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

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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·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·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_{salt}) through the Setschenow equation

$$\log(S_{\text{w}}/S) = K_{\text{s}}\, C_{\text{salt}} \tag{1}$$

where S_{w} is the solute solubility in pure water, S is the solute solubility in the salt solution, and K_{s} is the Setschenow 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]

$$\log(S_{\text{w}}/S) = K_{\text{s}}'\, I \tag{2}$$

where K_{s}' is a modified salting-out parameter. 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, while Luning Prak and O'Sullivan[10] reported average K_{s}' values of 0.11 L·mol^{-1} and 0.12 L·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 MΩ·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 μm 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 and

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

	c/(moles·L^{-1})			
	25 % seawater	50 % seawater	75 % seawater	100 % seawater
ion	(8.8 g of salt/kg of seawater)	(16.6 g of salt/kg of seawater)	(24.8 g of salt/kg of seawater)	(33.1 g of salt/kg of seawater)
Cl^-	0.1301	0.2625	0.3971	0.5340
SO_4^{2-}	0.0067	0.0136	0.0205	0.0276
HCO_3^-	0.0006	0.0012	0.0018	0.0024
Br^-	0.0002	0.0004	0.0006	0.0008
H_3BO_3	0.0001	0.0002	0.0003	0.0004
F^-	0.0000	0.0000	0.0000	0.0001
Na^+	0.1118	0.2256	0.3412	0.4589
Mg^{2+}	0.0126	0.0254	0.0384	0.0517
Ca^{2+}	0.0025	0.0049	0.0075	0.0101
K^+	0.0024	0.0049	0.0074	0.0100
Sr^{2+}	0.0000	0.0000	0.0001	0.0001
ionic strength	0.1662	0.3352	0.5071	0.6820

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]

% seawater	T K	no. of samples	c(NT) mg·L^{-1}	SD	T K	no. of samples	c(2,6-DNT) mg·L^{-1}	SD	T K	no. of samples	c(2,3-DNT) mg·L^{-1}	SD	T K	no. of samples	c(TNB) mg·L^{-1}	SD
MilliQ	278.5	3	190	0.4	278.0	3	74	0.3	278.1	3	67	0.7	277.5	3	270	2.5
25	278.5	3	178	0.2	278.0	3	70	0.3	278.1	3	63	0.4	277.5	6	268	7.4
50	278.5	3	168	0.3	278.0	3	68	0.3	278.1	3	59	0.8	277.5	6	254	3.9
75	278.5	3	157	0.5	278.0	3	64	0.3	278.1	3	56	0.4	277.5	6	249	3.3
100	278.5	3	149	0.6	278.0	3	62	0.5	278.1	3	54	0.2	277.5	6	241	2.2
MilliQ	281.0	3	219	13.7	280.7	3	90	0.6	280.6	3	80	0.4	ND	ND	ND	ND
25	281.0	3	205	0.4	280.7	3	86	0.1	280.6	3	76	0.2	ND	ND	ND	ND
50	281.0	2	189	1.4	280.7	3	82	0.2	280.6	3	73	0.5	ND	ND	ND	ND
75	281.0	3	179	1.5	280.7	3	78	0.3	280.6	3	69	0.3	ND	ND	ND	ND
100	281.0	3	168	1.0	280.7	3	75	1.6	280.6	3	65	1.0	ND	ND	ND	ND
MilliQ	292.0	3	295	1.9	292.1	3	147	0.2	292.1	3	122	0.9	290.1	3	390	2.2
25	292.0	2	275	0.2	292.1	3	140	0.3	292.1	3	115	0.5	290.1	3	378	2.8
50	292.0	2	258	0.6	292.1	3	134	0.3	292.1	3	109	0.4	290.1	3	357	3.2
75	292.0	3	243	0.6	292.1	3	128	0.1	292.1	3	104	0.3	290.1	3	343	1.3
100	292.0	3	230	0.8	292.1	3	123	0.6	292.1	3	99	0.5	290.1	3	335	0.6
MilliQ	297.6	3	361	25.1	297.5	3	204	0.4	297.5	3	161	0.6	297.7	3	492	30
MilliQ	303.4	3	422	0.8	303.3	3	266	0.5	303.4	3	202	0.2	304.0	4	565	1.8
25	303.4	3	399	0.7	303.3	3	252	0.1	303.4	3	192	0.4	304.0	4	541	1.1
50	303.4	3	382	0.2	303.3	3	240	0.2	303.4	3	183	0.7	304.0	3	520	0.4
75	303.4	5	376	34.7	303.3	3	227	0.2	303.4	3	179	1.1	304.0	3	501	0.8
100	303.4	3	339	0.3	303.3	3	217	0.5	303.4	3	165	0.1	304.0	3	486	0.6
MilliQ	308.9	3	495	0.7	308.7	3	338	2.1	308.7	3	249	1.5	308.5	3	667	3.6
MilliQ	313.6	3	578	7.0	314.0	3	423	6.4	313.6	3	313	1.0	313.6	4	749	3.0
25	313.6	3	550	6.2	314.0	3	403	0.8	313.6	3	298	0.7	313.6	4	713	3.6
50	313.6	3	522	0.5	314.0	3	378	4.5	313.6	3	284	0.5	313.6	3	687	1.9
75	313.6	3	491	1.7	314.0	3	366	3.2	313.6	3	268	0.3	313.6	3	662	2.0
100	313.6	3	467	0.2	314.0	3	346	7.2	313.6	3	255	0.5	313.6	3	641	2.2

