J. Chem. Eng. Data **1996,** *41,* 758−761

Solubility of 2,4,6-Trinitrotoluene (TNT) in Water

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Current literature values of 2,4,6-trinitrotoluene (TNT) solubility in water vary widely from 100 to 200 mg/L at room temperature. We investigated the effects of temperature and pH on the solubility of both reference TNT and field neat TNT obtained from the Alabama Army Ammunition Plant (AAAP), Childersburg, AL. The TNT solubility determined from this study was significantly lower than that of Taylor and Rinkenbach, which was cited by several reference chemical handbooks and articles. However, the values reported by the *Merck Index* and the *Lange's Handbook of Chemistry* compared well with our values. TNT solubility dropped rapidly as the pH increased. Three unknown HPLC peaks were observed at high pH, indicating a possibility of forming unknown transformation products. Both reference and field neat TNT solubility agreed well. A semiempirical solubility correlation was developed to predict the solubility of TNT at a temperature range from 6 °C to 42 °C.

Introduction

2,4,6-Trinitrotoluene (TNT) is one of many explosives contaminating soils in munitions facilities and military bases. It is toxic to humans, causing liver damage and anemia, inhibits growth of many fungi, yeasts, actinomycetes, and gram-positive bacteria, and exhibits mutagenicity in the Ames screening test (Maleki, 1994; Merck, 1976; Kaplan and Kaplan, 1982). Although TNT is no longer manufactured in the United States, crystalline TNT frequently found in contaminated sites is very persistent in soils (McGrath, 1995). The field TNT exists as chunks of weathered crystals, tiny crystals embedded in the soil matrix, and TNT molecules adsorbed on the soil surface. Large chunks of neat (pure) TNT materials pose a detonation hazard. In addition, these large and small TNT crystals in the soil matrix serve as a continued contamination source for the munitions facilities and military bases even long after activities which led to soil contamination cease. Knowledge of environmental fate and mass transport characteristics of TNT in the subsurface environment is essential for risk assessment and implementation of proper remediation technologies.

Solubility determines the maximum concentration of TNT in the aqueous phase and provides vital knowledge of the driving force for mass transfer. Temperature strongly affects the solubility, and an accurate estimation of TNT solubility at the site temperature is vital in successfully modeling the transport process. However, literature values of TNT solubility vary widely, as shown in Figure 1. One of the earliest works on TNT solubility was by Copisarow (1915), who reported that 100 g of water dissolved 0.021 g of TNT at 15 °C, which was equivalent to 210 mg TNT/L of water. Taylor and Rinkenbach (1923) investigated the solubility of TNT in various solvents and temperatures. Several reference chemical handbooks and articles later used the interpolated water solubility values reported by Taylor and Rinkenbach [*Solubilities of Organic Compounds* (Seidell, 1941), *Solubilities of Inorganic and Organic Compounds* (Stephen and Stephen, 1963), *Chemistry and Technology of Explosives* (Urbanski, 1964), Organic Explosives and Related Compounds (Rosenblatt et al., 1991)]. In addition, the *Handbook of Environmental Data on Organic Chemicals* (Verschueren, 1983) reported a value of 200 mg/L at 15 °C, whereas the *Lange's Handbook of Chemistry* (1985) and the *Merck Index* (1976) both reported a value of 100 mg/L at 25 °C for water solubility. Spanggord et al. (1983) reported TNT solubilities of (67, 104, and 165) mg/L at (10, 20, and 30) °C, respectively. Hale et al. (1979) determined a TNT solubility of 85.8 mg/L at 21 °C. Accurate values of TNT solubility are needed for research studies as well as for planning for contaminated site remediation measures.

