater (33.1 g of salt/kg of seawater)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$^-$</td>
<td>0.1301</td>
<td>0.2625</td>
<td>0.3971</td>
<td>0.3540</td>
<td></td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>0.0067</td>
<td>0.0136</td>
<td>0.0205</td>
<td>0.0276</td>
<td></td>
</tr>
<tr>
<td>HCO$_3^-$</td>
<td>0.0006</td>
<td>0.0012</td>
<td>0.0018</td>
<td>0.0024</td>
<td></td>
</tr>
<tr>
<td>Br$^-$</td>
<td>0.0002</td>
<td>0.0004</td>
<td>0.0006</td>
<td>0.0008</td>
<td></td>
</tr>
<tr>
<td>H$_2$BO$_3$</td>
<td>0.0001</td>
<td>0.0002</td>
<td>0.0003</td>
<td>0.0004</td>
<td></td>
</tr>
<tr>
<td>F$^-$</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0001</td>
<td></td>
</tr>
<tr>
<td>Na$^+$</td>
<td>0.1118</td>
<td>0.2256</td>
<td>0.3412</td>
<td>0.4589</td>
<td></td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>0.0126</td>
<td>0.0254</td>
<td>0.0384</td>
<td>0.0517</td>
<td></td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>0.0025</td>
<td>0.0049</td>
<td>0.0075</td>
<td>0.0103</td>
<td></td>
</tr>
<tr>
<td>K$^+$</td>
<td>0.0024</td>
<td>0.0049</td>
<td>0.0074</td>
<td>0.0100</td>
<td></td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0001</td>
<td>0.0001</td>
<td></td>
</tr>
<tr>
<td>Ionic strength</td>
<td>0.1662</td>
<td>0.3352</td>
<td>0.5071</td>
<td>0.6820</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Solubility, $c$, of NT, 2,6-DNT, 2,3-DNT and TNB in Pure Water and Seawater from $T = 277.5$ K to 314.0 K$^a$

<table>
<thead>
<tr>
<th>% seawater</th>
<th>$c$(NT)</th>
<th>$c$(2,6-DNT)</th>
<th>$c$(2,3-DNT)</th>
<th>$c$(TNB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MilliQ</td>
<td>278.5</td>
<td>3</td>
<td>74</td>
<td>67</td>
</tr>
<tr>
<td>25</td>
<td>278.5</td>
<td>3</td>
<td>74</td>
<td>67</td>
</tr>
<tr>
<td>50</td>
<td>278.5</td>
<td>3</td>
<td>74</td>
<td>67</td>
</tr>
<tr>
<td>75</td>
<td>278.5</td>
<td>3</td>
<td>74</td>
<td>67</td>
</tr>
<tr>
<td>100</td>
<td>278.5</td>
<td>3</td>
<td>74</td>
<td>67</td>
</tr>
<tr>
<td>MilliQ</td>
<td>281.0</td>
<td>3</td>
<td>77</td>
<td>69</td>
</tr>
<tr>
<td>25</td>
<td>281.0</td>
<td>3</td>
<td>77</td>
<td>69</td>
</tr>
<tr>
<td>50</td>
<td>281.0</td>
<td>3</td>
<td>77</td>
<td>69</td>
</tr>
<tr>
<td>75</td>
<td>281.0</td>
<td>3</td>
<td>77</td>
<td>69</td>
</tr>
<tr>
<td>100</td>
<td>281.0</td>
<td>3</td>
<td>77</td>
<td>69</td>
</tr>
<tr>
<td>MilliQ</td>
<td>294.0</td>
<td>3</td>
<td>80</td>
<td>73</td>
</tr>
<tr>
<td>25</td>
<td>294.0</td>
<td>3</td>
<td>80</td>
<td>73</td>
</tr>
<tr>
<td>50</td>
<td>294.0</td>
<td>3</td>
<td>80</td>
<td>73</td>
</tr>
<tr>
<td>75</td>
<td>294.0</td>
<td>3</td>
<td>80</td>
<td>73</td>
</tr>
<tr>
<td>100</td>
<td>294.0</td>
<td>3</td>
<td>80</td>
<td>73</td>
</tr>
<tr>
<td>MilliQ</td>
<td>309.6</td>
<td>3</td>
<td>82</td>
<td>74</td>
</tr>
<tr>
<td>25</td>
<td>309.6</td>
<td>3</td>
<td>82</td>
<td>74</td>
</tr>
<tr>
<td>50</td>
<td>309.6</td>
<td>3</td>
<td>82</td>
<td>74</td>
</tr>
<tr>
<td>75</td>
<td>309.6</td>
<td>3</td>
<td>82</td>
<td>74</td>
</tr>
<tr>
<td>100</td>
<td>309.6</td>
<td>3</td>
<td>82</td>
<td>74</td>
</tr>
</tbody>
</table>