[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

	NT		2,6-DNT		2,3-DNT		TNB	
	a	b	a	b	a	b	a	b
% sea water	10^4·mg·L^{-1}	K^{-1}	10^4 ·mg·L^{-1}	K^{-1}	10^4·mg·L^{-1}	K^{-1}	10^4·mg·L^{-1}	K^{-1}
0	352	0.0310	1.1	0.048	5.1	0.042	1040	0.0284
	(187, 664)	(±0.0021)	(0.50, 2.5)	(±0.003)	(2.60, 10.0)	(±0.002)	(582, 1860)	(±0.0019)
25	295	0.0314	1.2	0.048	4.7	0.043	1520	0.0269
	(129, 675)	(±0.0028)	(0.35, 3.9)	(±0.004)	(1.53, 14.6)	(±0.004)	(964, 2390)	(±0.0015)
50	228	0.0321	1.4	0.047	4.0	0.043	1190	0.0276
	(131, 400)	(±0.0019)	(0.46, 4.0)	(±0.004)	(1.0, 15)	(±0.005)	(844, 1670)	(±0.0011)
75	186	0.0326	1.2	0.048	3.7	0.043	1230	0.0273
	(53.7, 646)	(±0.0042)	(0.42, 3.2)	(±0.003)	(0.89, 16)	(±0.005)	(780, 1940)	(±0.0015)
100	198	0.0321	1.2	0.047	3.6	0.043	1380	0.0269
	(121, 326)	(±0.0017)	(0.45, 3.4)	(±0.003)	(1.3, 9.9)	(±0.003)	(816, 2330)	(±0.0018)

[a] Values in parentheses represent the 95 % confidence interval.

2,4-DNT in previous studies.[10] 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.[10]

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

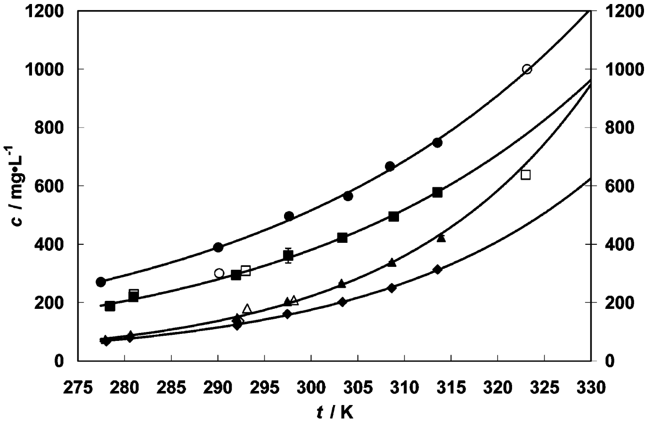

Figure 1. Solubility in pure water: □, NT, ref 15; ■, NT, this study; Δ, 2,6-DNT, ref 14 and 17; ▲, 2,6-DNT, this study; ○, TNB, ref 16; ●, TNB, this study; ◇, 2,3-DNT, ref 18; ◆, 2,3-DNT, this study. Error bars show the standard deviation of the concentration of replicate vials. Error bars for temperature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

