586 *J. Chem. Eng. Data* **2008,** *53,* 586–587

Solubility of 3,4-Dinitrotoluene in Pure Water and Seawater

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The solubility of 3,4-dinitrotoluene (3,4-DNT) in natural filtered seawater with ionic strength = (0.1662, 0.3352, 0.5071, and 0.6820) $\text{mol}\cdot\text{L}^{-1}$ and pure water was measured at temperatures ranging between (277 and 314) K. The solubility in seawater was lower than that in pure water. The average salting-out coefficient for 3,4-DNT was 0.13 $\text{L}\cdot\text{mol}^{-1}$, which is consistent with measurements for other isomers of dinitrotoluene. The salting-out coefficient did not show any significant variation with temperature over the range examined.

Introduction

Nitroaromatic compounds can enter and pollute the aquatic environment through poor manufacturing practices (explosives, dyes) and through the corrosion of unexploded ordnance casings at military training and battlefield sites. In an aquatic environment, aqueous solubility influences the chemical and biological degradation of these compounds. The presence of salts has been shown to alter solute solubility. This effect can be quantified using a version of the Setschenow equation, which relates solute solubility measurements to solution ionic strength, I

$$\log(S_w/S) = K_s'I \qquad (1)$$

where S_w is the solute solubility in pure water, S is the solute solubility in the salt solution, and K_s' is a salting-out parameter.[1–3]

The goal of this work was to continue studies that determine the influence of salinity and temperature on the solubility of nitroaromatic compounds.[1,2] Those studies investigated 2,4-dinitrotoluene (2,4-DNT), 2,3-dinitrotoluene (2,3-DNT), and 2,6-dinitrotoluene (2,6-DNT), while the present study investigates 3,4-dinitrotoluene (3,4-DNT). Unlike the other compounds, very little solubility information is available for 3,4-DNT ($CH_3C_6H_3(NO_2)_2$) though it is considered a persistent pollutant and has been found to be toxic to cells.[4–6]

Materials and Methods

The experiments were conducted using the methods described in Luning Prak and O'Sullivan.[2] The 3,4-DNT was obtained from Aldrich (99 % purity). The seawater was taken from the surface of Middle Atlantic Bight (salinity of 33.1 g of salt per kg of seawater, 63 μM DOC)[7] and filtered through 0.2 μm polysulfide filters (Gelman, Pall). Solid 3,4-DNT was mixed with either 18 $\text{M}\Omega\cdot\text{cm}^{-1}$ MilliQ (deionized water purified by a Millipore MilliQ Plus water system) or seawater diluted with various amounts of MilliQ water. The seawater solutions had ionic strengths of (0.1662, 0.3352, 0.5071, and 0.6820) $\text{mol}\cdot\text{L}^{-1}$. The distribution of salts producing these ionic strengths is given in ref 2. Four vials were run for each experimental condition. The vials were shaken at 45 rpm for over 24 h 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 benchtop (room-temperature samples) where the temperature varied within 0.6 K. Aqueous samples were analyzed by methods described by Luning Prak and O'Sullivan.[1]

Table 1. Solubility, *c*, of 3,4-DNT in Aqueous Samples at Various Temperatures, *T*

% seawater	T/K	c(3,4-DNT)/$\text{mg}\cdot\text{L}^{-1}$	standard deviation
0	278.2	69	2.1
25	278.2	65	1.0
50	278.2	61	0.2
75	278.2	58	0.2
100	278.2	56	1.0
0	285.1	98	1.9
0	291.7	121	0.6
0	293.1	134	0.7
25	293.1	127	0.3
50	293.1	120	0.7
75	293.1	115	0.2
100	293.1	109	0.3
0	298.3	179	1.1
0	304.2	206	0.9
25	304.2	198	0.3
50	304.2	188	1.5
75	304.2	179	1.0
100	304.2	171	2.0
0	308.3	262	1.0
0	312.6	324	0.9
25	312.6	305	1.4
50	312.6	289	1.1
75	312.6	275	1.0
100	312.6	262	1.5
0	313.2	326	0.1