$^a$ ND: not determined.

Table 3. Coefficients of Equation 3$^a$ for the Influence of Temperature on the Equilibrium Solubility of NT, 2,6-DNT, 2,3-DNT, and TNB in Pure Water and in Seawater at Various Concentrations

<table>
<thead>
<tr>
<th>% seawater</th>
<th>$a$</th>
<th>$b$</th>
<th>$a$</th>
<th>$b$</th>
<th>$a$</th>
<th>$b$</th>
<th>$a$</th>
<th>$b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>532</td>
<td>0.0310</td>
<td>343</td>
<td>0.0438</td>
<td>59.1</td>
<td>0.0384</td>
<td>104</td>
<td>0.0284</td>
</tr>
<tr>
<td>25</td>
<td>295</td>
<td>0.0314</td>
<td>228</td>
<td>0.0438</td>
<td>47.7</td>
<td>0.0438</td>
<td>58.2</td>
<td>0.0309</td>
</tr>
<tr>
<td>50</td>
<td>228</td>
<td>0.0321</td>
<td>145</td>
<td>0.0438</td>
<td>40.0</td>
<td>0.0438</td>
<td>52.0</td>
<td>0.0269</td>
</tr>
<tr>
<td>75</td>
<td>186</td>
<td>0.0326</td>
<td>126</td>
<td>0.0438</td>
<td>37.5</td>
<td>0.0438</td>
<td>47.5</td>
<td>0.0273</td>
</tr>
<tr>
<td>100</td>
<td>146</td>
<td>0.0326</td>
<td>100</td>
<td>0.0438</td>
<td>36.0</td>
<td>0.0438</td>
<td>39.0</td>
<td>0.0269</td>
</tr>
</tbody>
</table>

$^a$ Values in parentheses represent the 95% confidence interval.

2.4-DNT in previous studies. For all subsequent experiments, the vials were shaken for at least 24 h to establish equilibrium prior to sampling. Aqueous samples were analyzed by methods described in Luning Prak and O'Sullivan.

Results and Discussion

Table 2 shows the solubility data for NT, 2,6-DNT, 2,3-DNT, and TNB. The results for aqueous solubility of NT in pure water
Table 4. Comparison of Calculated (based on Equation 4) and Predicted (UNIFAC and Pierotti) Activity Coefficients, $\gamma$, of NT, 2,6-DNT, 2,3-DNT, and TNB in Pure Water Based on Using Heat of Fusion, $\Delta H_f$, Melting Temperature, $T_m$, and Sample Temperature, $T$

<table>
<thead>
<tr>
<th></th>
<th>NT</th>
<th>2,6-DNT</th>
<th>2,3-DNT</th>
<th>TNB</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H_f$ / kJ mol$^{-1}$</td>
<td>16.81$^{29}$</td>
<td>23.85$^{29}$</td>
<td>16.07$^{29}$</td>
<td>17.57$^{29}$</td>
</tr>
<tr>
<td>$T_m$ / K</td>
<td>325$^{10}$</td>
<td>340$^{29}$</td>
<td>330$^{29}$</td>
<td>398.4$^{10}$</td>
</tr>
<tr>
<td>$T_f$ / K</td>
<td>297.5</td>
<td>297.5</td>
<td>297.5</td>
<td>305</td>
</tr>
<tr>
<td>$\gamma$ (eq 4, exp)</td>
<td>1.13 - 10$^4$</td>
<td>1.96 - 10$^4$</td>
<td>1.25 - 10$^4$</td>
<td>2.89 - 10$^4$</td>
</tr>
<tr>
<td>$\gamma$ (UNIFAC)</td>
<td>2.14 - 10$^4$</td>
<td>9.86 - 10$^4$</td>
<td>9.86 - 10$^4$</td>
<td>6.67 - 10$^4$</td>
</tr>
<tr>
<td>$\gamma$ (Pierotti)</td>
<td>1.48 - 10$^4$</td>
<td>2.09 - 10$^4$</td>
<td>2.09 - 10$^4$</td>
<td>0.590 - 10$^4$</td>
</tr>
</tbody>
</table>

