

Physicochemical properties of an insensitive munitions compound, *N*-methyl-4-nitroaniline (MNA)

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Received 23 August 2007; received in revised form 16 November 2007; accepted 19 November 2007
Available online 23 November 2007

Abstract

Accurate information on physicochemical properties of an organic contaminant is essential for predicting its environmental impact and fate. These properties also provide invaluable information for the overall understanding of environmental distribution, biotransformation, and potential treatment processes. In this study the aqueous solubility (S_w), octanol–water partition coefficient (K_{ow}), and Henry's law constant (K_H) were determined for an insensitive munitions (IM) compound, *N*-methyl-4-nitroaniline (MNA), at 298.15, 308.15, and 318.15 K. Effect of ionic strength on solubility, using electrolytes such as NaCl and CaCl₂, was also studied. The data on the physicochemical 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.

Published by Elsevier B.V.

Keywords: Solubility; Octanol–water partition coefficient; Henry's law constant; *N*-Methyl-4-nitroaniline

1. Introduction

The objective of the insensitive munitions (IM) program is to develop new explosive materials and formulations that are more stable than the materials currently used. These new munitions may be incorporated into the Department of Defense (DoD) inventory and will be packed at current Load, Assemble, and Pack facilities. For example, China Lake 20 (CL-20) is a multi-ringed cyclic nitramine, and Picatinny Explosive 21 (PAX-21) is a mixture of ammonium perchlorate, RDX (a single-ring nitramine), dinitroanisole (DNAN), and *N*-methyl-*p*-nitroaniline (MNA). Production, loading, assembling, and packing of these munitions will generate new waste streams at Army industrial facilities. MNA is added as stabilizer in order to lengthen the useful service life of double-base and minimum smoke propellants [1]. Use of stabilizers, such as MNA, showed a decrease in absolute quantity of gases generated from polyglycidyl nitrate prepolymer and gumstock [2].

The fate and distribution of an IM compound released into the environment are primarily controlled by: (1) prevailing environmental conditions such as temperature, pH, salinity, presence of other hydrophilic and hydrophobic materials at the point(s) of discharge and (2) the physicochemical properties of the compound. Thus, accurate information of physicochemical properties is critical to developing valid environmental models and risk assessments. Conversely, the predictive/interpretive value of environmental studies is seriously compromised if the physicochemical data upon which they rely are of questionable or unknown quality [3]. Three of the most important thermo-physical 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). These parameters are used extensively in medicinal chemistry (pharmacokinetics, drug design, and anesthesiology), chromatography, and pesticide chemistry. Aqueous solubility is defined as the maximum amount of solute that can be dissolved in a given amount of solvent. Because S_w is the maximum solute concentration possible at equilibrium, it can also function as a limiting factor in concentration dependent processes [4]. Inorganic salts, present in large amounts in the environment, greatly

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influence the partitioning of organic compounds between different phases. The aqueous solubility of organic compounds usually decreases in the presence of inorganic salts, which is known as the salting-out effect. Salting-out offers several practical applications to (1) modify the physical behavior of the solution, (2) separate the components of a system, and (3) improve the sensitivity of analytical techniques.

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. Octanol is an organic solvent that is used as a surrogate for natural organic matter. This parameter is used in many environmental studies to determine the fate of chemicals in the environment. An example would be the prediction of the extent of bioaccumulation of a contaminant in fish using the coefficient. It is assumed that the molecular speciation of the solute is the same in both solvents and that the solutions are sufficiently dilute [5].

The distribution equilibrium of a compound between water phase and gas phase is characterized by Henry's law constant, which is equal to the ratio of concentration of the species in air and water in equilibrium. This law is very important in environmental studies and in chemical analyses: it affects the mass transfer of the 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 semi-volatile chemicals between gaseous and aqueous phases [6,7]. Solubility, octanol–water partition coefficient, and Henry's law constant quantify the extent to which a chemical partitions between solid–liquid, liquid–liquid, and air–water, respectively.