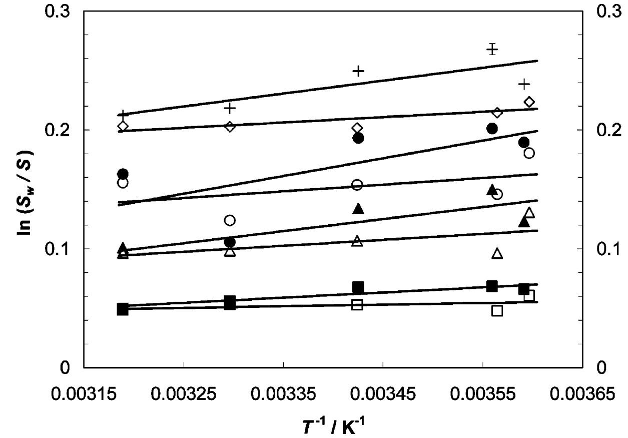

Figure 2. van't Hoff plot of NT and 2,3-DNT in seawater at various concentrations: □, NT, 25 % seawater; Δ, NT, 50 % seawater; ○, NT, 75 % seawater; ◇, NT, 100 % seawater; ■, 2,3-DNT, 25 % seawater; ▲, 2,3-DNT, 50 % seawater; ●, 2,3-DNT, 75 % seawater; +, 2,3-DNT, 100 % seawater.

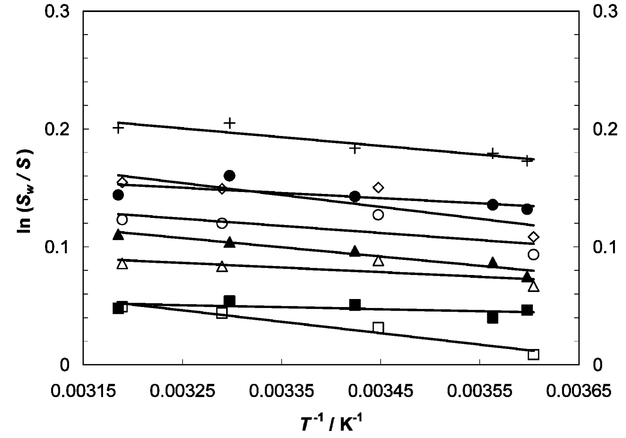

Figure 3. van't Hoff plot of TNB and 2,6-DNT in seawater at various concentrations: □, TNB, 25 % seawater; Δ, TNB, 50 % seawater; ○, TNB, 75 % seawater; ◇, TNB, 100 % seawater; ■, 2,6-DNT, 25 % seawater; ▲, 2,6-DNT, 50 % seawater; ●, 2,6-DNT, 75 % seawater; +, 2,6-DNT, 100 % seawater.

Table 4. Comparison of Calculated (based on Equation 4) and Predicted (UNIFAC and Pierotti) Activity Coefficients, γ, of NT, 2,6-DNT, 2,3-DNT, and TNB in Pure Water Based on Using Heat of Fusion, ΔH_f, Melting Temperature, T_m, and Sample Temperature, T

	NT	2,6-DNT	2,3-DNT	TNB
ΔH_f/ kJ•mol^{-1}	16.81[28,29]	23.85[29], 16.07[28]	17.57[29]	14.8[29]
T_m/ K	325[28]	340[28]	330[29]	398.4[28]
T/K	297.5	297.5	297.5	297.5
γ (eq 4, expt)	1.13•10^4	1.96•10^4, 1.25•10^4	2.89•10^4	0.314•10^4
γ (UNIFAC)	2.14•10^4	9.86•10^4	9.86•10^4	6.67•10^4
γ (Pierotti)	1.48•10^4	2.09•10^4	2.09•10^4	0.590•10^4

match those reported by Tzcheutschler and Gelbin[15] for lower temperatures (Figure 1, squares), while the results for the aqueous solubility of TNB are higher than those found by Urbanski[16] at low temperature and may match at higher temperatures (Figure 1, circles). The values measured for 2,6-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 of

$$c/\text{mg}\cdot\text{L}^{-1} = a \exp(b\ T/\text{K}) \tag{3}$$

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})[10] is similar to that of the dinitrotoluenes.

