Assessing the Salting-Out Behavior of Nitrobenzene, 2-Nitrotoluene, and 3-Nitrotoluene from Solubility Values in Pure Water and Seawater at Temperatures between (277 and 314) K

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The salting-out behavior of nitrobenzene (NB), 2-nitrotoluene (2-NT), and 3-nitrotoluene (3-NT) was determined from solubility measurements in pure water and seawater with ionic strengths = (0.1662, 0.3352, 0.5071, and 0.6820) $\text{mol}\cdot\text{L}^{-1}$ at temperatures between (277 and 314) K. For all compounds tested, the solubility increased with increasing temperature. Solubility values in pure water compare well with previously reported values. As the ionic strength of the solution increased, the solubility of the organic compounds decreased. The average salting-out coefficients for NB, 2-NT, and 3-NT were (0.12, 0.14, and 0.14) $\text{L}\cdot\text{mol}^{-1}$, respectively, which are consistent with measurements for other nitroaromatic compounds. Over the temperature range examined, the salting-out coefficients did not vary significantly.

Introduction

Pollution of the aquatic environment by nitroaromatic compounds can occur when chemical production (explosives, urethane, dyes) feedstocks are improperly handled or discarded and when unexploded ordnance casings rust at shooting ranges or battlefield sites.[1−3] As these organic compounds contact the aqueous phase, they dissolve and can be transported or transformed by chemical, biological, or physical processes. Most studies on nitroaromatic transformation processes have focused on freshwater or manufacturing effluent streams,[4−8] and very few studies have examined marine systems.[9,10] To accurately model the fate and transport of pollutants in marine systems, knowledge of the solubility of these compounds under various temperature and salinity conditions is needed.

The presence of dissolved salts has been found to alter the solubility of some organic compounds. When solubility decreases when salts are added (see review in Xie et al.[11]), the process is commonly called "salting-out". For solutions that are a complex mixture of salts such as seawater, the salting-out effect is quantified using a version of the Setschenow equation, which relates organic compound solubility to solution ionic strength, I ($\text{mol}\cdot\text{L}^{-1}$)[12−16]

$$\log(S_w/S) = K_s'I \tag{1}$$

where S_w is the solute solubility in pure water ($\text{mg}\cdot\text{L}^{-1}$); S is the solute solubility in the salt solution ($\text{mg}\cdot\text{L}^{-1}$); and K_s' is a salting-out parameter ($\text{L}\cdot\text{mol}^{-1}$). The ionic strength, I, is defined by

$$I = \frac{1}{2}\sum_i C_i Z_i^2 \tag{2}$$

where C_i is the concentration of ion i ($\text{mol}\cdot\text{L}^{-1}$) and Z_i is the charge on ion i. Values of K_s' in seawater have been reported to be between 0.08 and 0.16 for several nitroaromatic compounds.[13−15] The goal of this study was to measure the solubility of nitrobenzene (NB), 2-nitrotoluene (2-NT), and 3-nitrotoluene (3-NT) in seawater over a range of salinity encompassing most coastal waters and at various temperatures. These compounds are used as solvents and in the production of compounds such as pesticides, drugs, explosives, and dyes.

Materials and Methods

To determine the solubility, batch mixing experiments were conducted in Pierce 14 mL borosilicate glass vials (Rockford, IL) sealed with Teflon screw caps. Ten or twelve milliliters of either 18 $\text{M}\Omega\cdot\text{cm}^{-1}$ Milli-Q (deionized water purified by a Millipore Milli-Q Plus water system) or seawater diluted with various amounts of Milli-Q water (see Table 1) were added to each vial. The values in Table 1 have an uncertainty that is less than 1 %. The seawater was taken from the surface of the Middle Atlantic Bight (salinity of 33.1 g of salt/kg of seawater) and filtered through 0.2 μm polysulfide filters (Gelman, Pall) prior to use. Next, 50.0 μL of either NB (Aldrich, 98 % purity), 2-NT (Aldrich, 99 % purity), or 3-NT (Aldrich, 99 % purity) was added to the vials. Triplicate vials were run for most experimental conditions. The vials were shaken on a Labquake tube shaker (Barnstead International) that was placed in either a Thermax temperature-controlled room or a Precision 818 low-temperature incubator or on the benchtop (room-temperature samples). The temperature variation among vials for all three systems was at most 0.7 K. A rate study conducted at 294 K for NB in Milli-Q revealed that equilibrium was achieved in less than 24 h, an amount of time similar to that found for other nitroaromatic compounds.[13,14] For all subsequent experiments, the vials were shaken for more than 24 h 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, 3 μm, 53 mm by 7 mm, Alltech) and a variable wavelength detector set to 254 nm.

