Assessing the Salting-Out Behavior of 2,4-Dinitrobenzaldehyde and 2,6-Dinitrobenzaldehyde from Solubility Values in Pure Water and Seawater at Temperatures between (280 and 313) K

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ABSTRACT: The salting-out behavior of 2,4-dinitrobenzaldehyde (2,4-DNBA) and 2,6-dinitrobenzaldehyde (2,6-DNBA) was determined from solubility measurements in pure water and seawater with ionic strengths of (0.1662, 0.3352, 0.5071, and 0.6820) $mol \cdot kg^{-1}$ at temperatures between (280 and 314) K. For both compounds tested, the solubility increased with increasing temperature. As the ionic strength of the solution increased, the solubility of the organic compounds decreased. The average salting-out coefficients for 2,4-DNBA and 2,6-DNBA were (0.12 and 0.10) $kg \cdot mol^{-1}$, respectively, which are consistent with measurements for other nitroaromatic compounds. Over the temperature range examined, the salting-out coefficients did not vary significantly.

INTRODUCTION

Nitroaromatic compounds can cause pollution by entering the environment from the improper handling or disposal of feedstocks from chemical production (explosives, medicines) or from the corrosion of unexploded ordnance (UXO) casings at shooting ranges or off-shore dumping grounds.[1−3] Once dissolved in the aqueous phase, these compounds can be transported and undergo biological or chemical transformation. Since such processes depend on the amount of material dissolved, knowledge of the solubility of these compounds under various temperature and salinity conditions is needed to accurately model their fate and transport in marine systems. In the case of 2,4-dinitrobenzaldehyde (2,4-DNBA) and 2,6-dinitrobenzaldehyde (2,6-DNBA), the aqueous solubility has been estimated in pure water but not yet measured. These compounds are used in chemical synthesis and can also be formed by the photolysis of dinitrotoluenes (DNTs) that are leaking from UXOs or as a byproduct of the treatment of DNTs with ozone and peroxide.[4−8] Since 2,4-DNBA and 2,6-DNBA are mutagenic, knowledge of their solubility will help assess their impact on the environment.[9,10]

The solubility of neutral organic compounds can be altered by the presence of inorganic salts. When the solubility decreases, the process is commonly called "salting-out" (see review in Xie et al.[11]). When a solution contains a complex mixture of salts such as seawater, the salting-out effect can be quantified using a version of the Setschenow equation, which relates organic compound solubility to solution ionic strength, I ($mol \cdot kg^{-1}$):

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

where S_w is the solute solubility in pure water ($mg \cdot L^{-1}$), S is the solute solubility in the salt solution ($mg \cdot L^{-1}$), and $K_s{'}$ is a salting-out parameter ($kg \cdot mol^{-1}$).[13−17] 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 ($mol \cdot kg^{-1}$) 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, but no values have been reported for nitrobenzaldehydes.[12−16] One study did report that salting-out enhanced the aldol reaction of 4-nitrobenzaldehyde with cyclohexanone in the presence of a catalyst.[18] The goal of this study was to measure the solubility of 2,4-DNBA and 2,6-DNBA in seawater over a range of salinity encompassing most coastal waters and at various temperatures.

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. Approximately 0.05 g of solid 2,4-DNBA and 0.018 g of solid 2,6-DNBA were weighed into each vial. This mass was more than needed to reach solubility, so the solid remained in the vial after equilibrium was achieved. A total of 10 or 12 mL of either 18 $M\Omega \cdot cm^{-1}$ 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 $^0/_{00}$) and filtered through 0.2 μm polysulfide filters (Gelman, Pall) prior to use. 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 of the Thermax room was controlled by a Series 96 1/16 DIN temperature controller (Wetlow), while the temperature of the incubator was controlled by a compressor and a resistance temperature detector (RTD) located in the air stream that

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14. ABSTRACT
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Table 1. Ionic Strength and Molality, c, of Individual Ions in Seawater of Varying Composition (Salinity)

	$c/(\text{mol}\cdot\text{kg}^{-1})$			
ion	25 % seawater (8.8 g of salt/kg of seawater)	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^-	0.1301	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 2,6-Dinitrobenzaldehyde (1) and 2,4-Dinitrobenzaldehyde (2) in Pure Water and Seawater from T = (280 to 313) K

