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Experimental determination of solvent-water partition coefficients and Abraham parameters for munition constituents

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HIGHLIGHTS

- Physical-chemical properties of munition constituents were investigated.
- Partition coefficients in various solvent-water systems were determined.
- The Abraham solute parameters were determined from these experiments.
- Large errors were found for predictions using ABSOLV estimated solute parameters.
- Predictions using solute parameters from this work have smaller errors.

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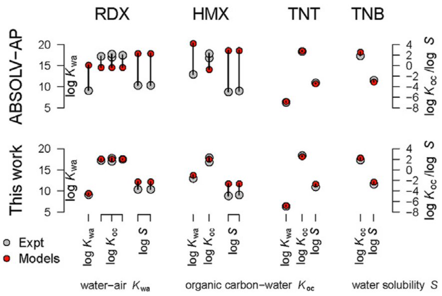
GRAPHICAL ABSTRACT



ABSTRACT

There is concern about the environmental fate and effects of munition constituents (MCs). Polyparameter linear free energy relationships (pp-LFERs) that employ Abraham solute parameters can aid in evaluating the risk of MCs to the environment. However, poor predictions using pp-LFERs and ABSOLV estimated Abraham solute parameters are found for some key physico-chemical properties. In this work, the Abraham solute parameters are determined using experimental partition coefficients in various solvent-water systems. The compounds investigated include hexahydro-1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX), hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX), hexahydro-1,3-dinitroso-5- nitro-1,3,5-triazine (DNX), 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitrobenzene (TNB), and 4-nitroanisole. The solvents in the solvent-water systems are hexane, dichloromethane, trichloromethane, octanol, and toluene. The only available reported solvent-water partition coefficients are for octanol-water for some of the investigated compounds and they are in good agreement with the experimental measurements from this study. Solvent-water partition coefficients fitted using experimentally derived solute parameters from this study have significantly smaller root mean square errors (RMSE = 0.38) than predictions using ABSOLV estimated solute parameters (RMSE = 3.56) for the investigated compounds. Additionally, the predictions for various physico-chemical properties using the experimentally derived solute parameters agree with available literature reported values with prediction errors within 0.79 log units except for water solubility of RDX and HMX with errors of 1.48 and 2.16 log units respectively. However, predictions using ABSOLV estimated solute parameters have larger prediction errors of up to 7.68 log units. This large discrepancy is

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probably due to the missing $-R_2N-NO_2$ and $-R_2N-NO_2$ functional groups in the ABSOLV fragment database.

1. Introduction

The US Department of Defense reported that 12,000 sites throughout the United States were contaminated by munition constituents (MCs) (Halasz et al., 2002). Concentrations in soil of hexahydro-1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), 2,4,6-trinitrotoluene (TNT), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) in some sites exceeded 3000 mg kg^{-1}, 87000 mg kg^{-1}, and 3000 mg kg^{-1}, respectively (Simini et al., 1995). Due to improper handling and disposal techniques, these MCs and their degradation products can enter into the environment, posing risks to a variety of organisms including microorganisms (Klausmeier et al., 1973; Smock et al., 1976; Spanggord et al., 1982; Won et al., 1976), algae (Smock et al., 1976), plants (Palazzo and Leggett, 1986), fish (Smock et al., 1976), and humans (Yinon, 1990).

In addition to MCs, metabolites, degradation products, or industrial by-products of MCs also pose an environmental risk. Hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX), hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX), and hexahydro-1,3-dinitroso-5- nitro-1,3,5-triazine (DNX), the degradation products of RDX, have been detected in soil and groundwater (Beller and Tiemeier, 2002; Moshe et al., 2010). It has been found that these degradation products are toxic to organisms (Zhang et al., 2006). 1,3,5-trinitrobenzene (TNB) is a high explosive used for mining and military application and is a degradation product of TNT and a by-product of TNT manufacturing (Reddy and Williams, 2015). With a structure similar to TNT, TNB is suggested to pose similar health problems and environmental risks (Reddy and Williams, 2015). The compound 4-nitroanisole (4NAN) was selected in this study because it is structurally similar to the investigated MCs. The compounds studied are listed in Table 1, together with their physico-chemical properties and chemical structures. Among them, RDX and HMX are cyclic nitramines with $-R_2N-NO_2$ structure (Sunahara et al., 2009); MNX, DNX, and TNX have R_2N-NO and/or R_2N-NO_2 and will be referred to as cyclic nitrosamines; TNT, TNB, and 4NAN are nitroaromatics with $Ar-NO_2$ structure (Sunahara et al., 2009).

