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Thermophysical Properties of an Insensitive Munitions Compound, 2,4-Dinitroanisole

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Accurate values of thermophysical properties of toxic chemical compounds over a range of temperatures are essential for understanding their environmental distribution, biotransformation, and development of potential water treatment processes. In this study, the aqueous solubility (s_w), octanol–water partition coefficient (K_{ow}), and Henry's law constant (k_H) were measured for an insensitive munitions compound, 2,4-dinitroanisole (DNAN), at the temperatures of (298.15, 308.15, and 318.15) K. The effect of ionic environment on solubility, using electrolytes such as NaCl and $CaCl_2$, was also studied. The data on the thermophysical parameters were correlated using the standard van't Hoff equation. All three properties exhibited a linear relationship with reciprocal temperature. The enthalpy and entropy of phase transfer were derived from the experimental data.

Introduction

The development of insensitive munitions (IM) is a key part of modern explosives research. In recent years, TNT has fallen out of favor as an ingredient in melt-cast explosive formulations, and alternatives with suitable chemical and physical properties have been sought. 2,4-Dinitroanisole (DNAN) is a promising alternative that prima facie appears to possess adequate properties and, by virtue of its reduced sensitivity, may enable the development of a new class of low sensitivity melt-cast formulations for use in IM.

One of the recoded first uses of DNAN in an explosive military device was as a main charge ingredient in Amatol 40 (50 % DNAN, 35 % ammonium nitrate, 15 % cyclotrimethylenetrinitramine) in the warhead of some V-1 flying bombs during the Second World War.[1] Its use was not necessarily due to any performance gains but more likely to its availability when higher performance materials such as TNT were becoming increasingly scarce.[2] Despite the performance shortcomings, the use of DNAN in explosive formulations is presently undergoing a renaissance as an IM compound. In addition, DNAN has many industrial applications such as an ingredient in the syntheses of dyes[3] and as an insecticide.[4] However, a review of more recent literature shows that current interest in DNAN is predominantly as an ingredient in explosive formulations. Exposure to DNAN via oral intake, skin absorption, and inhalation was found to be more acutely toxic than that of TNT for a single dose for a single exposure.[5]

Two main reasons exist for the renewed interest in DNAN. First, it is a less-sensitive melt-cast medium than TNT, and second, it is categorized as a Class 4.1 Flammable Solid and is therefore subject to less stringent international transportation requirements than Class 1 materials. Since the use of DNAN may increase considerably in the future, the possibility of this compound entering in to the environment is inevitable. The fate and distribution of DNAN released into the environment primarily depend on: (1) the physicochemical properties of the compound and (2) prevailing environmental conditions at the point(s) of discharge. Thus, accurate determination of physicochemical properties is critical in developing valid environmental models and impact assessments. The most important physicochemical properties relating to the environmental behavior of hydrophobic organic compounds are aqueous solubility (s_w), octanol–water partition coefficient (K_{ow}), and Henry's law constant (k_H). s_w is the maximum solute concentration possible at equilibrium, and it can also function as a limiting factor in concentration-dependent processes. Inorganic salts, present in solution, can influence the equilibrium solubility of organic compounds. The aqueous solubility of organic compounds usually decreases in the presence of inorganic salts, which is known as the salting-out effect.

The octanol–water partition coefficient is the ratio of the concentration of a chemical solute in octanol and in water at equilibrium and at a specified temperature. K_{ow} serves as an indicator for the tendency of the chemical to bioaccumulate. This parameter is used in many environmental studies to determine the fate of chemicals in the environment. The Henry's law constant (k_H) and its temperature dependence play an important role in all studies concerned with the fate and distribution of chemical species in the environment. k_H is very important in environmental studies and in chemical analyses: it facilitates the estimation of the mass transfer of a compound between water and air. In many industrial, toxicological, and environmental processes, the Henry's law constant and its dependency on temperature play an important role in modeling the exchange of semivolatile chemicals between gaseous and aqueous phases.[6,7] The solubility, octanol–water partition coefficient, and Henry's law constant quantify the extent to which a chemical partitions between solid–liquid, liquid–liquid, and water–air, respectively.

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Experimental data on aqueous solubility, octanol–water partition coefficient, and Henry's law constant for the explosive components are scarce. A search of the literature showed that no data on physicochemical properties of DNAN have been reported. However, aqueous solubility and dissolution rates were reported for other explosive components, TNT, RDX, and HMX, over the pH range of 4.2 to 6.2 in the temperature range of (3.1 to 33.3) °C studied using high-pressure liquid chromatography with ultraviolet detection.[8] Qasim et al.[9] predicted vapor pressure, Henry's law constants, aqueous solubility, octanol–water partition coefficients, enthalpies of formation, and ionization potentials of TNT and related species. In continuation of our efforts in the determination of physicochemical properties of insensitive munitions compounds,[10] we report new experimental data on s_w, K_{ow}, and k_H for DNAN at (298.15, 308.15, and 318.15) K. The salting-out effect on aqueous solubility of DNAN at these temperatures was investigated using (mass fraction of 1, 5, and 10) % of sodium chloride and calcium chloride in water. The effect of temperature on s_w, K_{ow}, and k_H was used to evaluate enthalpy and entropy of phase transfers.