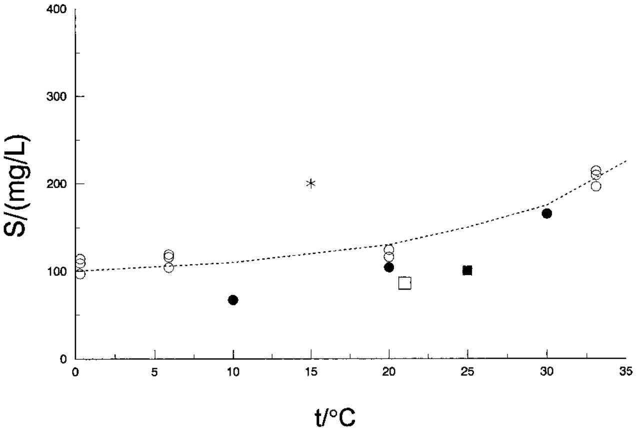

Figure 1. TNT solubilities in the literature: (○) original data of Taylor and Rinkenbach (1923); (---) interpolation of Taylor and Rinkenbach (1923), Seidell (1941), Urbanski (1964), Stephen and Stephen (1963), and Rosenblatt et al. (1991), and McGrath (1995); (∗) Verschueren (1983); (●) Spanggord et al. (1983); (■) *Merck Index* (1976) and *Lange's Handbook of Chemistry* (1985); (□) Hale et al. (1979).

Since several chemical reference handbooks cited the work by Talyor and Rinkenbach (1923) for TNT solubility, it is worthwhile to review their methodology and its limitations. They prepared analytical grade TNT by

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S0021-9568(95)00322-0 CCC: $12.00

recrystallizing grade I commercial TNT. They then determined the TNT solubility gravimetrically by collecting 30−50 g of saturated TNT solutions in specially designed pipets called wagon-pipets, evaporating solvents by dry air, and weighing the TNT residue in the pipets. They reported residue weights checked within 2 mg. Taylor and Rinkenbach also reported interpolated data for TNT solubility in water at various temperatures, which were later cited by the handbooks.

Although their wagon-pipet method was innovative and probably the only way of accurately measuring the TNT solubility at that time, it had several limitations compared to new spectroscopic analytical instrumental techniques. First, the purity of the prepared analytical grade TNT was uncertain. The purity of TNT crystals can now be quantitatively checked by X-ray diffraction and gas and liquid chromatography coupled with mass spectrometry. Second, the experimental variation of their gravimetric analysis was 2 mg of dried TNT residues in 30−50 g of water. In other words, the TNT solubility variation would be about 40 67 mg/L in water. Using modern analytical instruments such as spectrophotometers, HPLC, and others, this variance can be substantially reduced.

Use of existing empirical correlations for solubilities of general organic compounds (Rosenblatt et al., 1991; Yalkowsky and Banerjee, 1992) does not help us to estimate TNT solubility any better. The values of TNT solubilities estimated from these correlations were at least 1 order of magnitude higher than current solubility values.

The objectives of this paper are (1) to study the effects of temperature and pH on TNT solubility, (2) to develop a semiempirical correlation for TNT solubility as a function of temperature in the range that is environmentally relevant, and (3) to compare the solubility of field neat TNT found in contaminated sites to that of reference TNT.

Materials and Methods

Field Neat TNT Particles. A small portion of a large weathered crystalline TNT object (approximately 1 ft by 2 ft) found at the Alabama Army Ammunition Plant (AAAP), Childersburg, AL, was used to study the solubility of field TNT. This field TNT material was crushed into various size groups of semidried particles and will be referred to as field neat TNT hereafter.

Analytical Chemicals and Standard Solutions. Analytical-grade pure reference TNT crystals (99%, Chem Service, Inc.) were dried in a desiccator (Drierite, anhydrous $CaSO_4$) for several days before making stock solutions of about 1 mg/mL in HPLC-grade acetonitrile or methanol (Curtin Matheson Scientific, Inc., Houston, TX). The stock solution was then diluted with HPLC-grade water (Curtin Matheson Scientific, Inc., Houston, TX) to give concentrations of about 5, 10, 15, and 20 mg/L. These standard solutions were periodically prepared (at least once in a month) and used to calibrate a spectrophotometer (Hewlett Packard 8452A) and HPLC (Hewlett Packard, 1090 Series II).

Solubility Apparatus. Nine amber bottles (100−250 mL) with magnetic stirrers were placed in a constant-temperature water bath. A constant-temperature water recirculator (Cole Parmer, Model No. 01268-14) controlled the temperature of the water within ±0.5 °C. A multiposition magnetic stirrer (Cole Parmer, Model No. 51450) was used to stir all nine amber bottles simultaneously. About 500 mg of TNT and 100 mL of deionized (DI) water were added into the amber bottles. Some of the samples were adjusted to give a pH around 4, 7, and 9 using phosphate buffers (250 mg/100 mL each of mono- and dihydrogen potassium phosphates for a pH around 7 and addition of H_2SO_4 or NaOH to achieve a pH of about 4 or 9). For both buffered and nonbuffered samples, the values of pH did not change during the duration of the experiments. Each measurement temperature was approached from both lower and higher temperatures in order to prevent undersaturation or supersaturation. The samples were usually allowed to equilibrate for 1 week at the desired temperature before analysis.