DNT agree with the values reported by Verschueren$^{14}$ and EPA$^{17}$ (Figure 1, triangles), while the values measured for 2,3-DNT agree with a value reported by Luning Prak$^{18}$ (Figure 1, diamonds).

Using the data presented herein, exponential fits of pure water concentration as a function of temperature were generated for all four compounds in the functional form

$$c/\text{mg} \cdot \text{L}^{-1} = a \exp(b T/K)$$

where $c$ is the concentration, $T$ is temperature, and $a$ and $b$ are fitting parameters. Figure 1 shows the exponential fits (correlation coefficients $> 0.995$), and the values of $a$ and $b$ are given in Table 3 (along with their 95% confidence intervals). The temperature coefficients for 2,3-DNT and 2,6-DNT (0.042 ± 0.002, 0.048 ± 0.003) K$^{-1}$, respectively, are similar to the value found for 2,4-DNT (0.0408 ± 0.0024) K$^{-1}$ in the same seawater system.$^{10}$ NT has one less nitro group and has a smaller temperature coefficient (0.0310 ± 0.0021) K$^{-1}$. This trend of increasing temperature coefficient with increasing number of nitro groups is not followed, however, by TNT, whose temperature coefficient (0.0403 ± 0.0024 K$^{-1}$) is similar to that of the dinitrotoluenes.

A thermodynamic analysis of solubility data was used to calculate activity coefficients ($\gamma$), whose magnitudes depend on the standard state selected. For solid solutes, some researchers calculate activity coefficients using the standard state of a hypothetical pure subcooled liquid at the temperature and pressure of the solution.$^{19}$

$$\ln(x\gamma) = \frac{\Delta H_f}{RT} \left[ 1 - \frac{T}{T_f} \right] - \frac{\Delta C_p}{R} \left( \frac{T_t - T}{T} \right) + \frac{\Delta C_p}{R} \ln \frac{T_t}{T}$$

In this equation, $x$ is the mole fraction of the nitroaromatic compound from the solid—liquid equilibrium, $\Delta H_f$ is the heat of fusion at the melting point, $T_t$ is the triple point, $T$ is the temperature in Kelvin, $\Delta C_p$ is the difference between the liquid and solid heat capacity, and $R$ is the gas constant. In practice, researchers often substitute the melting point for the triple point and neglect the heat capacity terms because they tend to cancel each other out and are small when temperatures are close to the melting point.$^{19}$ Following that practice and using eq 4, the activity coefficients were calculated at 297.5 K for the NT, 2,3-DNT, 2,6-DNT, and TNB (Table 4). The activity coefficient for NT (1.13 - 10$^4$) at 297.5 K is close to the values reported by Tsonopoulou and Prausnitz$^{20}$ (1.6 - 10$^4$) for 298.2 K and by Benes and Dohnal$^{21}$ (1.6 - 10$^4$ and 1.54 - 10$^4$) for 293.2 K and 303.2 K, respectively. Activity coefficients can also be estimated using knowledge of the molecular structure. Grain$^{22}$ presented two methods for calculating the activity coefficient at infinite dilution: the Pierotti$^{23}$ and UNIFAC methods. The values predicted by these methods are given in Table 4. As can be seen, the UNIFAC analysis overestimates the activity coefficient for these compounds from 900 % (NT) to 2000 % (TNB), while the simpler Pierotti equation deviates by at most 31%.

Figure 1. Solubility in pure water: □, NT, ref 15; ■, NT, this study; Δ, 2,6-DNT, ref 14 and 17; ●, 2,6-DNT, this study; ○, TNB, ref 16; ●, TNB, this study; ◊, 2,3-DNT, ref 18; ●, 2,3-DNT, this study. Error bars show the standard deviation of the concentration of replicate vials. Error bars for temperature are not included.