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

	$c/(\text{mol}\cdot\text{L}^{-1})$			
	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 Nitrobenzene (1), 2-Nitrotoluene (2), and 3-Nitrotoluene (3) in Pure Water and Seawater from T = (277 to 314) K[a]

% seawater	T/K	no. of samples	c_1/mg·L^{-1}	SD	T/K	no. of samples	c_2/mg·L^{-1}	SD	T/K	no. of samples	c_3/mg·L^{-1}	SD
Milli-Q	278.3	3	1770	77	277.8	3	487	4	278.2	3	430	5
25	278.2	3	1640	5	277.9	3	469	4	278.0	ND	ND	ND
50	278.2	2	1560	1	277.8	2	441	4	277.9	ND	ND	ND
75	278.1	3	1480	8	277.8	3	413	5	277.9	ND	ND	ND
100	278.0	3	1400	13	277.8	3	393	2	278.0	ND	ND	ND
Milli-Q	287.2	3	1840	4	287.2	3	551	1	288.0	3	469	1
Milli-Q	293.8	3	1920	16	294.2	3	575	2	294.0	3	479	2
25	293.8	3	1800	8	293.9	3	537	4	294.1	3	449	3
50	293.8	3	1730	10	294.0	3	511	8	294.0	3	427	1
75	293.9	3	1650	15	294.0	3	478	1	294.0	3	401	1
100	294.0	3	1570	24	294.1	3	451	6	294.1	3	382	3
Milli-Q	296.7	3	2030	14	297.0	3	425	43	297.0	3	506	11
Milli-Q	303.6	3	2110	20	303.8	6	661	5	304.0	6	540	12
25	303.5	3	1980	5	303.8	6	609	8	303.7	6	502	2
50	303.7	3	1900	5	303.7	6	578	5	303.7	6	477	2
75	303.7	3	1790	144	303.9	3	548	3	304.0	3	450	1
100	303.8	3	1730	8	303.9	3	517	4	304.0	3	427	2
Milli-Q	308.7	3	2200	10	308.5	3	721	10	308.6	3	563	1
25	308.7	3	2090	6	308.7	3	656	3	308.7	3	528	4
50	308.7	3	2000	2	308.6	3	620	5	308.7	3	504	2
75	308.6	3	1900	1	308.7	3	583	2	308.6	3	476	3
100	308.8	3	1810	8	308.5	3	561	11	308.6	3	450	1
Milli-Q	313.7	3	2340	2	313.4	3	757	8	313.8	3	621	7
25	313.6	3	2210	7	313.4	3	707	3	313.6	3	569	9
50	313.7	3	2110	8	313.5	3	664	1	313.7	3	548	1
75	313.7	3	2010	11	313.4	3	627	1	313.6	3	514	8
100	313.6	3	1920	9	313.6	3	597	1	313.5	3	486	6

[a] ND: not determined. SD: standard deviation of replicate vials.

Samples (10 μL for 2-NT and 3-NT and 4 μL for NB) were injected into an eluent (methanol volume fraction of 50 % in water) for an isocratic separation with a flow rate of 0.75 mL·min^{-1}. To eliminate reforming the organic phase, all samples were maintained at their equilibration temperature prior to injection into the instrument.