Although the importance of IM compounds has been long recognized, experimental data of their aqueous solubility, octanol–water partition coefficient, and Henry's law constant are scarce. However, such data have been reported for some munitions compounds. Karakaya et al. [8] reported aqueous solubility and alkaline hydrolysis of novel high explosive hexanitrohexaazaisowurtzitane (CL-20). Kim et al. [9] studied the solubility, density, and metastable zone width of 3-nitro-1,2,4-triazol-5-one + water system. Physicochemical parameters of CL-20, which is considered to be a replacement for RDX and HMX, were measured by Monteil-Rivera et al. [10] for environmental applications. Aqueous solubility and dissolution rate were reported for TNT, RDX, and HMX over the pH range of 4.2–6.2 in the temperature range of 3.1–33.3 °C using high-pressure liquid chromatography with ultraviolet (UV) detection [11]. Qasim et al. [12] predicted vapor pressure, Henry's law constants, aqueous solubility, octanol/water partition coefficients, heats of formation, and ionization potentials of TNT and related species.

A comprehensive literature search revealed no experimental data on thermophysical properties of MNA. Here, we report experimental data on S_w , K_{ow} , and K_H for MNA at 298.15, 308.15, and 318.15 K. The salting-out effect on aqueous solubility of MNA at all the temperatures was investigated using 1, 5, and 10% solutions of sodium chloride and calcium chloride. The effect of temperature on S_w , K_{ow} , and K_H is used to evaluate enthalpy and entropy of phase transfer.

2. Materials and methods

2.1. Materials

N-Methyl-4-nitroaniline was obtained from Island Pyrochemical Industries, USA and used without further purification. Sodium chloride and calcium chloride were purchased from Sigma–Aldrich and Fischer Scientific, USA, respectively. Deionized water of resistivity >18 M Ω , obtained using US Filter Ion Exchanger, was used throughout the study. 1-Octanol and acetonitrile were obtained from Sigma–Aldrich, USA.

2.2. Solubility studies

The aqueous solubility of MNA was measured at temperatures of 298.15, 308.15 and 318.15 K by adding an excess amount of the solid compound (0.1 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 contents of the flasks were stirred at 150 rpm for about 36 h. Once thermodynamic equilibrium was established at a given temperature, three 2-mL samples were withdrawn with a syringe, centrifuged in a temperature-controlled centrifuge (Fisher Scientific, Marathon 21000R) for 10 min at 2000 rpm, and immediately diluted with water to avoid precipitation. To overcome MNA adsorption losses on the glassware during experimentation, all the glassware were soaked in MNA solution for about 24 h and rinsed with deionized water several times to remove excess MNA. To avoid re-crystallization of MNA, the hardware used for sampling and filtration was equilibrated at the test temperature. The concentration of MNA was determined spectrophotometrically.

2.3. Octanol–water partition coefficient

A stock solution of approximately 1 g/L of MNA in 1-octanol was prepared; this concentration is well below the solubility of MNA in octanol. The concentration of the solution was determined and was diluted to a desired concentration. The experiments were conducted in 40-mL vials with silicone septa at the temperatures of 298.15, 308.15 and 318.15 K. The two solvents (octanol and water) were mutually saturated at the temperature of the experiment before adding MNA dissolved in 1-octanol. To prevent loss of material due to volatilization, the vials were completely filled with the two-phase system. Three tests with different ratios of the two solvents in duplicate were conducted. Octanol and water were saturated with one another followed by the addition of MNA solution in octanol (92.5 mg/L). The volumetric ratios of octanol to water in the three tests were 0.60, 0.33 and 0.25. The vials were shaken in the shaker water bath (Julabo SW 23) at a desired temperature controlled to ± 0.5 K. The contents were then allowed to equilibrate at the set temperature bath for about 36 h to attain thermodynamic equilibrium. The vials were then centrifuged in a temperature controlled centrifuge (Fisher Scientific, Marathon

21000R) at 2000 rpm for about 10 min at the experimental temperature in order to achieve complete separation of the two phases. The aqueous phase from each vial was withdrawn using a 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 in order to prevent the entry of octanol into the needle. Once the syringe had an adequate quantity of the aqueous phase, it was quickly withdrawn and the needle was removed. This process of withdrawing the aqueous phase eliminated the risk of contamination with traces of 1-octanol. Both the phases were analyzed for MNA concentration. The octanol–water partition coefficient was obtained as the ratio of concentration of MNA in organic and aqueous phases.