Figure 2. van’t Hoff plot of NT and 2,3-DNT in seawater at various concentrations: □, NT, 25 % seawater; Δ, NT, 50 % seawater; ○, NT, 75 % seawater; ◊, NT, 100 % seawater; ■, 2,3-DNT, 25 % seawater; ●, 2,3-DNT, 50 % seawater; ●, 2,3-DNT, 75 % seawater; +, 2,3-DNT, 100 % seawater.

Figure 3. van’t Hoff plot of TNB and 2,6-DNT in seawater at various temperatures: □, TNB, 25 % seawater; Δ, TNB, 50 % seawater; ○, TNB, 75 % seawater; ◊, TNB, 100 % seawater; ■, 2,6-DNT, 25 % seawater; ●, 2,6-DNT, 50 % seawater; ●, 2,6-DNT, 75 % seawater; +, 2,6-DNT, 100 % seawater.

match those reported by Tzheutschler and Gelbin$^{15}$ for lower temperatures (Figure 1, squares), while the results for the aqueous solubility of TNB are higher than those found by Urbanskii$^{16}$ at low temperature and may match at higher temperatures (Figure 1, circles). The values measured for 2,6-
Table 5. Salting-Out Parameters, $K'_s$, for NT, 2,6-DNT, 2,3-DNT, and TNB at Various Temperatures, $T$.

<table>
<thead>
<tr>
<th></th>
<th>2,6-DNT</th>
<th>2,3-DNT</th>
<th>TNB</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$</td>
<td>$K'_s$</td>
<td>$T$</td>
<td>$K'_s$</td>
</tr>
<tr>
<td>K</td>
<td>L mol$^{-1}$ SE</td>
<td>K</td>
<td>L mol$^{-1}$ SE</td>
</tr>
<tr>
<td>278.5</td>
<td>0.15</td>
<td>0.006</td>
<td>278.0</td>
</tr>
<tr>
<td>281.0</td>
<td>0.16</td>
<td>0.011</td>
<td>280.7</td>
</tr>
<tr>
<td>292.0</td>
<td>0.15</td>
<td>0.005</td>
<td>292.1</td>
</tr>
<tr>
<td>303.4</td>
<td>0.13</td>
<td>0.037</td>
<td>303.3</td>
</tr>
<tr>
<td>313.6</td>
<td>0.14</td>
<td>0.004</td>
<td>314.0</td>
</tr>
</tbody>
</table>

$^a$ SE: standard error.

Table 6. Molar Free Energy of Transfer, $\Delta_m G^o$, Enthalpy of Transfer, $\Delta_m H^o$, and Entropy of Transfer, $\Delta_m S^o$, of Nitroaromatic Compounds from Pure Water to Seawater Solutions (L mol$^{-1}$) at 303.2 K.

<table>
<thead>
<tr>
<th></th>
<th>25% seawater</th>
<th>50% seawater</th>
<th>75% seawater</th>
<th>100% seawater</th>
</tr>
</thead>
<tbody>
<tr>
<td>NT</td>
<td>$\Delta_m G^o$</td>
<td>141 ± 0</td>
<td>248 ± 1</td>
<td>266 ± 2</td>
</tr>
<tr>
<td></td>
<td>$\Delta_m H^o$</td>
<td>363 ± 308</td>
<td>842 ± 1200</td>
<td>1240 ± 2640</td>
</tr>
<tr>
<td></td>
<td>$\Delta_m S^o$</td>
<td>0.73 ± 1.02</td>
<td>1.96 ± 3.95</td>
<td>3.21 ± 8.72</td>
</tr>
<tr>
<td>2,6-DNT</td>
<td>$\Delta_m G^o$</td>
<td>136 ± 0</td>
<td>263 ± 1</td>
<td>404 ± 1</td>
</tr>
<tr>
<td></td>
<td>$\Delta_m H^o$</td>
<td>-146 ± 376</td>
<td>-649 ± 322</td>
<td>-367 ± 679</td>
</tr>
<tr>
<td></td>
<td>$\Delta_m S^o$</td>
<td>-0.93 ± 1.24</td>
<td>-3.01 ± 1.06</td>
<td>-2.54 ± 2.24</td>
</tr>
<tr>
<td>2,3-DNT</td>
<td>$\Delta_m G^o$</td>
<td>134 ± 0</td>
<td>249 ± 1</td>
<td>312 ± 2</td>
</tr>
<tr>
<td></td>
<td>$\Delta_m H^o$</td>
<td>113 ± 403</td>
<td>416 ± 1030</td>
<td>467 ± 1570</td>
</tr>
<tr>
<td></td>
<td>$\Delta_m S^o$</td>
<td>-0.07 ± 0.96</td>
<td>0.55 ± 2.01</td>
<td>0.51 ± 3.64</td>
</tr>
<tr>
<td>TNB</td>
<td>$\Delta_m G^o$</td>
<td>111 ± 0</td>
<td>211 ± 1</td>
<td>303 ± 1</td>
</tr>
<tr>
<td></td>
<td>$\Delta_m H^o$</td>
<td>-305 ± 517</td>
<td>-324 ± 947</td>
<td>-502 ± 1480</td>
</tr>
<tr>
<td></td>
<td>$\Delta_m S^o$</td>
<td>-2.98 ± 1.70</td>
<td>-1.75 ± 3.12</td>
<td>-2.62 ± 4.86</td>
</tr>
</tbody>
</table>