Results and Discussion

Table 1 shows the solubility data for 3,4-DNT. The values given are an average and standard deviation of four replicate vials. The results for aqueous solubility of 3,4-DNT in pure water are between reported values of 1080 $\text{mg}\cdot\text{L}^{-1}$ (temperature was not given, likely to be 298.2 K)[6] and 100 $\text{mg}\cdot\text{L}^{-1}$ at 298.2 K[8] as shown in Figure 1. The latter value is consistent with an estimated value of 122 $\text{mg}\cdot\text{L}^{-1}$ at 298.2 K.[9] The solubility of 3,4-DNT in pure water, c(DNT), as a function of temperature (T) with an $R^2 = 0.995$ (p-value < 0.001) is

$$c(\text{DNT})/\text{mg}\cdot\text{L}^{-1} = 3.2\cdot 10^{-4}\exp(0.044\,T/\text{K}) \qquad (2)$$

This exponential fit is shown in Figure 1. The 95 % confidence interval for the temperature coefficient is $(0.044 \pm 0.003)\ \text{K}^{-1}$.

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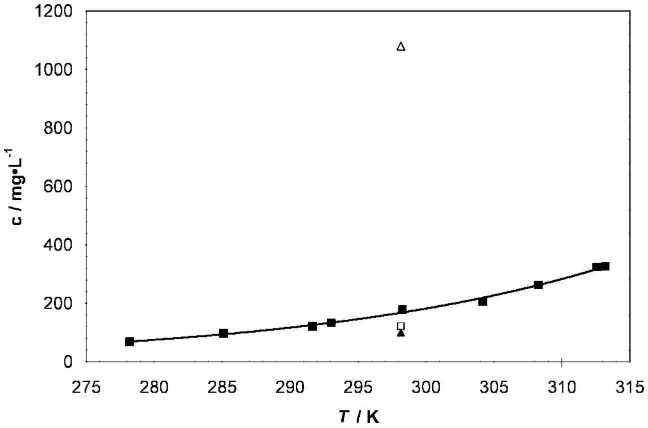

Figure 1. Solubility of 3,4-DNT in pure water: ■, this study; △, ref 4; ▲, ref 5; □, ref 6. Error bars show the standard deviation of the concentration and of replicate vials and the average temperature variation. In most cases, the error bars are smaller than the symbols.

Table 2. Salting-Out Coefficients, K_s', for 3,4-DNT at Various Temperatures, T^a

T / K	K_s' / L·mol^{-1}	SE
278.2	0.13	0.004
293.1	0.13	0.002
304.2	0.12	0.002
312.6	0.13	0.003

[a] SE = standard error from the linear regression.

This temperature coefficient is similar to the values of (0.0408 ± 0.0024, 0.042 ± 0.002, 0.048 ± 0.003) K^{-1} found for 2,4-DNT, 2,3-DNT, and 2,6-DNT, respectively, in the same seawater system.[1,2]

The presence of salt lowers the solubility of 3,4-DNT for all temperatures examined. Values of the modified salting-out parameter for 3,4-DNT, (0.13 ± 0.01) L·mol^{-1}, based on eq 1 do not vary significantly with temperature, assuming a 95 % confidence interval (Table 2). These parameters compare well with the average values of (0.11 ± 0.01, 0.13 ± 0.01, and, 0.12 ± 0.01) L·mol^{-1} for 2,4-DNT, 2,3-DNT, and 2,6-DNT, respectively.[1,2]

In an aquatic environment, chemical and biological degradation usually involves dissolved species, and dissolution rates are affected by solubility values. Very little experimental research has been done on the transformation of nitroaromatic compounds in marine systems.[10] The results of the present study provide starting information for that research. In this study, 3,4-DNT solubility in pure water increased from (69 to 326) mg·L^{-1} and in 100 % filtered seawater increased from (56 to 262) mg·L^{-1} as the temperature increased from (278 to 313) K. The range of salinity values tested [(0 to 33.1) mg of salt per kg of seawater] encompasses the values found for most costal waters, while the temperatures studied represent those found in ocean environments. The results also provide information that can be used in mathematical models of pollutant transformation in marine systems.

Acknowledgment

We would like to express our thanks to Dan O'Sullivan for providing the seawater.

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Received for review September 10, 2007. Accepted December 1, 2007. This work was sponsored in part by the Naval Academy Research Council and an ONR grant (N0001407WR20102) award to D. J. Luning Prak.

JE700520K