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Evaluation of the dependence of aqueous solubility of nitro compounds on temperature and salinity: A COSMO-RS simulation

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ABSTRACT

The solubility in pure and saline water at various temperatures was calculated for selected nitro compounds (nitrobenzene, 1,3,5-trinitrobenzene, 2-nitrotoluene, 3-nitrotoluene, 4-nitrotoluene, 2,4-dinitrotoluene, 2,6-dinitrotoluene, 2,3-dinitrotoluene, 3,4-dinitrotoluene, 2,4,6-trinitrotoluene) using the Conductor-like Screening model for Real Solvents (COSMO-RS). The results obtained were compared with experimental values. The COSMO-RS predictions have shown high accuracy in reproducing the trends of aqueous solubilities for both temperature and salinity. The proposed methodology was then applied to predict the aqueous solubilities of 19 nitro compounds in the temperature range of 5–50 °C in saline solutions. The salting-out parameters of the Setschenow equation were also calculated. The predicted salting-out parameters were overestimated when compared to the measured values, but these parameters can still be used for qualitative estimation of the trends.

1. Introduction

Wastes from high-energetic compounds have been known to impact the aquatic environment during manufacturing, storage, transportation, and utilization of munitions, leading to a potential hazard for humans and the ecosystem (Feuer and Nielsen, 1990; Neilson and Allard, 2008). The spontaneous transformation of hazardous chemicals, including explosives, to less hazardous forms under environmental conditions, as well as the efficiency of directed in-solution treatments is determined, to a large degree, by the solubility of these compounds in water. For many nitroaromatic compounds, including energetic materials, little is known about relevant physical and chemical properties under ambient conditions that can control their environmental fate. Furthermore, most available research data on the chemical, physical or biologically-powered transformation of explosives has focused on terrestrial and freshwater systems (Gorontzy et al., 1994; Lewandowski and DeFilippi, 1998; Hawari et al., 2000, 2004; Spain et al., 2000; Rodgers and Bunce, 2001; Garcia Einschlag et al., 2002; Liou et al., 2003; Qasim et al., 2005; Al Momani, 2006; Davis et al., 2006). Only a few studies investigated the fate of explosives in marine systems (Nipper et al., 2004; Zhao et al., 2004; Yang et al., 2008). However, the information on the solubility of contaminants in seawater systems under various temperature and salinity regimes is of high importance to develop effective methods of their remediation in the global framework. To our knowledge, the only available research where the solubility of nitroaromatic compounds in salt solutions has been measured is in recent studies by Luning Prak and O'Sullivan (2006, 2007, 2009) and Luning Prak and Morgan (2008). The aqueous solubility of most organic compounds decreases when inorganic salts are present in-solution; this process is commonly called "salting-out" effect (see Xie et al. (1997) for a general review, Luning Prak and O'Sullivan (2006, 2007, 2009) and Luning Prak and Morgan (2008) for the data on nitroaromatics). This effect can be quantitatively represented by the Setschenow equation, which relates organic compound solubility to solution ionic strength, I (mol L^{-1}) (Luning Prak and O'Sullivan, 2006)

$$Log\left(\frac{S_w}{S}\right) = K'_S I \quad (1)$$

where S_w is the solubility of a compound in pure water (mg L^{-1}); S is the solubility in the salt solution (mg L^{-1}); and K'_S is a salting-out coefficient (L mol^{-1}). The ionic strength, I, is defined by

$$I = \frac{1}{2}\sum_i C_i Z_i^2 \quad (2)$$

where C_i is the concentration of ion i (mol L^{-1}) and Z_i is the charge on ion i.