The presence of salt lowers the solubility of NT, 2,6-DNT, 2,3-DNT, and TNB for all temperatures. Values of the salting-out parameter based on eq 2 for NT (0.15 ± 0.01) L mol$^{-1}$, 2,3-DNT (0.13 ± 0.01) L mol$^{-1}$, 2,6-DNT (0.12 ± 0.01) L mol$^{-1}$, and TNB (0.09 ± 0.01) L mol$^{-1}$ do not vary significantly with temperature, assuming a 95% confidence interval (Table 5). These parameters compare well with the values given for NT (0.163 L mol$^{-1}$)$^{10}$ reported for sodium chloride solutions and average values given for TNT (0.12 L mol$^{-1}$)$^{10}$ and 2,4-DNT (0.11 L mol$^{-1}$)$^{10}$ in seawater solutions. As with the pure water systems, the solubility of 2,3-DNT, 2,6-DNT, NT, and TNB in saline solutions increased with increasing temperature. Comparison of the temperature coefficients based on eq 3 for pure water systems with saltwater systems shows that increasing the salinity does not change the temperature coefficient within the 95% confidence interval (Table 3). As was seen in the pure water system, the temperature coefficient in saltwater for NT, which has one less nitro group, is smaller (<0.032) K$^{-1}$ than those of the dinitrotoluences (<0.045) K$^{-1}$, but the trend of increasing temperature coefficients with increasing number of nitro groups is not followed by TNT, which has a reported temperature coefficient (~0.036) K$^{-1}$ in seawater.$^{10}$

The result that the salting-out parameters do not vary systematically with temperature suggests that the enthalpy of transfer from the pure to the salt-water phase, $\Delta_m H^o$, should be close to zero. A thermodynamic analysis by Long and McDevitt$^{24}$ provides a means for calculating the enthalpy of transfer from fresh water to saltwater. They define the overall chemical potential, $\mu_i$, of a nonelectrolyte species $i$ as

$$\mu_i = RT \ln(\gamma_i x_i) + \mu_i^\circ$$

with the chemical potential in the standard state, $\mu_i^\circ$, defined as

$$\mu_i^\circ = \lim_{x \to 0} (\mu_i - RT \ln(\gamma_i))$$

where $\gamma_i$ is the activity coefficient in the salt solution and $x_i$ is the mole fraction. Given these two equations, the free energy change upon transfer ($\Delta_m G^o$) of a nonelectrolyte from pure water to the aqueous phase would be$^{24}$

$$\Delta_m G^o = \Delta_m H^o - T\Delta_m S^o = RT \ln\left(\frac{\gamma_i^W}{\gamma_i^S}\right)$$

(5)