A thermodynamic analysis of solubility data was used to calculate activity coefficients (γ), 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]

$$\ln(x\gamma) = \frac{\Delta H_f}{RT}\left[1 - \frac{T}{T_t}\right] - \frac{\Delta c_p}{R}\left(\frac{T_t - T}{T}\right) + \frac{\Delta c_p}{R}\ln\frac{T_t}{T} \tag{4}$$

In this equation, x is the mole fraction of the nitroaromatic compound from the solid−liquid equilibrium, ΔH_f is the heat of fusion at the melting point, T_t is the triple point, T is the temperature in Kelvin, Δc_p is the difference between the liquid and solid heat capacity, and R is the gas coefficient. 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 Tsonopoulos 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 800 % (NT) to 2000 % (TNB), while the simpler Pierotti equation deviates by at most 31%.

Table 5. Salting-Out Parameters, K_s', for NT, 2,6-DNT, 2,3-DNT, and TNB at Various Temperatures, T[a]

NT			2,6-DNT			2,3-DNT			TNB		
T	K_s'		T	K_s'		T	K_s'		T	K_s'	
K	$L\cdot mol^{-1}$	SE	K	$L\cdot mol^{-1}$	SE	K	$L\cdot mol^{-1}$	SE	K	$L\cdot mol^{-1}$	SE
278.5	0.15	0.006	278.0	0.11	0.009	278.1	0.14	0.012	277.5	0.08	0.014
281.0	0.16	0.011	280.7	0.12	0.002	280.6	0.14	0.008			
292.0	0.15	0.005	292.1	0.11	0.003	292.1	0.12	0.003	290.1	0.10	0.014
303.4	0.13	0.037	303.3	0.13	0.004	303.4	0.12	0.018	304.0	0.09	0.005
313.6	0.14	0.004	314.0	0.12	0.010	313.6	0.13	0.004	313.6	0.09	0.003

[a] SE: standard error.

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

		25 % seawater	50 % seawater	75 % seawater	100 % seawater
NT	$\Delta_{tr}G^o$	141 ± 0	248 ± 1	266 ± 24	551 ± 1
	$\Delta_{tr}H^o$	363 ± 308	842 ± 1200	1240 ± 2640	902 ± 1190
	$\Delta_{tr}S^o$	0.73 ± 1.02	1.96 ± 3.95	3.21 ± 8.72	1.16 ± 3.91
2,6-DNT	$\Delta_{tr}G^o$	136 ± 0	263 ± 1	404 ± 1	517 ± 1
	$\Delta_{tr}H^o$	−146 ± 376	−649 ± 322	−367 ± 679	−617 ± 452
	$\Delta_{tr}S^o$	−0.93 ± 1.24	−3.01 ± 1.06	−2.54 ± 2.24	−3.74 ± 1.49
2,3-DNT	$\Delta_{tr}G^o$	134 ± 0	249 ± 1	312 ± 2	511 ± 1
	$\Delta_{tr}H^o$	113 ± 403	416 ± 1030	467 ± 1570	376 ± 495
	$\Delta_{tr}S^o$	−0.07 ± 0.96	0.55 ± 2.01	0.51 ± 3.64	−0.44 ± 0.39
TNB	$\Delta_{tr}G^o$	111 ± 0	211 ± 1	303 ± 1	377 ± 1
	$\Delta_{tr}H^o$	−805 ± 517	−324 ± 947	−502 ± 1480	−843 ± 1590
	$\Delta_{tr}S^o$	−2.98 ± 1.70	−1.75 ± 3.12	−2.62 ± 4.86	−3.97 ± 5.23