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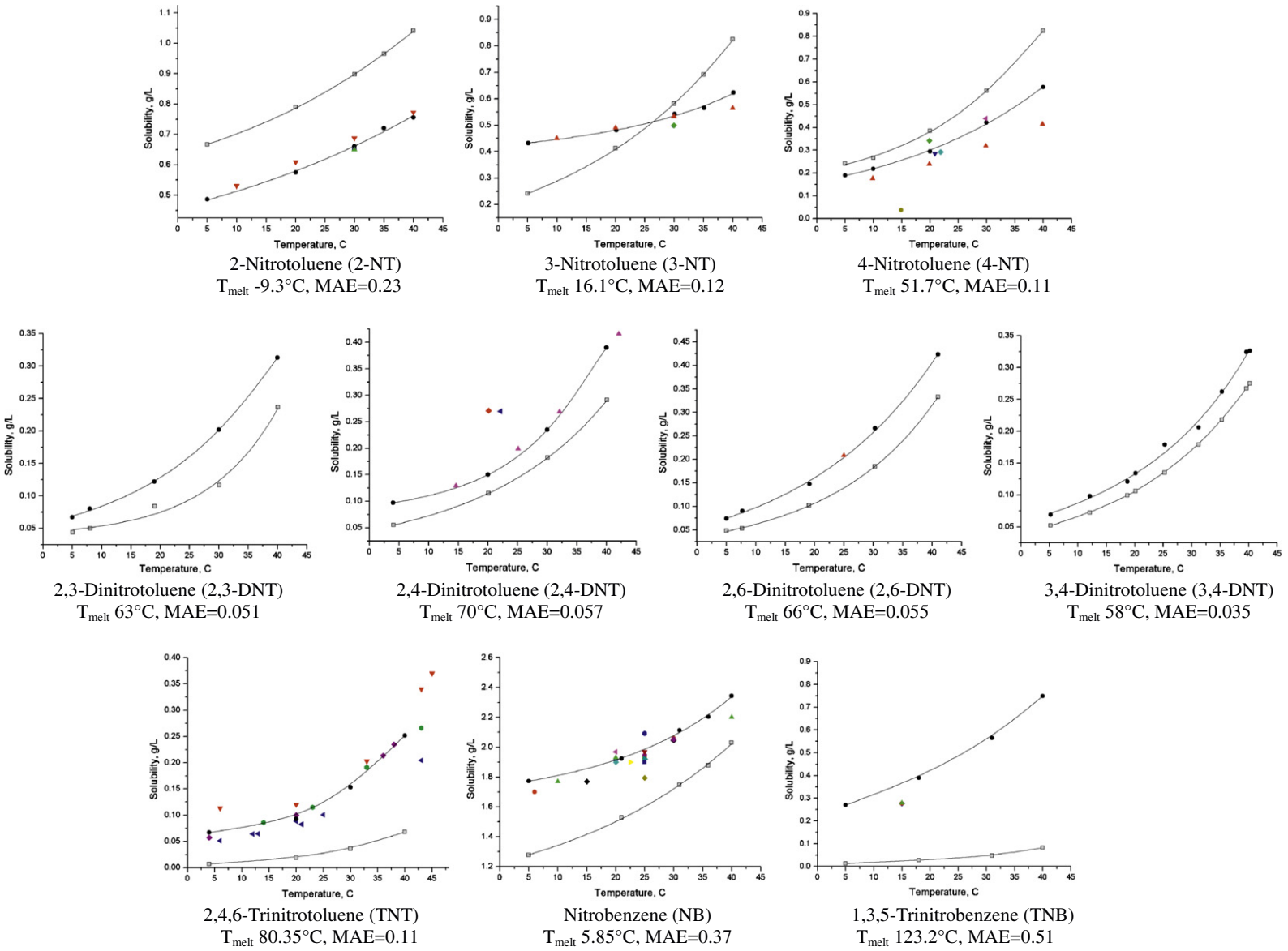

Fig. 1. Theoretically predicted (grey squares) vs. experimentally measured (black circles) by Luning Prak and O'Sullivan (2006, 2007, 2009) and Luning Prak and Morgan (2008) and earlier experimental data (remaining symbols) collected by Yalkowsky and He (2003) on aqueous solubilities of nitroaromatic compounds at various temperatures. Numerical data with corresponding references for all experimental data are given in Supplementary materials (Tables S1–S5). Melting point temperatures from PhysProp database and mean absolute errors (MAE, g L^{-1}) of theoretical predictions are shown for each solute.