Here $\Delta_m S^o$ is the entropy of transfer and $\gamma_i^W$ is the activity coefficient in the salt-free solution. Because the difference between the molar activity coefficient ($\gamma$) and the activity coefficient ($\gamma_i$) is small, the ratio of the activity coefficients is related to the aqueous solubility by$^{24}$

$$\left(\frac{\gamma_i^W}{\gamma_i^S}\right) = \left(\frac{S_w}{S}\right)$$

(6)

Substituting eq 6 into eq 5 yields

$$\Delta_m G^o = \Delta_m H^o - T\Delta_m S^o = RT \ln\left(\frac{S_w}{S}\right)$$

(7)

or

$$\frac{\Delta_m H^o}{R} - \frac{1}{T} = \frac{\Delta_m S^o}{R} = \ln\left(\frac{S_w}{S}\right)$$

(8)

The values of $\Delta_m H^o$ were obtained from plots of $\ln(S_w/S)$ versus inverse temperature, and enthalpy values obtained in this fashion are often called van’t Hoff enthalpies.$^{25}$ For the compounds studied here, the linear fits were variable and often poor (correlation coefficients ranged from 0.21 to 0.96) as shown in Figures 2 and 3, so the 95% confidence interval for $\Delta_m H^o$ is presented with the results in Table 6. The values for $\Delta_m G^o$ and $\Delta_m S^o$ (Table 6 for 303.2 K) were determined using eq 7, and the errors for $\Delta_m G^o$ were determined by propagating solubility errors, while the errors for $\Delta_m S^o$ were determined by propagating the errors in $\Delta_m G^o$ and $\Delta_m H^o$. The $\Delta_m G^o$ values are positive for all nitroaromatic compounds tested, (111 to 551) J mol$^{-1}$, showing that it is not thermodynamically favorable to transfer a nitroaromatic nonelectrolyte from a pure water system to a
salt water system. Positive values of $\Delta_n G^\circ$ would be found for any compound that is salted-out. The signs of $\Delta_n H^\circ$ and $\Delta_n S^\circ$ do not follow a simple pattern with increasing number of nitro groups for compounds examined in this work. For most compounds and salt concentrations, the 95% confidence interval straddles zero for both thermodynamic parameters. When studying naphthalene solubility in seawater, Gold and Rodriguez26 found that the enthalpy of dissolution into fresh water was the same as dissolution into seawater ($\Delta_n H^\circ = 0$), and they attributed the increase in free energy to a decrease in entropy as the nonelectrolyte moves into seawater ($\Delta_n S^\circ < 0$). In contrast, Noubigh et al.27 reported that the positive values of $\Delta_n G^\circ$ of several phenolic compounds from fresh water to salt water (KCl, NaCl, LiCl) was caused by positive values of both $\Delta_n H^\circ$ and $\Delta_n S^\circ$. More work is needed with compounds with additional substituents to elucidate their effect on $\Delta_n H^\circ$ and $\Delta_n S^\circ$.

Conclusions

The solubility of NT, 2,6-DNT, 2,3-DNT, and TNB was measured in pure water and seawater. The pure water solubility for the compounds determined in this study agree fairly well with values observed in earlier studies.14-18 Equations describing the aqueous solubility as a function of temperature were empirically generated (eq 3). Equations describing the solubility of NT, 2,6-DNT, 2,3-DNT, and TNB as a function of ionic strength for seawater have been generated in the form of eq 2. The average values of the salting out coefficient for NT, 2,3-DNT, 2,6-DNT, and TNB were $0.15 \pm 0.01 \text{ L} \cdot \text{mol}^{-1}$, $(0.13 \pm 0.01) \text{ L} \cdot \text{mol}^{-1}$, $(0.12 \pm 0.01) \text{ L} \cdot \text{mol}^{-1}$, and $(0.09 \pm 0.01) \text{ L} \cdot \text{mol}^{-1}$, respectively, and did not vary significantly with temperature.

Literature Cited

(17) Drinking Water Health Advisory for 2,4-dinitrotoluene and 2,6-dinitrotoluene, EPA-822-R-06-06; U.S. Environmental Protection Agency: Washington, DC, 2006.

Received for review July 3, 2007. Accepted September 8, 2007. This work was sponsored in part by the Naval Academy Research Council and ONR grant (N00014071W20102) award to D.J.L.P. and by a Strategic Environmental Research and Development Program (SERDP ER 1431) award to D.W.O.