Analytical Protocols. U.S. EPA Standard Method 8330 (1990) was used initially to analyze TNT and other transformation products. This method involved the use of an HPLC (Hewlett Packard, 1090 Series II). An isocratic mobile phase, 50/50 water/methanol and a 5-μm reversed-phase C_{18} column (Supelco LC-18, 250 × 4.6) at 40 °C were used. The compound was detected at 254 nm.

The spectrophotometer (Hewlett Packard 8452A) became the major analytical instrument for TNT analysis after we learned that the neat TNT particles were composed of mostly pure TNT crystals. Absorbances at multiple wavelengths (224, 234, 238, and 244 nm) were analyzed to determine TNT concentrations and to check possible interference from other impurities. If any interference was suspected, HPLC was used to verify the results.

The samples for spectrophotometric analysis were prepared by collecting 2−3 mL of the saturated solution from the amber bottles using a 10-mL multifit interchangeable glass syringe (Becton-Dickinson). The needle was then replaced with a 0.2-μm nylon syringe filter (Nalgene, New York), and the filtrate was collected in a 4-mL amber sample vial. One milliliter of the filtrate was pipeted into a 20-mL bottle and diluted with 10 mL of deionized water. Approximately 2 mL of the prepared sample was placed in a quartz cuvette and subsequently analyzed using the spectrophotometer.

In order to assess the potential adsorptive loss of TNT in the syringe filter, a sample was centrifuged at 15 000 rpm for 15 min (Brinkmann Instrument Inc., New York). The liquid supernatant was not clear, which indicated that the centrifugation technique was not adequate for the spectrophotometric analysis. As a result, the absorbance and the corresponding concentration was almost twice as high as it was in the the filtered samples. In order to assess the adsorptive loss during filtration, the filtered samples were filtered for a second time. There was no difference at a significance level of 0.05 in TNT concentrations between the samples filtered once and twice, indicating no significant adsorptive loss through the nylon filter.

Results and Discussion

TNT Solubility as a Function of pH and Temperature. Tables 1 and 2 summarize the solubility data for both reference and field neat TNT in water at different pH and temperatures. As expected, TNT solubility increases with an increase in temperature, from about 52 mg/L at 6 °C to 205 mg/L at 42 °C for reference TNT. The solubility of the field neat TNT was very similar to that of reference TNT. The solubilities of samples approaching equilibrium from the lower temperature were also comparable to those of samples approaching equilibrium from the higher temperature at the same pH. Generally, the solubility determined from this study is about 33% below the solubility reported by Taylor and Rinkenbach (1923).

At high temperatures, the TNT solubility dropped sharply as the pH was increased to 9.3 and its standard deviation substantially increased. At 25 °C, the solubility of both reference TNT and the field neat TNT was about 101.5 mg/L (an average value excluding the value at pH = 9.1) at different pH levels (3.5, 6.8, and 9.1 for reference TNT

Table 1. Solubility (S) of Reference TNT

t/°C	pH	S/(mg/L)	no. of measurements	remarks[a]
6	3.7	52.5	1	H-T
6	6.9	51.3 ± 1.3	5	H-T, L-T
12	6.9	64.0 ± 2.4	11	L-T
13	3.7	72.2	1	L-T
13	6.9	64.4 ± 2.9	2	L-T
20	4.2	86.2 ± 0.2	2	L-T
20	7.3	88.5 ± 0.4	2	L-T
20	9.2	96.8 ± 0.3	2	L-T
20	9.4	95.7 ± 0.5	2	L-T
20	10.1	91.2 ± 0.3	2	L-T
21	3.5	74.5	1	H-T
21	6.8	82.5	1	H-T
21	9.1	88.2	1	H-T
25	3.5	101.6 ± 1.6	3	L-T
25	6.8	100.5 ± 2.0	6	L-T, H-T
25	9.1	110.5 ± 1.8	3	L-T
42	4.0	204.9 ± 3.4	3	L-T
42	6.8	204.5 ± 4.9	6	H-T, L-T
42	9.3	167.6 ± 60.5	3	L-T

L-T: approach equilibrium from lower temperature. [b] H-T: approach equilibrium from higher temperature.