| % seawater	T/K	no. of samples	$c_1/\text{mg}\cdot\text{L}^{-1}$	SD[a]	T/K	no. of samples	$c_2/\text{mg}\cdot\text{L}^{-1}$	SD[a]
Milli-Q	280.0	3	61.3	1.4	280.1	3	1420	26
25	280.0	3	60.0	2.5	280.2	3	1390	24
50	280.0	3	54.8	3.2	280.4	3	1320	7
75	280.0	3	55.8	1.7	280.5	3	1280	9
100	280.1	3	53.2	1.4	280.5	3	1220	8
Milli-Q	289.2	3	96	2	289.0	3	1810	20
Milli-Q	294.0	11	147	5	294.2	3	2230	20
25	294.1	3	139	4	294.2	4	2110	10
50	294.1	3	135	4	294.2	4	1980	10
75	294.1	3	131	2	294.2	3	1910	10
100	294.2	3	126	4	294.2	3	1830	30
Milli-Q	297.5	3	175	6	297.7	3	2370	27
Milli-Q	303.9	3	251	12	303.8	3	2740	20
25	303.8	3	242	9	303.9	4	2640	30
50	303.9	3	233	3	303.8	3	2510	37
75	303.9	3	221	6	303.8	3	2400	61
100	303.9	3	213	1	303.7	3	2280	15
Milli-Q	308.4	3	345	10	308.6	3	3280	80
25	308.4	3	323	5	308.6	3	3070	20
50	308.5	3	308	4	308.7	3	2960	20
75	308.6	3	300	9	308.6	3	2810	30
100	308.5	3	280	1	308.7	3	2730	30
Milli-Q	313.4	3	420	7	313.3	3	3750	28
25	313.3	3	405	6	313.4	3	3610	65
50	313.3	3	390	8	313.3	3	3460	35
75	313.4	3	372	5	313.3	3	3280	39
100	313.4	3	365	5	313.6	3	3130	85

[a] SD: standard deviation of replicate vials.

changed the heating to maintain the desired temperature. A thermometer with a range of (276.15 to 287.15) K was used to measure the temperature of each sample. Its accuracy was determined by measuring the temperature in ice water, which was measured multiple times to be 0.05 K as compared to 0.00 K, and by comparing the temperatures measured by this

thermometer with a thermometer that had been calibrated in ice water and in boiling water. On the basis of this comparison, the accuracy of this thermometer is 0.1 K. The temperature variation among vials for all three systems was at most 0.5 K. A rate study conducted at 294 K for both compounds 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 48 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. The 2,6-DNBA standards were prepared in a mixture of 50 % acetonitrile in water as was previously done for other nitroaromatic compounds.[14-17] Since such conditions resulted in poor chromatography for the 2,4-DNBA, the 2,4-DNBA standards were prepared in a mixture of 50 % methanol in water. Aqueous samples of 2,6-DNBA (10 μL) and 2,4-DNBA diluted 50 % in methanol (5 μL) 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.
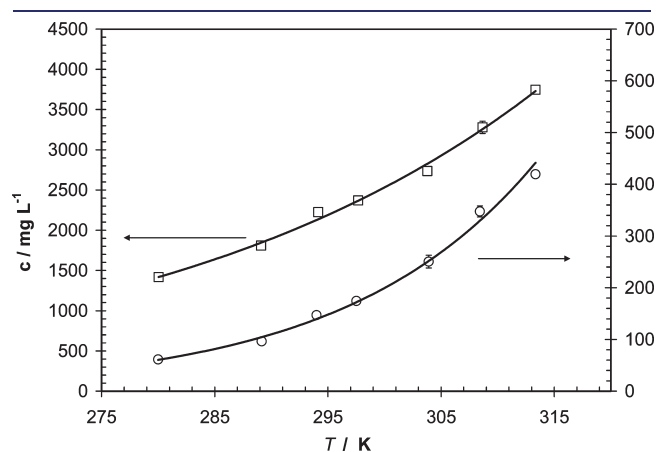
Figure 1. Solubility of 2,4-dinitrobenzaldehyde (2,4-DNBA), □, and 2,6-dinitrobenzaldehyde (2,6-DNBA), ○, in pure water: Error bars show either the standard deviation of the concentration of replicate vials or the analytical error (1.3 % for 2,6-DNBA except for 280 K samples with 4 % error; and 1.9 % for 2,4-DNBA), whichever is larger. The lines shown are for the empirical correlations: c(2,4-DNBA)/mg·L^{-1} = 0.419 exp(0.0290T/K) and c(2,6-DNBA)/mg·L^{-1} = 3.43·10^{-6} exp(0.0596 T/K).

■ RESULTS AND DISCUSSION

Solubility data for 2,6-DNBA and 2,4-DNBA 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 1.9 % for 2,4-DNBA and 1.3 % for 2,6-DNBA, except for the 280 K samples which are approximately 4 %. Solubility values for 2,4-DNBA and 2,6-DNBA have not been reported, but estimates have been made using computer software. The solubility of 2,4-DNBA has been estimated using various computer software packages to be between (160 and 7540) mg·L^{-1} in pure water at 298 K.[19-21] The experimentally measured value reported herein, 2370 ± 27 mg·L^{-1} for 297.7 K, falls within the range of numbers predicted by numerical models. Solubility estimates for 2,6-DNBA range from (140 to 3800) mg·L^{-1} at 298 K.[20,21] The lower estimated value is close to the 176 ± 6 mg·L^{-1} reported herein for 297.5 K. The use of this experimental method for structurally similar compounds resulted in an average accuracy of 3.6 %.[13,14,16] This accuracy is based on comparing values determined by this method and results reported by other researchers. Based on these previous results, the current accuracy is estimated at 3.6 %.