2.4. Henry's law constant

The gas-purging bubble column system used for the experimental determination of Henry's law constant was similar to that of Mackay et al. [13]. Dilute aqueous solution of MNA was prepared in deionized water. High purity compressed air was bubbled through the aqueous solution containing MNA, which was stripped from the solution into the gas phase. The Henry's law constant was calculated from the rate of decrease in aqueous concentration of MNA. 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 temperature maintenance. Gas was introduced at the bottom of the column through a fritted metal disk. The liquid temperature was kept constant by a coolant flowing from a temperature-controlled water bath (Isotemp, 1013D) through the jacket surrounding the bubble column.

Experiments were conducted at 10 K intervals between 298 and 318 K. Vigorous mixing of the liquid in the bubble column occurred; random tests confirmed a uniform liquid concentration over the whole column height. The gas flow was controlled by calibrated mass flow meter (Gilmont Instruments, GF-1160). Volumetric gas flows were corrected to prevailing temperature and pressure. To prevent water evaporation from the purging column, the gas was humidified prior to entering the bubble column by passing the flow through a vessel containing deionized water. This vessel was immersed in the water bath at the same temperature as the bubble column. No change of liquid volume was noted, even after purging for several hours. The gas exited from the upper end of the column through a three-way stopcock and 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 the eluate. Coolant was circulated through the condenser from a Haake K10 cooling system. One milliliter of the sample was withdrawn at 1-h intervals through the tubing and the concentration in the liquid phase was measured using UV absorption spectroscopy. All precautions were taken to ensure loss-free transfer of each aliquot. At least three absorption measurements were taken for each sample. Recovery of MNA in the gas purge experiment was calculated from the mass balance between the initial aqueous concentration and the total amount of MNA collected in the cooled acetonitrile

plus the remainder in the water phase after the experiment. This recovery value was used to estimate the uncontrolled losses of MNA and to validate the measured K_H . The values of K_H were obtained following the procedure reported by Fu et al. [14].

In a dilute aqueous solution, Henry's law constant ($\text{m}^3 \text{Pa mol}^{-1}$) is represented as the ratio of solute partial pressure (p) in Pascal (Pa) and aqueous-phase solute concentration (C) in mol m^{-3} . Application of the mass balance on MNA at equilibrium between MNA in the liquid phase and vapor phase, leads to the following equation,

$$-V \frac{dC}{dt} = \frac{pU}{RT} = \frac{K_H UC}{RT} \quad (1)$$

where U is the gas flow rate ($\text{m}^3 \text{min}^{-1}$), V is the volume of the liquid (m^3), R is the gas constant ($8.314 \text{ m}^3 \text{Pa mol}^{-1} \text{K}^{-1}$), T is the system temperature (K), and t is the gas stripping time (min). Integration of the above equation from initial conditions ($t=0$ and $C=C_0$) gives,

$$\ln C = \ln C_0 - \left(\frac{K_H U}{VRT} \right) t \quad (2)$$

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 time of 12 h, the sample volume undergoes a change of 8%. Obviously, it is inappropriate to ignore this change in volume and assume volume to be constant, while integrating Eq. (1) from time = 0 to t . Instead, a modified approach is adopted as indicated by Fu et al. [14]. Since the volume of aqueous solution is constant between two sampling intervals, Eq. (1) is applied to each time interval separately. All the resulting equations on summation results the following equation,

$$\ln C_n = \ln C_0 - \left[\frac{K_H U \Delta t}{RT} \right] \sum \left(\frac{1}{V} \right)_n \quad (3)$$

where Δt represents the time difference between two successive sampling intervals and $\sum (1/V)_n$ is the sum of reciprocal volumes of solution left in the column at different time intervals, that is, $\sum (1/V)_n = (1/V_0 + 1/V_1 + \dots + 1/V_{n-2} + 1/V_{n-1})$, where $V_0, V_1, V_2, \dots, V_{n-2}$ and V_{n-1} represent the volume of solution left in the column at different sampling intervals. Eq. (3) demonstrates that a plot of $\ln C_n$ versus $\sum (1/V)_n$ gives a straight line with a slope of $((-K_H U \Delta t)/RT)$, from which K_H can be determined.