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) $L\cdot mol^{-1}$, 2,3-DNT (0.13 ± 0.01) $L\cdot mol^{-1}$, 2,6-DNT (0.12 ± 0.01) $L\cdot mol^{-1}$, and TNB (0.09 ± 0.01) $L\cdot mol^{-1}$ 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 $L\cdot mol^{-1}$)[9] reported for sodium chloride solutions and average values given for TNT (0.12 $L\cdot mol^{-1}$)[10] and 2,4-DNT (0.11 $L\cdot mol^{-1}$)[10] in seawater systems. 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 dinitrotoluenes (∼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, $\Delta_{tr}H^o$, should be close to zero. A thermodynamic analysis by Long and McDevit[24] provides a means for calculating the enthalpy of transfer from fresh water to saltwater. They define the overall chemical potential, μ_i, of a nonelectrolyte species i as

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

with the chemical potential in the standard state, μ_i^*, defined as

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

where γ_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 ($\Delta_{tr}G^o$) of a nonelectrolyte from pure water to the aqueous phase would be[24]

$$\Delta_{tr}G^o = \Delta_{tr}H^o - T\Delta_{tr}S^o = RT\ln\left(\frac{\gamma_i}{\gamma_i^o}\right) \tag{5}$$

Here $\Delta_{tr}S^o$ is the entropy of transfer and γ_i^o is the activity coefficient in the salt-free solution. Because the difference between the molar activity coefficient (f_i) and the activity coefficient (γ_i) is small, the ratio of the activity coefficients is related to the aqueous solubility by[24]

$$\left(\frac{\gamma_i}{\gamma_i^o}\right) = \left(\frac{S_w}{S}\right) \tag{6}$$

Substituting eq 6 into eq 5 yields

$$\Delta_{tr}G^o = \Delta_{tr}H^o - T\Delta_{tr}S^o = RT\ln\left(\frac{S_w}{S}\right) \tag{7}$$

or

$$\frac{\Delta_{tr}H^o}{R}\left(\frac{1}{T}\right) - \frac{\Delta_{tr}S^o}{R} = \ln\left(\frac{S_w}{S}\right) \tag{8}$$

The values of $\Delta_{tr}H^o$ 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 $\Delta_{tr}H^o$ is presented with the results in Table 6. The values for $\Delta_{tr}G^o$ and $\Delta_{tr}S^o$ (Table 6 for 303.2 K) were determined using eq 7, and the errors for $\Delta_{tr}G^o$ were determined by propagating solubility errors, while the errors for $\Delta_{tr}S^o$ were determined by propagating the errors in $\Delta_{tr}G^o$ and $\Delta_{tr}H^o$. The $\Delta_{tr}G^o$ values are positive for all nitroaromatic compounds tested, (111 to 551) $J\cdot mol^{-1}$, 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 $\Delta_{tr}G^o$ would be found for any compound that is salted-out. The signs of $\Delta_{tr}H^o$ and $\Delta_{tr}S^o$ 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 Rodriguez[26] found that the enthalpy of dissolution into fresh water was the same as dissolution into seawater ($\Delta_{tr}H^o = 0$), and they attributed the increase in free energy to a decrease in entropy as the nonelectrolyte moves into seawater ($\Delta_{tr}S^o < 0$). In contrast, Noubigh et al.[27] reported that the positive values of $\Delta_{tr}G^o$ of several phenolic compounds from fresh water to salt water (KCl, NaCl, LiCl) was caused by positive values of both $\Delta_{tr}H^o$ and $\Delta_{tr}S^o$. More work is needed with compounds with additional substituents to elucidate their effect on $\Delta_{tr}H^o$ and $\Delta_{tr}S^o$.

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 ± 0.01) $\text{L}\cdot\text{mol}^{-1}$, (0.13 ± 0.01) $\text{L}\cdot\text{mol}^{-1}$, (0.12 ± 0.01) $\text{L}\cdot\text{mol}^{-1}$, and (0.09 ± 0.01) $\text{L}\cdot\text{mol}^{-1}$, respectively, and did not vary significantly with temperature.

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