Experimental Section

DNAN (CAS No: 119-27-7) was manufactured by Ordnance Systems, Inc., Kingsport, Tennessee, USA, and used without further purification. ACS reagent grade sodium chloride and calcium chloride were purchased from Sigma-Aldrich and Fisher Scientific, respectively. Deionized water of resistivity $> 18\ \mathrm{M\Omega}$, obtained using US Filter Ion Exchanger and Reverse Osmosis Setup (UHQ-II-MK3), was used throughout the study. 1-Octanol (ACS reagent grade) and acetonitrile (ACS reagent grade) were obtained from Sigma-Aldrich and used without further purification.

The concentration of DNAN in water as well as in 1-octanol was determined using HPLC (DIONEX ICS 3000) with a UV detector (UVD170U) at a wavelength of 254 nm. The flow rate of the mobile phase was set to $1.00\ \mathrm{mL \cdot min^{-1}}$ within the column (Acclaim Explosive E2), and the column compartment temperature was set to 30 °C. A mixture of 57 vol % of helium purged deionized water and 43 vol % of HPLC grade methanol was used as the mobile phase. Data acquisition and analysis were carried out using Chromeleon software (DIONEX). The method was simple, quick, and reproducible. In the determination of DNAN, Beer–Lambert's law was applicable up to $50\ \mathrm{mg \cdot L^{-1}}$ with a regression coefficient value equal to 0.9985. The concentration of DNAN was reproducible to $\pm\ 0.1\ \mathrm{mg \cdot L^{-1}}$. The solutions were diluted appropriately prior to analysis.

The aqueous solubility of DNAN was measured at temperatures of (298.15, 308.15, and 318.15) K by adding an excess amount of the solid compound (0.2 g) to glass flasks containing deionized water (100 mL). The flasks were stoppered and sealed with parafilm and Teflon tape to prevent evaporation of water. Experiments were conducted in a shaker water bath (Julabo SW 23), and the temperature was controlled within ± 0.5 °C. The flasks were shaken at 150 rpm for about 36 h. Once thermodynamic equilibrium was established at a given temperature, three samples (2 mL each) were withdrawn with a syringe, centrifuged in a temperature-controlled centrifuge (Fisher Scientific, MARATHON 21000R) for 10 min at 2000 rpm, and immediately diluted to avoid precipitation. To overcome DNAN adsorption losses on the glassware during experimentation, all the glassware was soaked in DNAN solution for about 24 h and rinsed with deionized water several times to remove excess DNAN. To avoid recrystallization of DNAN, the hardware used for sampling and filtration was equilibrated at the test temperature. The concentration of DNAN in aqueous medium was determined using the above HPLC method.

A stock solution of DNAN in 1-octanol was prepared and diluted to a required concentration. The concentration of DNAN in the solution was determined using the HPLC method. The experiments were conducted in 40 mL glass vials with silicone septa. The two solvents (octanol and water) were mutually saturated at the temperature of the experiment before adding DNAN dissolved in 1-octanol. To prevent loss of material due to volatilization, the vials were completely filled with the two-phase system. Three sets of experiments were conducted with different ratios of the two solvents in duplicate. The vials were shaken for 36 h in the shaking water bath (Julabo SW 23) at a desired temperature controlled to ± 0.5 K. The contents were then allowed to equilibrate in the set temperature bath for about 36 h. The vials were centrifuged at 2000 rpm for about 10 min at the experimental temperature to achieve complete separation of the two phases. The aqueous phase from each vial was withdrawn using a glass syringe with a removable stainless steel needle. The syringe was filled partially with air, and the air was gently expelled while the needle was passing through the top octanol layer to prevent entry of octanol in to the needle. The syringe with an adequate quantity of the aqueous phase was quickly withdrawn, and the needle was removed. This process of withdrawing the aqueous phase eliminated any risk of contamination with traces of 1-octanol. Both the phases were analyzed for DNAN concentration following the HPLC-UV detection method described earlier. The octanol–water partition coefficient was obtained as the ratio of the concentration of DNAN in organic and aqueous phases.