Results and Discussion

Solubility data for NB, 2-NT, and 3-NT are shown in Table 2. The values given are an average and standard deviation of replicate vials. Errors due to standard preparation and instrument variability are approximately 0.8 % for NB, 1.1 % for 2-NT, and 1.9 % for 3-NT. The results for the aqueous solubility of NB in pure water compare well with those reported by other researchers[17−21] as shown in Figure 1. Variability in reported NB solubility values can be high, as illustrated by a greater than 8 % variation in values compiled by MacKay et al.[22] for 298 K (six values between (1930 and 2093) mg·L^{-1} and a seventh value was 1204 mg·L^{-1}). The results for 2-NT tend to

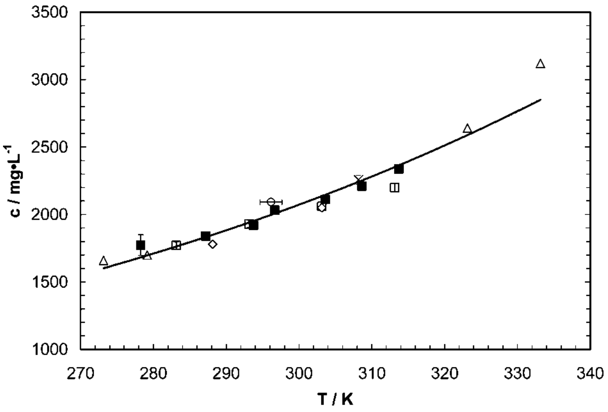

Figure 1. Solubility of nitrobenzene in pure water: □, ref 17; ○, ref 18; ◇, ref 19; △, ref 20; ×, ref 21; ■, this study. Error bars show the standard deviation of the concentration of replicate vials or 0.8 %, whichever is larger. The line shown is for the empirical correlation, $c/\text{mg}\cdot\text{L}^{-1} = 116 \exp(0.00961\ T/\text{K})$.

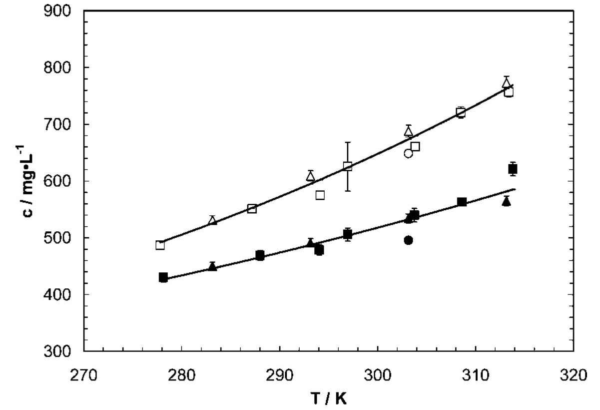

Figure 2. Solubility of 3-nitrotoluene and 2-nitrotoluene in pure water: ▲, 3-NT, ref 17; ●, 2-NT, ref 23; ■, 3-NT, this study; Δ, 2-NT, ref 17; ○, 2-NT, ref 23; □, 2-NT, this study. Error bars show either the standard deviation of the concentration of replicate vials or the analytical error (1.9 % for 3-NT and 1.1 % for 2-NT), whichever is larger. The lines shown are for the empirical correlations: $c(\text{2-NT})/\text{mg}\cdot\text{L}^{-1} = 15.7 \exp(0.0124\ T/\text{K})$ and $c(\text{3-NT})/\text{mg}\cdot\text{L}^{-1} = 36.4 \exp(0.00885\ T/\text{K})$.

fall slightly below values reported by Benes and Dohnal[17] and slightly above the value reported by Gross et al.[23] as shown in Figure 2. Figure 2 also shows that the results for 3-NT compare well with those of Benes and Dohnal[17] up to 304 K and are higher than those of Gross et al.[23] at 304 K and Benes and Dohnal[17] at 314 K. At the lowest temperature studied, both 3-NT (melting point of 288.7 K)[24] and NB (melting point of 278.9 K)[22] remained liquid (supercooled) during the gentle mixing process, so their solubility values represent quasi-equilibrium measurements. The value for NB reported by Vermillion et al.[20] for 273 K was also for a supercooled liquid.