Table 2. Solubility (S^*) of Field Neat TNT

/°C	pH	S^*/(mg/L)	no. of measurements	remarks[a]
6	3.9	50.0 ± 0.2	2	H-T
6	6.9	54.8 ± 5.0	4	H-T, L-T
12	6.9	61.9 ± 1.7	11	L-T
13	3.9	70.5	1	L-T
13	6.9	68.9 ± 2.4	5	L-T
17	6.8	83.3 ± 1.2	9	L-T
20	6.8	90.9 ± 1.3	2	L-T
21	3.9	69.7	1	H-T
21	6.8	81.5	1	H-T
21	9.1	85.2	1	H-T
25	3.8	92.3 ± 0.3	3	L-T
25	6.8	108.2 ± 5.5	6	H-T, L-T
25	7.9	105.1 ± 1.5	3	L-T
42	4.0	185.7 ± 4.2	3	L-T
42	6.8	198.0 ± 15.1	6	L-T, H-T
42	9.3	125.8 ± 32.3	3	L-T

L-T: approach equilibrium from lower temperature. [b] H-T: approach equilibrium from higher temperature.

and 3.8, 6.8, and 7.9 for field neat TNT). This solubility is much lower than 150 mg/L suggested by Taylor and Rinkenbach (1923), but was very close to that by the *Lange's Handbook of Chemistry* and the *Merck Index* (100 mg/L). At 42 °C, TNT solubility almost doubled to about 198 mg/L at pH levels of 4.0 and 6.8. The measured TNT solubility varied widely at pH 9.3 with the standard deviations ranging from 32.3 mg/L to 60.5 mg/L.

We initially suspected formation of dimerized or polymerized azoxy compounds at this high pH, as suggested by Funk et al. (1993), which caused the large decrease in solubility values due to adsorptive loss of the macromolecules. The samples were further analyzed using HPLC. For samples with pH ranging from 3.5 to 9.1 at 25 °C and 4.0 to 6.8 at 42 °C, only TNT peaks were observed during the 14 min of HPLC runs. However, three additional unknown peaks (retention times of 6.1, 7.5, and 9.7 min) were observed at pH 9.3 and 42 °C before the TNT peak (a retention time of 11.2 min). The fact that the peaks appeared before TNT suggested the unknown products would be more polar and/or smaller molecules than TNT, instead of the dimerized or polymerized azoxy compounds. We did not pursue this matter any further due to lack of available reference chemicals at the time of experiment.

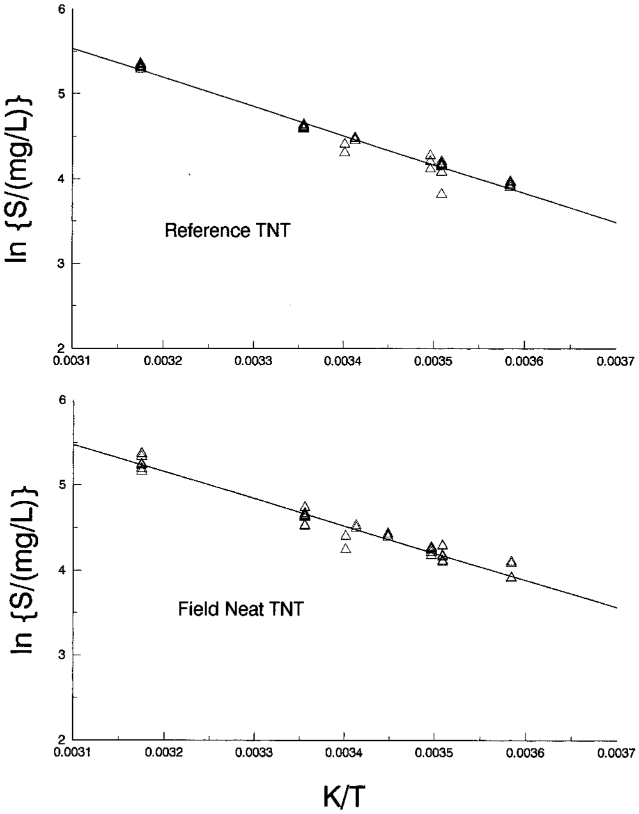

Figure 2. ln S vs $1/T$.