The gas-purging bubble column system used for the experimental determination of Henry's law constant was similar to that of Mackay et al.[11] and of Muller and Heal.[12] The schematic diagram is shown in Figure 1. High purity compressed air was bubbled through the aqueous solution containing DNAN at a constant flow rate. The air stripped DNAN from the solution into the gas phase. The volume of the gas passed through the column was obtained from the flow rate and the stripping time. The Henry's law constant was calculated from the rate of decrease in an aqueous concentration of DNAN. The Pyrex glass bubble column used in these experiments was 30 cm high with an internal diameter of 2 cm and with a water jacket to facilitate water circulation for maintaining constant temperature. Air was introduced at the bottom of the column through a fritted disk. The temperature of the liquid in the bubble column was kept constant by circulating water from a temperature-controlled water bath (Fisher Scientific, Isotemp 1013D) through the jacket surrounding the bubble column. Experiments were conducted at 10 K intervals between (298.15 and 318.15) K. Vigorous mixing of the liquid occurred in the bubble column. The air flow was controlled and measured by accalibrated mass flow meter (Gilmont Instruments, GF-1160). To prevent water evaporation from the purging column, the gas was humidified prior to entering the bubble column by passing the flow through a U-tube containing deionized water. The U-tube was immersed in the water bath at the temperature of the bubble column. No change of liquid volume was observed in the bubble column, even after purging the gas for several hours. The gas exiting from the upper end of the column was discharged into cooled acetonitrile through Teflon tubing. A reflux condenser was attached to the top of the acetonitrile trap to minimize the loss of acetonitrile and DNAN. Coolant was circulated through the condenser from a Haake K-10 (Fisher Scientific) cooling system. An amount of 150 mL of dilute solution of DNAN was taken

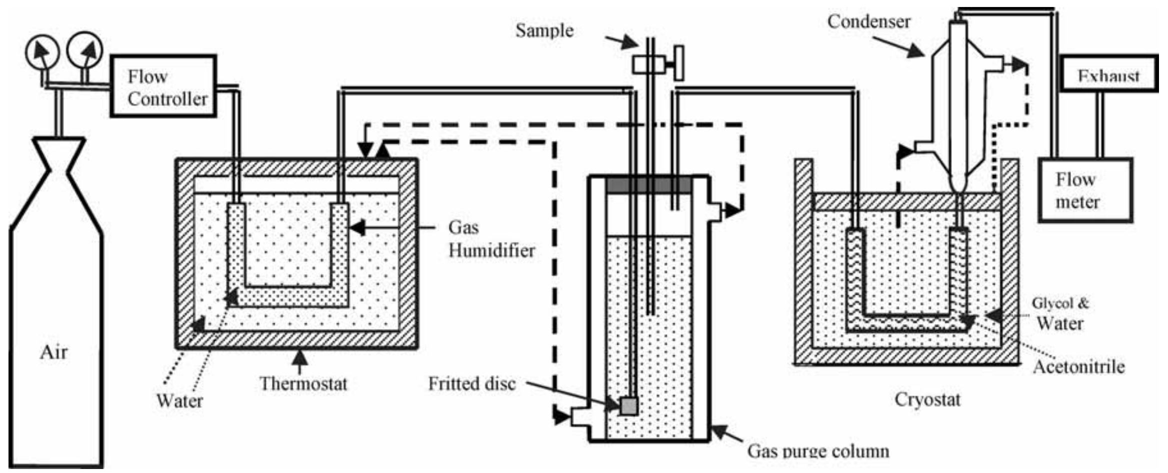

Figure 1. Experimental setup for the determination of Henry's law constant.

in the bubble column, and air was allowed to flow at a desired flow rate. An amount 1 mL of the samples was withdrawn at 1 h time intervals through the tubing and the concentration of DNAN in the liquid phase was determined. All precautions were taken to ensure loss-free transfer of each aliquot. The values of k_H were obtained following the procedure reported by Fu et al.[13]

In a dilute aqueous solution, the Henry's law constant, k_H, is represented as the ratio of solute partial pressure (p) and aqueous-phase solute concentration (c). Application of the mass balance on DNAN at equilibrium between DNAN in the liquid phase and vapor phase leads to the following equation

$$-V\frac{dc}{dt} = \frac{pU}{RT} = \frac{k_H Uc}{RT} \tag{1}$$

where U is the gas flow rate; V is the volume of the liquid; R is the gas constant; T is the system temperature; and t is the gas stripping time. Integration of the above equation from initial conditions ($t = 0$ and $C = C_0$) gives

$$\ln c = \ln c_0 - \left(\frac{k_H U}{VRT}\right)t \tag{2}$$

A plot of ln c against t should be linear, with a slope of ($-k_H U/VRT$) if the water volume is constant. Since 1 mL of the sample is withdrawn each time, the volume of the sample changes. In this study, the initial volume of aqueous solution (V_0) for gas purge was 150 mL. For an experimental run of 12 h, the sample volume undergoes a change of 8 %. Correction to this volume change was incorporated, while integrating eq 1 from time = 0 to time = t. The modified approach as described by Fu et al.[12] was adopted to account for the volume change. Since the volume of aqueous solution was constant between two sampling intervals, eq 1 is applied to each time interval separately. All the resulting equations on summation result in the following equation in place of eq 2