Using the data in Table 2, exponential fits of pure water concentration as a function of temperature were generated for both compounds in the functional form of

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

where c is the concentration, T is temperature, and a and b are fitting parameters. The values of a and b were determined using linear regression (Microsoft Excel 2003) of the log−linearized form of eq 3:

$$\ln c/\mathrm{mg\cdot L^{-1}} = b\cdot T/\mathrm{K} + \ln a \qquad (4)$$

Figure 1 shows the exponential fits for the pure water systems (correlation coefficients of 0.995 for both), and the values of a and b,

Table 4. Salting-Out Parameters, K_s', for 2,6-Dinitrobenzaldehyde (1) and 2,4-Dinitrobenzaldehyde (2) at Various Temperatures, T^a

	1			2	
T/K	K_s'/kg·mol^{-1}	SE	T/K	K_s'/kg·mol^{-1}	SE
280.0	0.089	0.033	280.3	0.11	0.003
294.0	0.082	0.007	294.2	0.12	0.007
303.9	0.11	0.007	303.8	0.13	0.002
308.5	0.12	0.012	308.6	0.11	0.011
313.4	0.090	0.011	313.4	0.12	0.006

^{a} SE: standard error.

Table 3. Coefficients^a of eq 3 and Standard Deviation of the Regression (SE) for eq 4 for the Influence of Temperature on the Equilibrium Solubility of 2,6-Dinitrobenzaldehyde (1) and 2,4-Dinitrobenzaldehyde (2) in Pure Water and in Seawater at Various Concentrations

% seawater	$a_1/10^6\cdot$mg·L^{-1}	b_1/K^{-1}	SE$_1$	a_2/mg·L^{-1}	b_2/K^{-1}	SE$_2$
0	3.43 ± 2.00	0.0596 ± 0.0020	0.055	0.419 ± 0.110	0.0290 ± 0.0009	0.025
25	5.23 ± 2.06	0.0581 ± 0.0013	0.034	0.528 ± 0.136	0.0281 ± 0.0009	0.023
50	3.77 ± 1.51	0.0590 ± 0.0013	0.035	0.432 ± 0.105	0.0286 ± 0.0008	0.021
75	6.32 ± 2.22	0.0572 ± 0.0012	0.031	0.481 ± 0.117	0.0281 ± 0.0008	0.021
100	5.30 ± 1.29	0.0576 ± 0.0008	0.021	0.440 ± 0.117	0.0283 ± 0.0009	0.023

^{a} The "±" values represent the standard error.

their standard error, and the standard deviation about the regression (standard error of the estimate) for eq 4 are given in Table 3. The temperature coefficient for 2,6-DNBA, (0.0596 ± 0.0020) K^{-1}, is much higher than that of 2,4-DNBA, (0.0290 ± 0.0009) K^{-1}. The temperature coefficient for 2,6-DNBA is higher than that of 2,6-dinitrotoluene (2,6-DNT) (0.048 ± 0.003) K^{-1}, while the temperature coefficient for 2,4-DNBA is lower than that of 2,4-dinitrotoluene (2,4-DNT) (0.0408 ± 0.0024) K^{-1} in the same seawater system.[13,14]

The presence of salt lowers the solubility of 2,6-DNBA and 2,4-DNBA for all temperatures. Values of the salting-out parameter based on eq 1 for 2,6-DNBA, (0.10 ± 0.02) kg·mol^{-1}, and 2,4-DNBA, (0.12 ± 0.01) kg·mol^{-1}, do not vary significantly with temperature (Table 4). These salting-out coefficients for dinitrobenzaldehydes are similar to $(0.11 \pm 0.01$ and $0.12 \pm 0.01)$ for 2,4-DNT and 2,6-DNT, respectively. As with the pure water systems, the solubility of 2,6-DNBA and 2,4-DNBA in seawater solutions increased with increasing temperature. A 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 significantly, as shown by error bars that overlap (Table 3). Similar behavior has been found for other nitroaromatic compounds.[13,14]

CONCLUSIONS

On the basis of the solubility measurements of 2,6-DNBA and 2,4-DNBA in pure water and seawater, the salting-out coefficients were determined to be (0.10 ± 0.02) kg·mol^{-1} and (0.12 ± 0.01) kg·mol^{-1}, respectively. These values are similar to those reported for 2,6-DNT and 2.4-DNT in the same seawater system.[13,14] The salting-out coefficients did not vary significantly with temperature. A comparison of measured pure water solubility values with those predicted in the literature using computer models shows that the measured value at 298 K for 2,6-DNBA is close to the lower predicted value, while the measured value for 2,4-DNBA falls within the wide range of predicted values.

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