Using the data shown in Figures 1 and 2, exponential fits of pure water concentration as a function of temperature were generated for all three compounds in the functional form of

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

where c is the concentration; T is temperature; and a and b are fitting parameters. Figures 1 and 2 show the exponential fits for the pure water systems (correlation coefficients of 0.94, 0.97, and 0.90 for NB, 2-NT, and 3-NT, respectively), and the values of a and b are given in Table 3 (along with their 95 % confidence intervals). The temperature coefficients for 2-NT, $(0.0124 \pm 0.0014)\ \text{K}^{-1}$, and 3-NT, $(0.00885 \pm 0.00195)\ \text{K}^{-1}$, the two liquid isomers of nitrotoluene, are smaller than that of the solid 4-nitrotoluene, 4-NT, $(0.0310 \pm 0.0024)\ \text{K}^{-1}$.[14]

The presence of salt lowers the solubility of NB, 2-NT, and 3-NT for all temperatures. Values of the salting-out parameter based on eq 1 for NB, $(0.12 \pm 0.01)\ \text{L}\cdot\text{mol}^{-1}$, 2-NT, $(0.14 \pm 0.01)\ \text{L}\cdot\text{mol}^{-1}$, and 3-NT, $(0.14 \pm 0.01)\ \text{L}\cdot\text{mol}^{-1}$, do not vary significantly with temperature, assuming a 95 % confidence interval (Table 4). Saylor et al.[25] reported both salting-in and salting-out behavior for NB at 303 K in the presence of organic and inorganic ions. Hashimoto et al.[12] reported that sodium chloride solutions behaved similarly to Pacific Ocean seawater when calculating the K_s' values. Using the sodium chloride data from Saylor et al.,[25] a salting-out coefficient of approximately $0.13\ \text{L}\cdot\text{mol}^{-1}$ can be calculated. This value is consistent with the value of $0.12\ \text{L}\cdot\text{mol}^{-1}$ reported herein. The K_s' values for 2-NT and 3-NT, both $(0.14 \pm 0.01)\ \text{L}\cdot\text{mol}^{-1}$, are similar to the values found for 4-NT, $(0.15 \pm 0.01)\ \text{L}\cdot\text{mol}^{-1}$,[14] in the same seawater system.

The salting-out coefficient for NB is slightly less that those of the nitrotoluenes. Such a result is expected. Positive correlations have been found between salting-out coefficients based on sodium chloride concentration and both octanol–water partition coefficients, K_{ow},[26] and LeBas molar volumes.[11] It would be expected, then that NB with a K_{ow} of approximately 1.85 and a LeBas molar volume of $112.0\ \text{cm}^3\cdot\text{mol}^{-1}$ should have a lower salting-out coefficient than those of 2-NT, 3-NT, and 4-NT, which have higher K_{ow} values (approximately 2.30, 2.40, and 2.30, respectively) and higher LeBas molar volumes (all are $153.0\ \text{cm}^3\cdot\text{mol}^{-1}$).[22,24] Hasimoto et al.[12] developed a correlation that showed that K_s' values increased as the logarithm of S_w decreased. NB, which has the largest pure water solubility of the compounds studied herein, does have the smallest K_s'. In the plot of their correlation, Hasimoto et al.[12] also showed that the values of K_s' for isomers of nitrophenol do not follow this correlation. Similarly, the values of K_s' for isomers of nitrotoluene reported herein also do not follow the correlation.

As with the pure water systems, the solubility of NB, 2-NT, and 3-NT in seawater solutions increased with increasing temperature. Comparison of the temperature coefficients based on eq 2 for pure water systems with saltwater systems (correlation coefficients > 0.97) shows that increasing the salinity does not change the temperature coefficient within the 95 % confidence interval (Table 3). Similar behavior has been found for other nitroaromatic compounds.[13,14]

A thermodynamic analysis of the data can provide some insight into the processes involved in salting-out nitroaromatic compounds. Long and McDevit[27] provide a thermodynamic analysis for calculating the free energy change upon transfer ($\Delta_{tr}G°$) of a nonelectrolyte from pure water to the salt water with the net result being[14]

$$\Delta_{tr}G° = \Delta_{tr}H° - T\Delta_{tr}S° = RT\ln\left(\frac{S_w}{S}\right) \tag{4}$$

or

$$\frac{\Delta_{tr}H°}{R}\left(\frac{1}{T}\right) - \frac{\Delta_{tr}S°}{R} = \ln\left(\frac{S_w}{S}\right) \tag{5}$$