2.5. Analysis of MNA

The concentration of aqueous solutions of MNA was determined by measuring absorbance at 406.5 nm using a UV Visible Spectrophotometer (Thermo Supertonic Aqua mate). About 50 mg of MNA was weighed using a Sartorius Electronic Balance with an accuracy of ± 0.01 mg and dissolved in 1000 mL of deionized water. From this stock solution, appropriate concentrations were obtained by dilution. An aqueous solution of MNA obeys the Beer–Lambert's law up to 10 mg/L with regression

Table 1
Aqueous solubility of MNA in presence of NaCl and CaCl₂ salts at different temperatures

Medium	Solubility (mg/L)		
	298.15 K	308.15 K	318.15 K
Water	85.42 ± 0.85	111.51 ± 1.12	141.93 ± 1.42
1% NaCl	79.49 ± 0.80	96.65 ± 0.97	128.17 ± 1.28
5% NaCl	63.69 ± 0.64	75.51 ± 0.76	113.96 ± 1.14
10% NaCl	49.56 ± 0.50	58.22 ± 0.58	76.28 ± 0.76
1% CaCl ₂	82.82 ± 0.83	104.99 ± 1.05	134.81 ± 1.35
5% CaCl ₂	72.30 ± 0.72	95.03 ± 0.95	117.29 ± 1.17
10% CaCl ₂	60.62 ± 0.61	85.84 ± 0.86	101.28 ± 1.01

coefficient equal to 0.9997. Using this method the concentration of MNA could be determined with an accuracy of ±0.1 mg/L. The concentration of MNA in 1-octanol was determined using an HPLC (DIONEX ICS 3000) with UV detector (UVD170U). In this case the Beer–Lambert law is applicable up to 50 mg/L with regression coefficient value equal to 0.9985. The values were reproducible to ±0.1 mg/L.

3. Results and discussion

3.1. Solubility

The solubility of MNA in water and salt solutions of NaCl and CaCl₂ (1, 5, and 10%) at 298.15, 308.15, and 318.15 K are shown in Table 1. The variation of solubility of MNA with reciprocal temperatures at different salt concentrations is graphically represented in Figs. 1 and 2, respectively. As observed from the data and plots the solubility of MNA 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. Usually in an endothermic process, the added heat at higher temperatures helps to overcome the intermolecular forces that operate between solute molecules, thereby resulting in an increase in solubility with increased temperature. In a saturated solution, excess solid solute is in equilibrium with the dissolved solute and can be considered thermodynamically like any other equilibrium process. The most generally used method of determining the effect of temperature on solubility is to calculate the

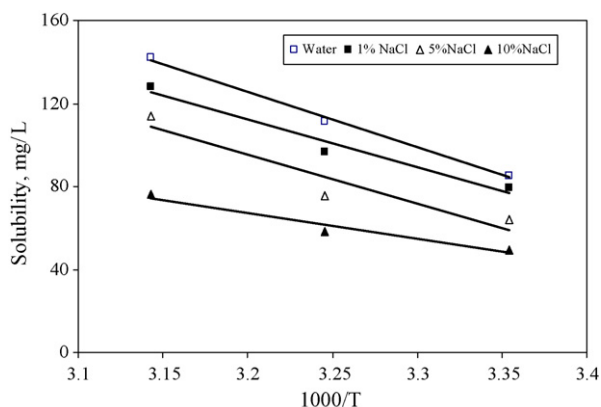


Fig. 1. Solubility of MNA versus reciprocal temperature in the presence of NaCl.

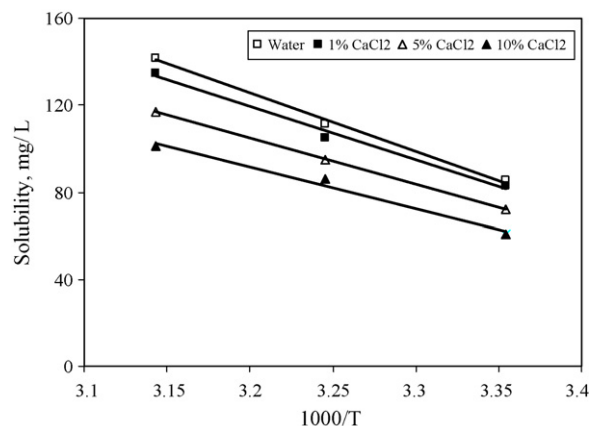


Fig. 2. Solubility of MNA versus reciprocal temperature in the presence of CaCl₂.