In order to assess the fate of MCs and their degradation products in the environment, physico-chemical properties are required, such as vapor pressure, water solubility, and particularly partition coefficients. The partition coefficient K is defined as the ratio of the concentrations of a compound in a two-immiscible-phase system at equilibrium (Schwarzenbach et al., 2003):

$$K_{i12} = \frac{C_{i1}}{C_{i2}} \tag{1}$$

where C_{i1} and C_{i2} denote the equilibrium concentrations of substance i in phase 1 and in phase 2, respectively. K_{i12} denotes the partition coefficient of the substance i.

1.1. Polyparameter linear free energy relationships (pp-LFERs)

Experimentally measured physico-chemical properties are available for only 1% of the approximately 70,000 industrial compounds compiled in EPA's Toxic Substances Control Act (TSCA) inventory (Karickhoff et al., 1989). Many attempts have been made to develop predictive models since it is not practical to measure all the required physico-chemical properties for all existing and newly emerging environmental contaminants. Among the available models, the polyparameter linear free energy relationships (pp-LFERs), such as the Abraham solvation model, have been proposed to predict partitioning in a broad variety of environmental systems and chemicals (Abraham, 1993a; Endo and Goss, 2014). This model evaluates the logarithm of the partition coefficient (K) between two phases using the equation:

$$\log K = c + eE + sS + aA + bB + vV \tag{2}$$

where the lower case parameters pertain to the two phases, e.g. the solvent-water system, and the upper case parameters pertain to the solute. The model assumes that the Gibbs free energy contributions to the partitioning process are separable and additive (Abraham et al., 1988): eE describes the dispersion van der Waals interaction, sS describes the dipole-dipole and dipole-induced dipole interactions, aA and bB measure the hydrogen-bond interactions, and vV describes the energy required for cavity formations. The pp-LFER model assumes that the effects of the solute are independent from those of the solvent (Endo and Goss, 2014). That is, a set of solute parameters for a given substance is considered constant, regardless of the solvent, and vice versa. The upper case letters E, S, A, B, and V denote the solute's excess molar refraction, dipolarity/polarizability, effective hydrogen-bond acidity (i.e. the ability of the solute to donate a hydrogen bond), effective hydrogen-bond basicity (i.e. the ability of the solute to accept a hydrogen bond), and molar volume, respectively. The lowercase letters c, e, s, a, b, v are solvent/system parameters, which represent the complimentary effects of the solvent phase, relative to the water phase.

Over the years, Abraham and co-workers have successfully correlated the solute parameters to more than 400 properties or processes (Endo et al., 2015). The properties include partitioning between solvent-solvent, solvent-water, gas-solvent, and aqueous solubility; partitioning to bio-materials of plant, protein, lipid, and blood; sorption to organic carbon, mineral surfaces, and coal tar; narcotic toxicity, skin permeation, eye irritation, nasal pungency, and odor thresholds. Once the solute parameters are obtained, the properties or processes of the solute can be predicted.

A common method to estimate Abraham solute parameters is the ABSOLV prediction module, which is a fragment based method (ACD/Percepta, 2015). The estimations of each solute parameter are based on the Platts-type fragment descriptors (Platts et al., 1999). A set of 81 atom and functional group fragments is used to estimate the E, S, and B parameters and a separate set of 51 fragments for the A parameter (Platts et al., 1999). The coefficients of the atom/fragments have been further optimized by performing statistical analysis on available experimental partitioning data and experimentally-based solute parameters (ACD/Percepta, 2015). The V parameter is calculated as McGowan characteristic volume (Abraham and McGowan, 1987). The reported root mean square errors (RMSE) of the ABSOLV parameters are 0.12, 0.22, 0.07, 0.15, and 0.01 for E, S, A, B, and V respectively (ACD/Percepta, 2015). Stenzel et al. (2014) performed a rigorous validation of ABSOLV for a diverse set of complex multifunctional compounds in various partition systems. They concluded that the overall