Here, $\Delta_{tr}S°$ is the entropy of transfer and $\Delta_{tr}H°$ is the enthalpy of transfer. On the basis of this equation, $\Delta_{tr}H°$ values were obtained from plots of $\ln(S_w/S)$ versus inverse temperature. When enthalpy values are obtained in this fashion, they are often called van't Hoff enthalpies.[28] For the compounds studied here, the linear fits spanned a wide range of correlation coefficients ranging from 0.10 to 0.93 as shown in Figures 3 and 4. The values of $\Delta_{tr}H°$ and the 95 % confidence interval from the linear regression are given in Table 5. Equation 4 was used to calculate $\Delta_{tr}G°$ and $\Delta_{tr}S°$ at 303.2 K (Table 5). The errors for $\Delta_{tr}G°$ were determined by propagating solubility errors, and the errors for $\Delta_{tr}S°$ were determined by propagating the errors in $\Delta_{tr}G°$ and $\Delta_{tr}H°$.

The positive values of $\Delta_{tr}G°$ for NB, 2-NT, and 3-NT, (160 to 618) $\text{J}\cdot\text{mol}^{-1}$, show that it is not thermodynamically favorable to transfer these compounds from a pure water system to a salt water system. The magnitude of the values increases as the salt concentration increases, a result that is expected when compounds are salted-out. The $\Delta_{tr}G°$ values determined in this work are similar to previously reported values for 4-NT, 2,6-dinitrotoluene (2,6-DNT), 2,3-dinitrotoluene (2,3-DNT), and

Table 3. Coefficients[a] of Equation 3 for the Influence of Temperature on the Equilibrium Solubility of Nitrobenzene (1), 2-Nitrotoluene (2), and 3-Nitrotoluene (3) in Pure Water and in Seawater at Various Concentrations

% seawater	a_1 / mg·L^{-1}	b_1 / 10^3·K^{-1}	a_2 / mg·L^{-1}	b_2 / 10^3·K^{-1}	a_3 / mg·L^{-1}	b_3 / 10^3·K^{-1}
0	116	9.61	15.7	12.4	36.4	8.85
	(81, 166)	(8.40, 10.8)	(10.5, 23.5)	(11.0, 13.7)	(20.4, 65.0)	(6.90, 10.8)
25	160	8.32	19.1	11.5	13.6	11.9
	(82, 313)	(6.08, 10.6)	(7.78, 46.7)	(8.46, 14.4)	(6.28, 29.4)	(9.37, 14.4)
50	143	8.53	18.2	11.4	11.1	12.4
	(89, 231)	(6.95, 10.1)	(9.05, 36.5)	(9.10, 13.8)	(3.62, 34.3)	(8.70, 16.1)
75	137	8.52	15.7	11.7	10.4	12.4
	(79, 237)	(6.68, 10.3)	(7.73, 32.0)	(9.33, 14.1)	(5.13, 21.1)	(10.1, 14.7)
100	122	8.72	14.3	11.8	10.9	12.1
	(76, 199)	(7.11, 10.3)	(5.79, 35.5)	(8.82, 14.9)	(4.67, 25.2)	(9.33, 14.9)

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

Table 4. Salting-Out Parameters K_s' for Nitrobenzene (1), 2-Nitrotoluene (2), and 3-Nitrotoluene (3) at Various Temperatures, T[a]

1			2			3		
T / K	K_s' / L·mol^{-1}	SE	T / K	K_s' / L·mol^{-1}	SE	T / K	K_s' / L·mol^{-1}	SE
278.1	0.13	0.001	277.8	0.15	0.004			
293.9	0.12	0.005	294.0	0.15	0.010	294.0	0.14	0.009
303.7	0.12	0.011	303.8	0.14	0.002	303.9	0.14	0.003
308.7	0.12	0.007	308.6	0.14	0.010	308.6	0.13	0.007
313.4	0.12	0.002	313.4	0.14	0.005	313.4	0.14	0.013

[a] SE: standard error.