value of the equilibrium constant on the basis of the solubility at different temperatures. An alternative approach is based on the estimation of the enthalpy at equilibrium, which can be considered as independent of temperature over the studied temperature range. Assuming that the saturated solution of MNA has an ideal behavior (which is justified in solutions of limited solubility of hydrophobic materials [15]), the influence of temperature on the solubility of MNA can be quantitatively described by the Van't Hoff equation as,

$$\log S_w = \frac{-\Delta_{\text{sol}}H^\circ}{RT} + b \quad (4)$$

The enthalpy of fusion of MNA, $\Delta_{\text{sol}}H^\circ$, has been determined by plotting $\log S_w$ versus $1/T$ and found to be 20.02 kJ mol⁻¹. No experimental data are available in the literature for comparison. However, the value reported here is in good agreement with enthalpy of fusion (18.85 kJ/mol) predicted by Toghiani et al. [16] on the basis of chemical structure.

The solubility of MNA decreases gradually with the increase in concentration of sodium chloride and calcium chloride at all three temperatures studied. This may be attributed to ions in solution binding tightly to several water molecules in hydration shells [17]. This process (electrostriction) results in a reduction of the volume of the aqueous solution. A smaller number of water molecules are available for cavity formation, therefore a fewer number of organic molecules are accommodated in solution, consequently resulting in a decrease in their solubility. Similar decreases in aqueous solubility of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans 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,

$$\log \left(\frac{S_w}{S_s} \right) = K_s C \quad (5)$$

where S_w is the solubility of MNA in pure water, S_s is the solubility in presence of a salt, K_s is the Setschenow constant, and C is the concentration of the salt (mol/L). $\log (S_0/S_s)$ versus concentration plots are shown in Figs. 3 and 4. The values of Setschenow constants, obtained from experimental data, are

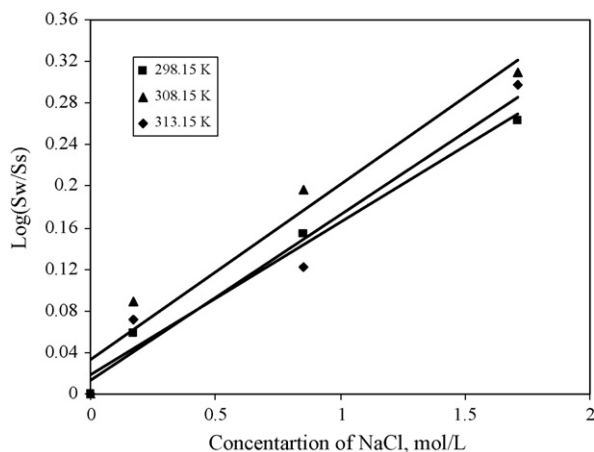
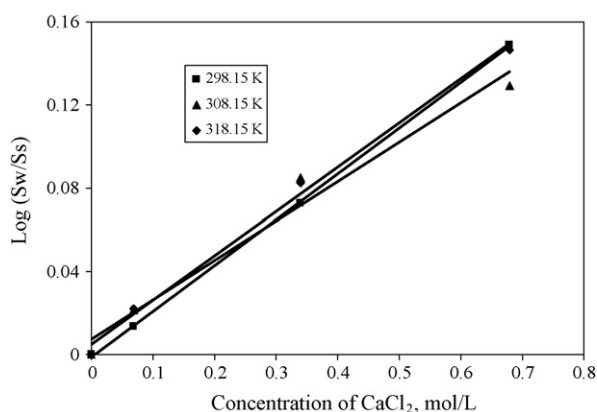


Fig. 3. Setschenow plots for variation of solubility of MNA in presence of NaCl.

Fig. 4. Setschenow plots for variation of solubility of MNA in presence of CaCl₂.

included in Table 2. The positive value of K_s ($S_w > S_s$) indicates the salting-out effect, whereas the negative K_s ($S_w < S_s$) indicates a salting-in effect. The values of K_s are positive and fairly constant over the temperature range studied. The linear relationship between $\log(S_w/S_s)$ and salt concentration has been observed in several investigations over a wide concentration range [20]. The observed salting-out effect is stronger in the presence of calcium chloride in the aqueous phase compared to sodium chloride corresponding to the same concentration. This is in agreement with the observations of Koga et al. [21], who found that the salting-out tendency is significantly higher with divalent salt in the aqueous phase compared to monovalent salt at equal concentrations. This behavior may be attributed to the higher ionic strength of the divalent salts compared to monovalent salts at the same concentration.