$$\ln c_n = \ln c_0 - \left(\frac{k_H U \Delta t}{RT}\right)\Sigma\left(\frac{1}{V}\right)_n \tag{3}$$

where Δt represents the time difference between two successive sampling intervals and $\Sigma(1/V)_n$ is the sum of reciprocal volumes of solution left in the column at different time intervals; that is, $\Sigma(1/V)_n = (1/V_0 + 1/V_1 + \cdots + 1/V_{n-2} + 1/V_{n-1})$, where V_0, V_1, V_2, ... V_{n-2} and V_{n-1} represent the volume of solution left in the column at different sampling intervals. Equation 3 demonstrates that a plot of ln c_n versus $\Sigma(1/V)_n$ gives a straight line with a slope of ($-k_H U \Delta t/RT$), from which Henry's Law constant (k_H) was determined.

Table 1. Aqueous Solubility of DNAN in the Presence of NaCl and $CaCl_2$ Salts at Different Temperatures

	S/mg·L^{-1}		
vol % of salt solution	298.15 K	308.15 K	318.15 K
0	276.2 ± 2.5	399.2 ± 4.0	560.0 ± 5.0
1 % NaCl	267.1 ± 2.5	388.6 ± 3.0	527.2 ± 5.0
5 % NaCl	233.5 ± 2.5	320.1 ± 2.5	437.2 ± 4.0
10 % NaCl	190.7 ± 2.5	240.0 ± 2.5	321.4 ± 2.5
1 % $CaCl_2$	268.1 ± 2.5	388.8 ± 3.0	537.5 ± 5.0
5 % $CaCl_2$	249.0 ± 2.5	333.5 ± 3.0	463.5 ± 4.0
10 % $CaCl_2$	224.2 ± 2.5	276.7 ± 2.5	378.7 ± 3.0

Results and Discussion

The solubilities of DNAN in water and salt solutions of NaCl and $CaCl_2$ [(mass fraction of 1, 5, and 10) %] at (298.15, 308.15, and 318.15) K are shown in Table 1. The variation of solubility of DNAN with reciprocal temperatures at different salt concentrations is graphically represented in Figures 2 and 3, respectively. No experimental data on aqueous solubility of DNAN are available in the literature for comparison. Toghiani et al.[14] estimated the aqueous solubility of DNAN at 298.15 K as (140 and 159) mg·L^{-1} on the basis of Klopman and COSMOtherm prediction methods, respectively. Samuel and

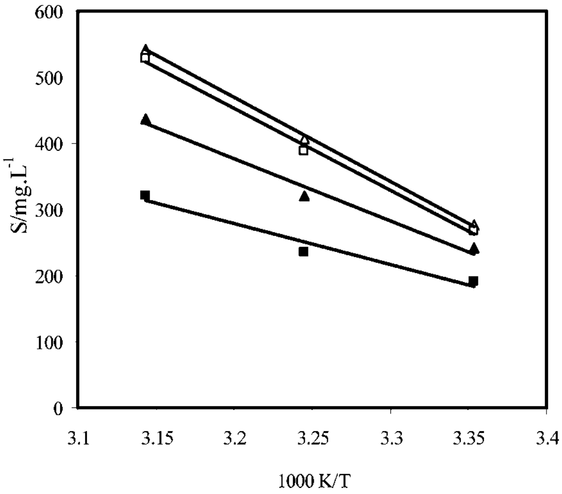

Figure 2. Solubility of DNAN versus reciprocal temperature in the presence of NaCl. △, water; □, w = 1 % NaCl; ▲, w = 5 % NaCl; ■, w = 10 % NaCl.

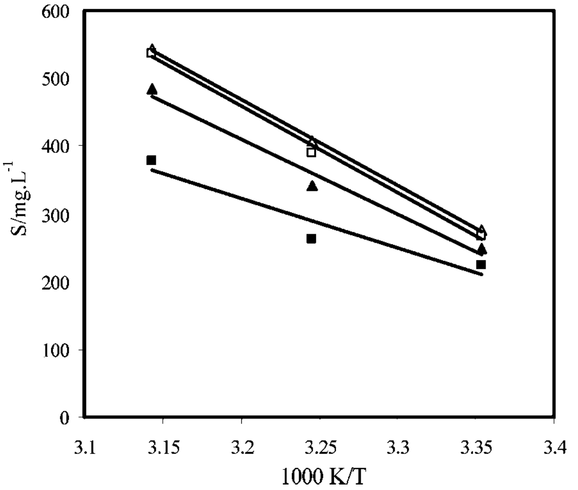

Figure 3. Solubility of DNAN versus reciprocal temperature in the presence of $CaCl_2$. △, water; □, $w = 1$ % $CaCl_2$; ▲, $w = 5$ % $CaCl_2$; ■, $w = 10$ % $CaCl_2$.