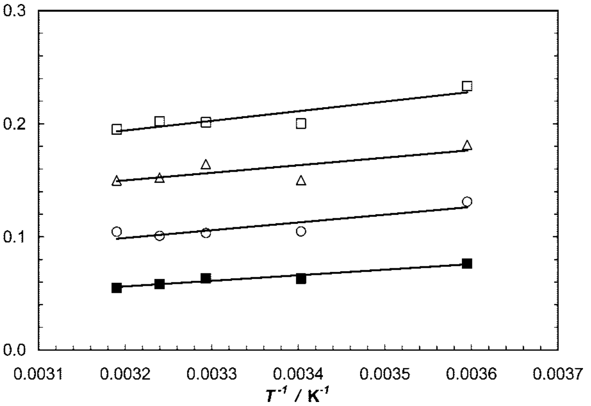

Figure 3. van't Hoff plot of nitrobenzene in seawater at various concentrations: ■, 25 % seawater; ○, 50 % seawater; Δ, 75 % seawater; □, 100 % seawater.

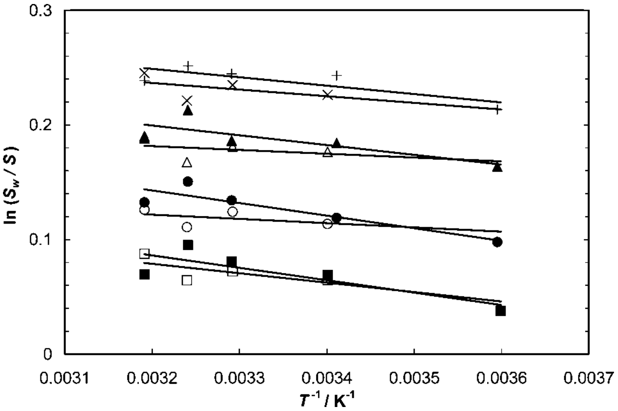

Figure 4. van't Hoff plot of 2-nitrotoluene and 3-nitrotoluene in seawater at various concentrations: □, 3-NT, 25 % seawater; ○, 3-NT, 50 % seawater; Δ, 3-NT, 75 % seawater; ×, 3-NT, 100 % seawater; ■, 2-NT, 25 % seawater; ●, 2-NT, 50 % seawater; ▲, 2-NT, 75 % seawater; +, 2-NT, 100 % seawater.

Table 5. Molar Free Energy of Transfer $\Delta_{tr}G°$, Enthalpy of Transfer $\Delta_{tr}H°$, and Entropy of Transfer $\Delta_{tr}S°$ of Nitrobenzene (1), 2-Nitrotoluene (2), and 3-Nitrotoluene (3) from Pure Water to Seawater Solutions (J·mol^{-1}) at 303.2 K[a]

	25 % seawater	50 % seawater	75 % seawater	100 % seawater
$\Delta_{tr}G^\circ_1$	160 ± 2	261 ± 3	415 ± 33	508 ± 2
$\Delta_{tr}H^\circ_1$	410 ± 64	570 ± 172	556 ± 243	709 ± 202
	(207, 612)	(22, 1120)	(−217, 1330)	(67, 1352)
$\Delta_{tr}S^\circ_1$	0.82 ± 0.21	1.02 ± 0.57	0.46 ± 0.81	0.66 ± 0.66
$\Delta_{tr}G^\circ_2$	204 ± 3	339 ± 2	470 ± 2	618 ± 2
$\Delta_{tr}H^\circ_2$	−900 ± 350	−916 ± 249	−709 ± 323	−609 ± 253
	(−2020, 215)	(−1710, −122)	(−1738, 319)	(−1414, 196)
$\Delta_{tr}S^\circ_2$	−3.63 ± 1.15	−4.13 ± 0.82	−3.88 ± 1.06	−4.04 ± 0.83
$\Delta_{tr}G^\circ_3$	182 ± 4	314 ± 4	457 ± 4	593 ± 4
$\Delta_{tr}H^\circ_3$	−683 ± 527	−307 ± 450	−278 ± 581	−483 ± 603
	(−2950, 1590)	(−2240, 1630)	(−2780, 2220)	(−3080, 2110)
$\Delta_{tr}S^\circ_3$	−2.85 ± 1.74	−2.04 ± 1.48	−2.42 ± 1.91	−3.54 ± 1.98

[a] The error for $\Delta_{tr}G°$ and $\Delta_{tr}S°$ was determined by error propagation. The values in parentheses for $\Delta_{tr}H°$ are the 95 % confidence interval from the regression using eq 5.