Table 2
Constants of Setschenow equation for MNA solubility at different temperatures

Temperature (K)	Sodium chloride		Calcium chloride	
	K_s	R^2	K_s	R^2
298.15	0.1368	0.9980	0.2195	0.9998
308.15	0.1580	0.9807	0.1884	0.9733
318.15	0.1490	0.9617	0.2121	0.9945

Table 3
Octanol–water partition coefficients ($\log K_{ow}$) for MNA at different temperatures

Temperature (K)	$\log K_{ow}$
298.15	2.1028 ± 0.0209
308.15	1.9846 ± 0.0305
318.15	1.9377 ± 0.0146

3.2. Octanol–water partition coefficient

The experimental values of octanol–water partition coefficient ($\log K_{ow}$) of MNA at 298.15, 308.15, and 328.15 K are given in Table 3 and variation of $\log K_{ow}$ with reciprocal temperature is shown in Fig. 5. The partition coefficient represents equilibrium between the compositions of a component in two liquids and hence, from the Van't Hoff isotherm, the free energy of transfer from water to octanol is given by,

$$\Delta G = -2.303RT \log K_{ow} \quad (6)$$

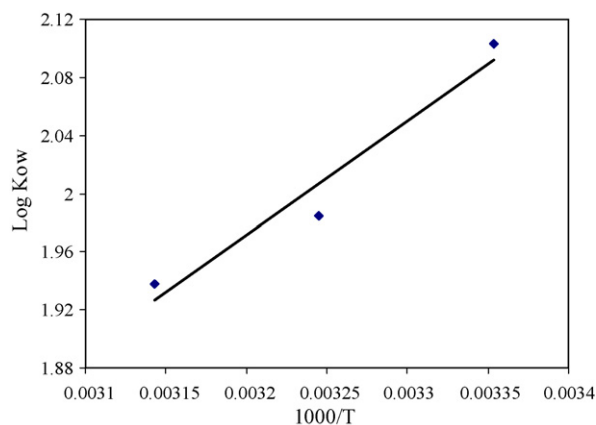
However, the Gibbs free energy is the difference between the enthalpy (ΔH) and the entropy (ΔS) of transfer,

$$\Delta G = \Delta H - T \Delta S \quad (7)$$

where T is the temperature (K). It is thus 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, which involves plotting the $\log K_{ow}$ of a substance versus reciprocal temperatures, and obtaining from the Van't Hoff isochors (Eq. (8)) the enthalpy and entropy of partitioning.

$$\log K_{ow} = \frac{-\Delta H}{2.303RT} + \frac{\Delta S}{2.303R} \quad (8)$$

The method relies on the enthalpy and entropy of partitioning being constant over the temperature range studied. The Gibbs free energy (at 298.15 K), enthalpy and entropy of partitioning of MNA in the water–octanol are $-11.95 \text{ kJ mol}^{-1}$, $-15.06 \text{ kJ mol}^{-1}$, and $-10.44 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively.

Fig. 5. Octanol–water partition coefficient ($\log K_{ow}$) of MNA versus reciprocal temperature.

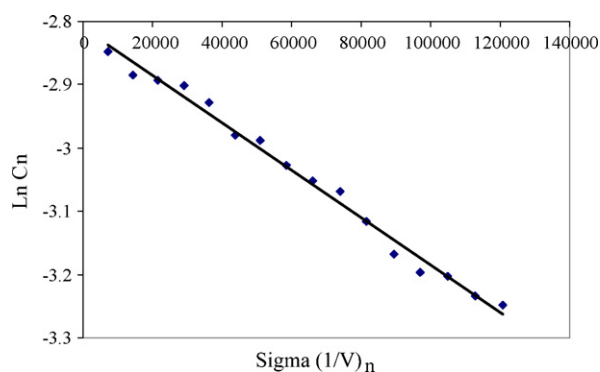


Fig. 6. Typical plot of $\ln C$ versus $\Sigma (I/V)_n$ for MNA at 298.15 K.