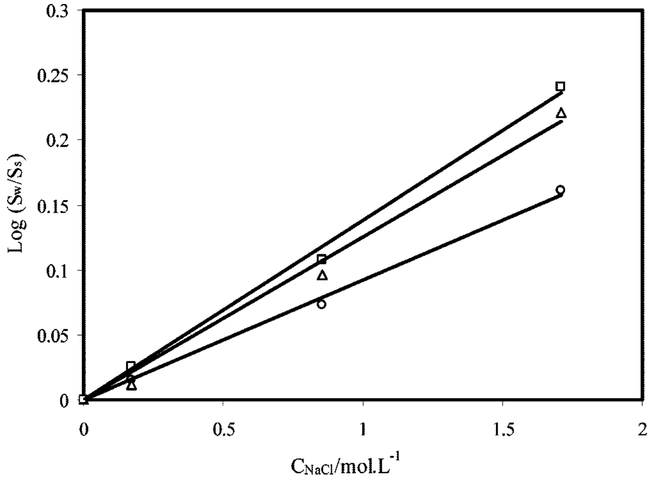

Figure 4. Setschenow plots for variation of solubility of DNAN in the presence of NaCl. ○, 298.15 K; △, 308.15 K; □, 318.15 K.

Yan[15] compiled the solubility of DNAN as 155 mg·L^{-1} at 22 °C, 136 mg·L^{-1} at 50 °C, and 4757 mg·L^{-1} at 100 °C. All the predicted values are not in agreement with the experimentally determined aqueous solubility of DNAN. As observed from the data, the solubility of DNAN is a strong function of temperature. The increase in temperature results in an increase in solubility in pure water as well as in solutions of electrolytes. The saturated solution of DNAN can be assumed to exhibit ideal behavior, which is justified in solutions of limited solubility of hydrophobic materials.[16] The influence of temperature on the solubility of DNAN can be quantitatively estimated by the van't Hoff equation as

$$\log s_{\mathrm{w}} = \frac{-\Delta_{\mathrm{fus}} H^0}{RT} + b \tag{4}$$

The enthalpy of fusion of DNAN, $\Delta_{\mathrm{fus}}H$, has been determined by plotting $\log(s_{\mathrm{w}})$ versus $1/T$ and found to be 11.59 kJ·mol^{-1}. No experimental data on enthalpy of fusion for DNAN are available in the literature for comparison. However, Toghiani et al.[14] (2007) predicted the enthalpy of fusion of DNAN as 19.91 kJ·mol^{-1}.

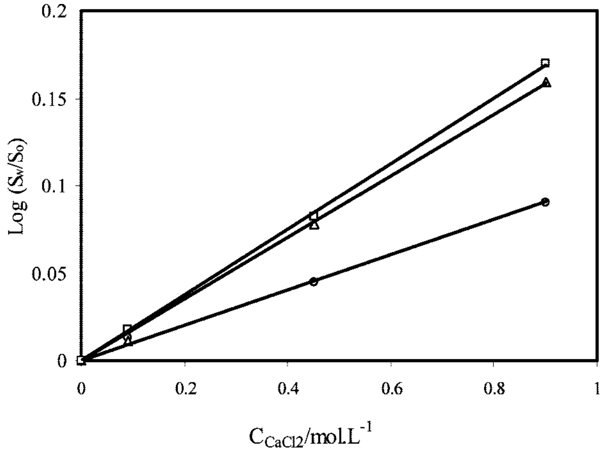

Figure 5. Setschenow plots for variation of solubility of DNAN in the presence of $CaCl_2$. ○, 298.15 K; △, 308.15 K; □, 318.15 K.

Table 2. Constants of the Setschenow Equation for DNAN Solubility at Different Temperatures

	sodium chloride		calcium chloride	
T/K	K_{s}	R^2	K_{s}	R^2
298.15	0.0922 ± 0.006	0.9971	0.1007 ± 0.0003	0.9970
308.15	0.1253 ± 0.0011	0.9914	0.1756 ± 0.0003	0.9987
313.15	0.1380 ± 0.0006	0.9960	0.1874 ± 0.0001	0.9996

The solubility of DNAN decreases gradually with an increase in the concentration of sodium chloride and calcium chloride at all three temperatures studied. This may be attributed to binding of ions in solution tightly to several water molecules into hydration shells.[17] A smaller number of water molecules are freely available for cavity formation, therefore a fewer number of organic molecules are accommodated in solution, consequently resulting in a decrease in their solubility. A similar decrease in the aqueous solubility of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) was reported recently by Sylwia et al.[18] The decrease in solubility of a solute in the presence of an electrolyte is correlated by the classical Setschenow equation[19] as given below

$$\log\left(\frac{s_{\mathrm{w}}}{s_{\mathrm{s}}}\right) = K_{\mathrm{s}} c \tag{5}$$

where s_{w} is the solubility of DNAN in pure water; s_{s} is the solubility in the presence of a salt; K_{s} is the Setschenow constant; and c is the concentration of the salt. $\mathrm{Log}(s_{\mathrm{w}}/s_{\mathrm{s}})$ versus concentration plots are shown in Figures 4 and 5. The values of Setschenow constants, obtained from experimental data, are included in Table 2. The positive value of K_{s} indicates the salting-out effect, whereas the negative K_{s} indicates a salting-in effect. The values of K_{s} are positive for DNAN and increase with an increase in temperature. The linear relationship between $\log(s_{\mathrm{w}}/s_{\mathrm{s}})$ and salt concentration has been observed in several investigations over a wide concentration range.[20]