1,3,5-trinitrobenzene (TNB) in the same seawater matrix, which ranged from (111 to 551) J·mol^{-1}.[14]

The thermodynamically unfavorable transfer could be caused by an endothermic process, $\Delta_{tr}H°$ being positive, or by the system becoming more ordered, negative $\Delta_{tr}S°$. For 2-NT and 3-NT, the 95 % confidence interval for $\Delta_{tr}H°$ values straddle zero for most salt concentrations, suggesting that an endothermic process is not causing the unfavorable transfer. Similar behavior was found for $\Delta_{tr}H°$ values of 4-NT, 2,6-DNT, 2,3-DNT, and TNB in the same seawater systems as used in the experiments reported herein.[14] These results are also consistent with results found by Gold and Rodriguez[29] when studying naphthalene solubility in seawater. They found that the enthalpy of dissolution into fresh water was the same as dissolution into seawater ($\Delta_{tr}H° = 0$). For 2-NT and 3-NT in our experiments, the $\Delta_{tr}S°$ values are negative, which suggests that an increase in order in the system causes the transfer of these compounds from fresh water to seawater to be unfavorable. Gold and Rodriguez[29] also attribute the increase in free energy to a decrease in entropy as the nonelectrolyte moves into seawater ($\Delta_{tr}S° < 0$). Such results could occur if the ions in solution force the water to be more organized around the 2-NT and 3-NT than they would be in pure water.

In contrast to these results, the 95 % confidence intervals for $\Delta_{tr}H°$ for NB in our experiments are slightly greater than zero except for the 75 % salt concentration, which straddles zero. These results suggest that an endothermic process contributes to the unfavorable transfer of the solute from pure water to the salt solution. Arnett et al.[30] reported positive $\Delta_{tr}H°$ for the transfer of acetone, diacetone alcohol, butanone, and piperidine from fresh water to sodium chloride solutions. Noubigh et al.[31] also reported positive values of $\Delta_{tr}H^\circ$ for the transfer of several phenolic compounds from fresh water to salt water (KCl, NaCl, LiCl) solutions, though not all phenolic compounds behaved in this manner. For NB in our experiments, the $\Delta_{tr}S^\circ$ values are positive or straddle zero, which suggests that the unfavorable transfer is not caused by an increase in order in the system. Noubigh et al.[31] also reported positive values of $\Delta_{tr}S^\circ$ for those compounds with positive $\Delta_{tr}H^\circ$, while Arnett[30] found both positive and negative values of $\Delta_{tr}S^\circ$ for those compounds with positive $\Delta_{tr}H^\circ$ values.

Conclusions

On the basis of the solubility measurements of NB, 2-NT, and 3-NT in pure water and seawater, the salting-out coefficients were determined to be $(0.12 \pm 0.01)\ \text{L}\cdot\text{mol}^{-1}$, $(0.14 \pm 0.01)\ \text{L}\cdot\text{mol}^{-1}$, and $(0.14 \pm 0.01)\ \text{L}\cdot\text{mol}^{-1}$, respectively. For NB, the value is close to the value determined for sodium chloride solutions.[25] All the values are similar to those reported for other nitroaromatic compounds in the same seawater system.[14] The salting-out coefficients did not vary significantly with temperature, and a thermodynamic analysis shows that the transfer of these organic compounds from pure water to seawater is thermodynamically unfavorable; the free energy is greater than zero. The data suggest that this unfavorable condition is caused by an increase in entropy for 2-NT and 3-NT and by an increase in enthalpy for NB. The pure water solubilities for the compounds determined in this study agree fairly well with values observed in earlier studies.[17−23]

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