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

$$\log K_{ow} = -\log S_w - \log \bar{V}_0^* \quad (9)$$

where \bar{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,

$$\log K_{ow} = -0.9859 \log S_w + 1.9453 \quad (10)$$

This equation is capable of predicting $\log K_{ow}$ values of MNA with an average absolute deviation of 0.2371 with $R^2 = 0.9999$.

3.3. Henry's law constant

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

$$K_H = \frac{p_g}{C_w} \quad (11)$$

where p_g is the gas-phase partial pressure and C_w is the aqueous concentration in units of mass of MNA per volume of water, or as the dimensionless Henry's law constant ($K_{H'}$),

$$K_{H'} = \frac{C_g}{C_w} \quad (12)$$

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

$$K_{H'} = \frac{K_H}{RT} \quad (13)$$

where R is the gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$) and T is the absolute temperature. The experimental values of Henry's law constants for MNA obtained from the slopes of typical lines as shown in Fig. 6 are given in Table 4. The temperature dependence of K_H is described by the equation,

$$-RT \ln K_{H'} = \Delta H_H - T \Delta S_H \quad (14)$$

Table 4
Henry law constants for MNA at different temperatures

Temperature (K)	K_H ($\text{M}^3 \text{ Pa mol}^{-1}$)	$K_{H'}$ (dimensionless g/aq)
298.15	0.6100	2.46×10^{-4}
308.15	0.5566	2.25×10^{-4}
318.15	0.5160	2.08×10^{-4}

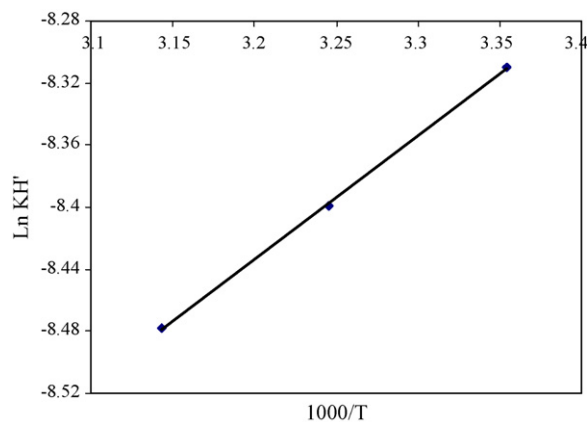


Fig. 7. $\ln K_{H'}$ of MNA versus reciprocal temperature.

where ΔH_H and ΔS_H are the enthalpy and entropy of the phase transfer from the dissolved phase to the gas phase. Solving Eq. (12) for $\ln K_{H'}$ gives the Gibbs–Helmholtz equation,

$$\ln K_{H'} = \frac{-\Delta H_H}{RT} + \frac{\Delta S_H}{R} \quad (15)$$

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 or $K_{H'}$ experimentally at different temperatures and plotting $\ln K_{H'}$ versus $1/T$, ΔH_H and ΔS_H are determined from the slope and intercept, respectively. The enthalpy and entropy for gas to liquid transfer of MNA are determined by plotting $\ln K_{H'}$ versus $1/T$ (Fig. 7), assuming that these quantities are invariant over the considered temperature interval. The good linear fit with regression coefficient of 0.9997 confirms that this assumption is true. The slope and intercept of the fitted line yield values for ΔH_H and ΔS_H , respectively. The values of ΔH_H and ΔS_H are $-6.62 \text{ kJ mol}^{-1}$ and $-91.30 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. On the basis of the measured temperature dependence, the following expression represents the Henry's law coefficient of MNA between 298 and 318 K,

$$\ln K_{H'} = \frac{786.08}{T} - 10.981 \quad (16)$$

4. Conclusions

Aqueous solubility, octanol–water partition coefficient, and Henry's law constant have been determined experimentally for MNA in the temperature range of 298.15–318.15 K. The effect of temperature and electrolytes on aqueous solubility of MNA was studied. The solubility increases with increasing temperature and decreases with increasing 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. These data enable prediction of the concentrations of MNA to be expected in wastewater and air from munitions facilities. Projectiles will normally be loaded by melt pour techniques, and the facilities are cleaned with hot water or steam. Thus MNA would be at a higher concentration than expected at the hot water or steam temperatures due to the temperature dependence of the physical parameters studied.

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