The experimental values of the octanol–water partition coefficient ($\log K_{\mathrm{ow}}$) of DNAN at (298.15, 308.15, and 318.15) K are given in Table 3, and the variation of $\log K_{\mathrm{ow}}$ with reciprocal temperature is shown in Figure 6. The value of $\log k_{\mathrm{ow}}$ at 298 K, as reported by Debnath et al.,[21] is about 7 % higher than the value reported in this study. The partition coefficient represents equilibrium between the compositions of a component in two liquids, and hence, from the Van't Hoff isotherm, the Gibbs energy of transfer from water to octanol is given by

$$\Delta G = -2.303RT \log K_{\mathrm{ow}} \tag{6}$$

However, the Gibbs energy is the difference between the enthalpy (ΔH) and the entropy (ΔS) of transfer. It is thus

Table 3. Composition of DNAN in Octonol and Aqueous Phases and Octanol−Water Partition Coefficients (log K_{ow}) at Different Temperatures

T K	C in octanol $mg \cdot L^{-1}$	C in water $mg \cdot L^{-1}$	log K_{OW}
298.15	39.77	0.97	1.612 ± 0.014
	56.19	1.38	
	59.17	1.65	
	86.61	2.24	
	108.08	2.48	
308.15	45.60	1.28	1.549 ± 0.013
	48.18	1.34	
	93.94	2.66	
	78.39	2.34	
	147.83	4.03	
	149.15	4.22	
318.15	64.56	2.30	1.472 ± 0.025
	67.22	2.36	
	88.48	2.72	
	121.71	4.30	
	125.20	4.04	

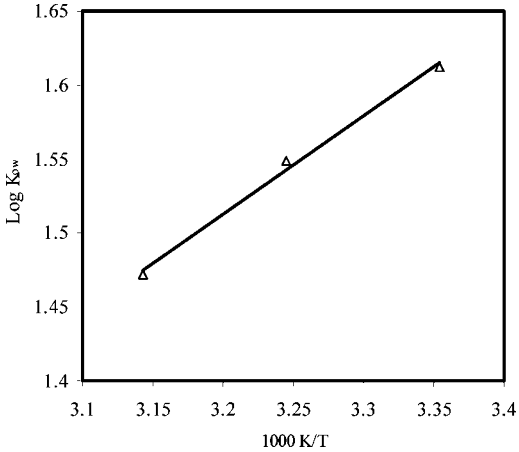

Figure 6. Octanol–water partition coefficient (log K_{ow}) of DNAN versus reciprocal temperature.

possible for two compounds with very similar log K_{ow} values to have widely differing enthalpies and entropies of partitioning, indicating different partitioning mechanisms. We have used the van't Hoff approach to obtain from the van't Hoff isochore (eq 7) the enthalpy and entropy of partitioning.

$$\log K_{ow} = \frac{-\Delta H}{2.303RT} + \frac{\Delta S}{2.303R} \tag{7}$$

The method relies on the assumption that enthalpy and entropy of partitioning are constant over the temperature range studied. The Gibbs energy (at 298.15 K), enthalpy, and entropy of partitioning of DNAN between octanol and water are –9.22 $kJ \cdot mol^{-1}$, -12.70 $kJ \cdot mol^{-1}$, and -11.68 $J \cdot mol^{-1} \cdot K^{-1}$, respectively.

Chiou et al.[22] derived the following correlation between aqueous solubility and K_{ow} for solutes of partial solubility, assuming perfect solution behavior

$$\log K_{ow} = -\log s_w - \log V_0^* \tag{8}$$

where V_0^* is molar volume of the solvent. The experimental data on log S_w and log K_{ow} at different temperatures are fitted to the above equation. The regression analysis between log S_w and log K_{ow} gives the following relation

$$\log K_{ow} = -\log s_w + \log V_0^* \tag{9}$$

This equation is capable of predicting log K_{ow} values of DNAN with an average absolute deviation of 0.008 and $R^2 = 0.98$.