Semiempirical Correlation for TNT Solubility in Water. Hildebrand (1924) derived an equation relating the solubility and temperature based on Raoult's law of an ideal solution. Assuming that the solid is transformed into a hypothetical, supercooled liquid (also referred to as a subcooled liquid by several authors of recent literature), and the enthalpy of fusion does not change much with the small change in temperature, the following solubility equation can be derived using the Clausius–Clapeyron equation.

$$\ln x = -H_{\text{fusion}}/R(1/T - 1/T_{\text{m}}) \tag{1}$$

where x is the mole fraction, H_{fusion} is the enthalpy of fusion, R is the universal gas constant, T is absolute temperature, and T_{m} is the melting point.

The solubility estimated from eq 1 with L_{f} of 98.3 J/g (Rosenblatt, 1991) at 25 °C is 4007 g/L. This unreasonably high predicted value indicates that the TNT–water system is not an ideal solution. Although the TNT–water system is far from the ideal solution, eq 1 infers the temperature dependency of solubility (S) as

$$\ln S = A - B/T \tag{2}$$

where A and B are empirical constants.

Figure 2 shows the applicability of eq 2 for both reference and field neat TNT solubilities. All solubility data at pH less than 8 were incorporated into the graphs. Both reference and field neat TNT solubility data fitted to eq 2 well with R^2 values of 0.97 and 0.96, respectively. The correlations of reference and field neat TNT for the temperature range from 6 °C to 42 °C were found to be statistically equal at the significance level of 0.05. The semiempirical TNT solubility correlation based on the reference TNT was

$$\ln\{S/(\text{mg/L})\} = 16.12 - 3413/(T/\text{K}) \qquad \text{for } 279\text{ K} < T < 315\text{ K} \tag{3}$$

This correlation was compared with existing TNT solubility data in the literature (Figure 3). The solubility

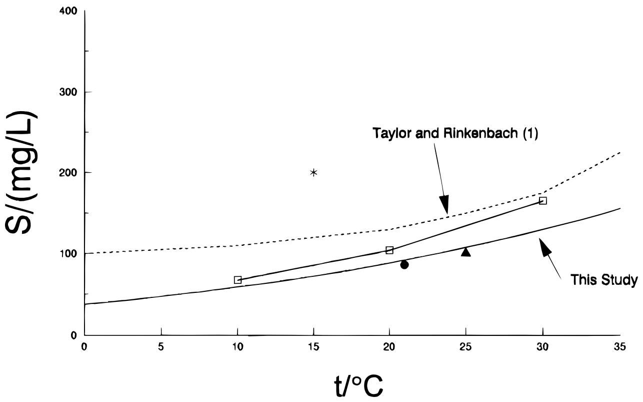

Figure 3. Comparison of literature TNT solubility with this study: (∗) Verschueren (1983); (▲) *Merck Index* (1976) and *Lange's Handbook of Chemistry* (1985); (●) Hale et al. (1979); (□) Spanggord et al. (1983).

determined by Taylor and Rinkenbach (1923) and the value of 200 mg/L at 25 °C reported in the *Handbook of Environmental Data on Organic Compounds* significantly overestimated TNT solubility compared to this study. The solubilities determined by Spanggord et al. (1983) were similar to those of this study at 10 °C but approached those of Taylor and Rinkenbach (1923) at 30 °C. The values of 100 mg/L at 25 °C reported by the *Merck Index* and *Lange's Handbook of Chemistry* and 85.8 mg/L at 21 °C reported by Hale et al. (1979) agreed reasonably well with the solubility predicted from eq 3, i.e., 106 and 91 mg/L, respectively.

Conclusions

The solubility of both reference and field neat TNT increased with an increase in temperature. Solubility data at higher pH varied widely, especially at high temperature, and subsequent HPLC analysis showed three unknown peaks at high pH and temperature. The solubility found from this study was significantly lower than the most frequently cited literature TNT solubility by Taylor and Rinkenbach (1923) but compared well to that from the *Merck Index*, *Lange's Handbook of Chemistry*, Hale et al. (1979), and Spanggord et al. (1983). A semiempirical correlation of solubility to temperature, based on ideal solution theory, fitted the experimental data well.

Acknowledgment

We thank Drs. D. L. Kaplan and D. H. Rosenblatt and an anonymous peer reviewer for their constructive comments and input.

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Received for review December 18, 1995. Accepted March 28, 1996.[⊗] This work was supported by the U.S. EPA Hazardous Substance Research Center/S & SW Contract No. 127-70-5108.

JE950322W

[⊗] Abstract published in *Advance ACS Abstracts*, May 1, 1996.