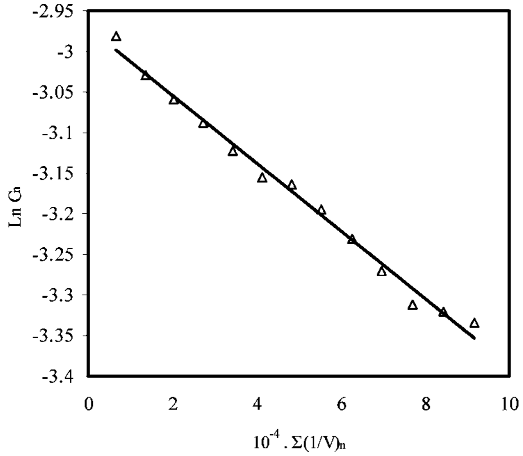

Figure 7. Typical plot of ln C versus $\Sigma(1/V)$ for DNAN at 298.15 K.

Table 4. Henry's Law Constants for DNAN at Different Temperatures

T/K	$k_H/(m^3 \cdot Pa \cdot mol^{-1})$	$10^4\ k_H'$
298.15	1.366	$5.51 \cdot 10^{-4}$
308.15	1.397	$5.64 \cdot 10^{-4}$
318.15	1.442	$5.82 \cdot 10^{-4}$

Henry's law constant (k_H) is also often expressed as a dimensional quantity with units of (pressure·volume)/mass

$$k_H = \frac{p_g}{c_w} \tag{10}$$

where p_g is the gas-phase partial pressure and c_w is the aqueous concentration in units of mass of DNAN per volume of water or as the dimensionless Henry's law constant (k_H')

$$k_H' = \frac{c_g}{c_w} \tag{11}$$

where the gas-phase concentration (c_g) is expressed in units of mass of the compound chemical per volume of air. The partial pressure can be expressed in moles per cubic meter of air assuming ideal behavior, [$p_i = (n_i/V)RT$]. The relationship between k_H and k_H' is as follows

$$k_H' = \frac{k_H}{RT} \tag{12}$$

where R is the ideal gas constant (8.314 $J \cdot K^{-1} \cdot mol^{-1}$) and T is the absolute temperature. The experimental values of Henry's law constants, obtained from plots of ln c_n versus $\Sigma(1/V)_n$ (a typical plot is shown in Figure 7), for DNAN are given in Table 4. The temperature dependence of k_H' is described by the equation

$$-RT \ln k_H' = \Delta H_H - T\Delta S_H \tag{13}$$

where ΔH_H and ΔS_H are the enthalpy and entropy of the phase transfer from the dissolved phase to the gas phase. Solving for ln k_H' gives

$$\ln k_H' = \frac{-\Delta H_H}{RT} + \frac{\Delta S_H}{R} \tag{14}$$

Assuming ΔH_H and ΔS_H are independent of temperature (a reasonable assumption over small temperature ranges), this equation describes the dependence of k_H' on temperature. By measuring k_H' experimentally at different temperatures and plotting ln k_H' versus $1/T$ (Figure 8), ΔH_H and ΔS_H are determined from the slope and intercept, respectively. The values

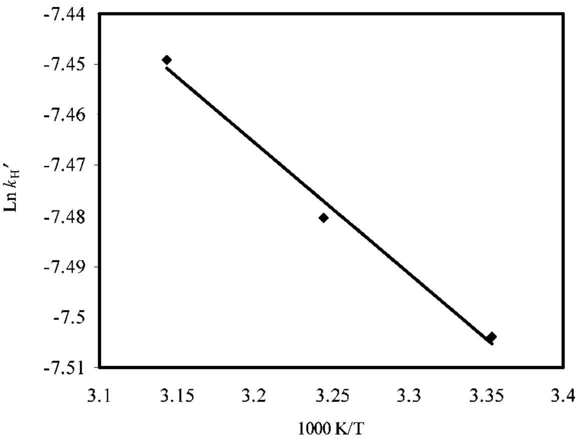

Figure 8. Ln k_{H}' of DNAN versus reciprocal temperature.

of ΔH_{H} and ΔS_{H} are 2.15 $\mathrm{kJ \cdot mol^{-1}}$ and –55.18 $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$, respectively.

Conclusions

To date, to the best of our knowledge, the data presented here are the most comprehensive experimentally determined values for aqueous solubility, octanol–water partition coefficient, and Henry's law constant for DNAN in the temperature range (298.15 to 318.15) K. The effect of temperature and electrolytes on aqueous solubility of DNAN was studied. The solubility increases with an increase in temperature and decreases with an increase in electrolyte concentration. Enthalpies of phase change from solid to liquid, liquid to liquid, and liquid to vapor were obtained by fitting the experimental data on s_{w}, K_{ow}, and k_{H}', respectively, to the van't Hoff equation.

Literature Cited

(1) Fedoroff, B. T. Dictionary of Explosives, Ammunition and Weapons (German Section),Picatinny Arsenal Technical Report 2510, 1958.
(2) Fedoroff, B. T. *Encyclopedia of Explosives and Related Items*; Picatinny Arsenal: Dover, New Jersey, C616, 1960; *Vol. 3*.
(3) Chuddar, R. J.; Oakes, J. *Kirk-Other Encyclopedia of Chemical Technology - Section on Ago Dyes*, John Wiley & Sons, Inc., 2003.
(4) Nelson, A. A. Toxicological Investigations of Compounds Proposed for use as Insect repellents. C. Pathological Examination. *J. Pharm. Exp. Therap.* **1948**, *93*, 26–39.
(5) Dodd, D. E.; McDougal, J. N. Recommendation of an Occupational Exposure Level for PAX-21, AFRL-HE-WP-TR-2001–0103, 2002.
(6) Mackay, D.; Paterson, S.; Schroeder, W. H. Model Describing the Rates of Transfer Processes of Organic Chemicals between Atmosphere and Water. *Environ. Sci. Technol.* **1986**, *20*, 810–816.
(7) Holly, A. B.; Dianne, L. P.; Joel, E. B. Henry's Law Constants of Polychlorinated Biphenyl Congeners and their Variation with Temperature. *J. Chem. Eng. Data* **2000**, *45*, 1069–1074.
(8) Jason, C. L.; Karen, F. M.; James, M. B.; Joseph, J. D. Effects of pH and Temperature on the Aqueous Solubility and Dissolution Rate of 2,4,6-Trinitrotoluene (TNT), Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX). *J. Chem. Eng. Data* **2001**, *46*, 1549–1555.
(9) Qasim, M.; Kholod, Y.; Gorb, L.; Magers, D.; Honea, P.; Leszczynsk, J. Application of Quantum-chemical Approximations to Environmental Problems: Prediction of Physical and Chemical Properties of TNT and Related Species. *Chemosphere* **2007**, *69*, 1144–1150.
(10) Boddu, V. M.; Krishnaiah, A.; Maloney, S. W.; Damavarapu, R. Physicochemical properties of an insensitive munitions compound, N-methyl-4-nitroaniline (MNA). *J. Hazard. Mater.* **2008**,in press, doi: 10.1016/j.jhazmat.2007.11.074.
(11) Mackay, D.; Shih, W. Y.; Sutherland, R. P. Determination of Air-water Henry's Law Constants for Hydrophobic Pollutants. *Environ. Sci. Technol.* **1979**, *13*, 333–337.
(12) Muller, B.; Heal, M. R. The Henry's Law Coefficient for 2-Nitrophenol in the Temperature Range 278–303 K. *Chemosphere* **2001**, *45*, 309–314.
(13) Fu, F.; Shaogang, C.; Hong, C. -S. Air-water Henry's Law Constants for PCB Congeners: Experimental Determination and Modeling of Structure-property Relationship. *Anal. Chem.* **2006**, *78*, 5412–5418.
(14) Toghiani, R. K.; Tohiani, H.; Maloney, S. W.; Boddu, V. M. Prediction of Physicochemical properties of energetic materials. *Fluid Phase Equilib.* **2008**, *264*, 86–92.
(15) Samuel, H. Y.; Yan, H. *Handbook of Aqueous Solubility Data*; CRC Press: Boca Raton, FL, 2003.
(16) Adel, N.; Manef, A.; Elise, P. Temperature and Salt Addition Effects on the Solubility Behavior of some Phenolic Compounds in Water. *J. Chem. Thermodyn.* **2007**, *39*, 297–303.
(17) Long, F. A.; McDevit, W. F. Activity Coefficients of Nonelectrolyte Solutes in Aqueous Salt Solutions. *Chem. Rev.* **1952**, *51*, 119–169.
(18) Sylwia, O.- K.; Etsuro, S.; Takashi, N. Solubilities of Selected PCDDs and PCDFs in Water and Various Chloride Solutions. *J. Chem. Eng. Data* **2007**, *52*, 1824–1829.
(19) Setschenow, J. Uber die Konstitution der Salzlosungen auf Grund ihres Verhaltens zu Kohlensaure. *Z. Phys. Chem. Vierter Band.* **1889**, *1*, 117–125.
(20) Miklós, G.; Jo, D.; Herman, V. L.; Károly, H. Aqueous Salting-out Effect of Inorganic Cations and Anions on Non-electrolytes. *Chemosphere* **2006**, *65*, 802–810.
(21) Debnath, A. K.; Compadre, R. L, L. D.; Shusterman, A. J.; Hansch, C. Quantitative Structure-Activity Relationship Investigation of the Role of Hydrophobicity in Regulating Mutagenicity in the Ames test: 2. Mutagenicity of Aromatic and Heteroaromatic Nitro Compounds in Salmonella typhimurium TA100. *Environ. Mol. Mutagen.* **1992**, *19*, 53–70.
(22) Chiou, C.; Schmedding, D. W.; Manes, M. Improved Prediction of Octanol-Water Partition Coefficients from Liquid-solute Water Solubilities and Molar Volumes. *Environ. Sci. Technol.* **2005**, *39*, 8840–8846.

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