Full Paper

Predicting Solubility of Military, Homemade, and Green Explosives in Pure and Saline Water using COSMO-RS

Sufian Alnemrat[a] and Joseph P. Hooper*[a]

Abstract: The conductor-like screening model for real solvents (COSMO-RS) has previously been shown to give accurate aqueous solubilities for a range of organic compounds using only quantum chemical simulation data. Application of this method for solid organic explosives, however, faces two difficulties; it requires correction for the free energy of fusion (a generally unknown quantity for these compounds) and it shows considerable error for common explosive classes such as nitramines. Herein we introduce a correction factor for COSMO-RS that is applicable to a wide range of explosives, and requires no data beyond a quantum chemistry calculation. This modification allows COSMO-RS to be used as a predictive tool for new proposed explosives or for systems lacking experimental data. We use this method to predict the temperature-dependent solubility of solid explosives in pure and saline water to an average accuracy of approximately 0.25 log units at ambient temperature. Setschenow (salting-out) coefficients predicted by this method show considerable improvement over previous COSMO-RS results, but are still slightly overestimated compared to the limited experimental data available. We apply this method to a range of military, homemade, and "green" explosives that lack experimental seawater solubility data, an important property for environmental fate and transport modeling.

Keywords: Solubility · Explosives · Salting-out coefficient · COSMO-RS

1 Introduction

The physical and chemical properties of explosives in soil and water are important concerns for both environmental contamination and in explosive detection. Contamination from military explosives such as TNT, RDX, and their by-products are found on a number of military ranges, many of which are adjacent to fresh or saltwater environments [1–9]. There is increasing concern with the environmental fate and transport of contaminants from underwater munitions, particularly in shallow water. The relatively low solubility of explosive materials such as TNT (115 mg L^{-1}) and RDX (59 mg L^{-1}) in water maintains a continuous release of contaminant to the surrounding environment [10–16]. The aqueous solubility is also important for explosive detection; a primary transport mechanism for vapors from buried explosives or landmines is upward advection due to evaporation of soil water [10]. Accurate solubility data, including the effects of inorganic salts in saline environments, are needed to understand the fate, extraction, and detection of these compounds [1, 10, 13, 17–21].

The experimental data on solubility of explosives is limited to a few common compounds and very little data exists on seawater solubility save for the work of Luning-Prak and O'Sullivan on TNT and other nitroaromatics [22]. To address this lack of data, previous work by Kholod et al. (2009) and Toghiani et al. (2008) used the conductor-like screening model for real solvents (COSMO-RS) to estimate water solubility for several common explosive compounds [23, 24].

COSMO-RS combines a continuum solvation model with data from standard quantum chemistry calculation; see references [25–27] for detailed information on the methodology. While the aqueous solubility predictions by COSMO-RS are quite accurate for certain explosives (especially nitroaromatics), there are difficulties with this approach. First, for solid phase solubilities one must correct the COSMO-RS predictions using a free energy of fusion term, which is typically unknown and must be estimated with experimental data or an empirical relationship. Second, the COSMO-RS method performs very poorly for certain compounds, with solubility errors on the order of three to four orders of magnitude for important nitramines such as RDX and HMX. Finally, Toghiani et al. showed that even with a correction for the free energy of fusion from experimental data, the solubility in saline solutions using COSMO-RS is problematic [24]. Setschenow (salting-out) coefficients were found to be significantly overestimated compared to experimental data on several nitroar-

[a] S. Alnemrat, J. P. Hooper
Department of Physics
Naval Postgraduate School
Monterey, CA 93943, USA
*e-mail: jphooper@nps.edu

omatics [28]; the seawater solubility varies exponentially with the Setschenow coefficient, magnifying any errors in the prediction of this term. It is now standard to explore new potential explosives and propellants using quantum chemistry methods before synthesis efforts even begin, and a method that can reasonably estimate pure and saline water solubility without experimental data or even knowledge of the crystalline packing is highly desirable [22, 23, 27].

In this work, we present a simple correction term for COSMO-RS that addresses these issues, bringing the accuracy for aqueous solubility of a range of military and homemade explosives down to approximately 0.25 log units. The correction term requires only data from a standard quantum chemistry calculation and a COSMO-RS analysis. Salting-out coefficients are improved considerably from previous results, and though still slightly overestimated they fall close to the range of experimental scatter in the limited data on nitroaromatics that is available. We use this modified approach to explore the variation of explosives' solubilities with temperature and ionic strength, covering a wide range of energetic materials from volatile homemade explosives to recent high-nitrogen "green" propellants.

2 Theoretical Methodolody

The COSMO-RS method extends the COSMO continuum solvation model, which places a solute molecule inside a screening cavity and embeds this within an ideal conductor representing the solvent (in this case, pure and saline water). COSMO-RS uses the same molecular cavity and its ideal screening charges to then construct a statistical thermodynamics theory of interacting screening surface charges between solute and solvent molecules in a liquid. Hydrogen bonding and van der Waals terms are added to the energy of these interacting surface charges, and used to construct a partition function for the molecule in solution. References [25, 26, 29] contain a full description of the methodology. All density functional theory calculations used for solvation analysis in this work were performed using Turbomole with the Becke-Perdew (BP) functional [30, 31] and triple zeta valence and polarization (TZVP) [32] basis sets are for all atoms. COSMO-RS analysis was done using the COSMOtherm code (version C30_1201).

COSMO-RS is properly a theory for liquids and, for temperatures below a compounds melting point; it computes the properties of a supercooled disordered liquid. COSMO-RS allows for the estimation of solubility by calculating the chemical potentials and energies of a solvent and pure solute liquid phase. The solubility of solute X in a solution can then be computed from these chemical potentials using the relation:

$$\log X = \frac{\mu_{\text{self}} - \mu_{\text{solvent}}}{RT \ \ln(10)} \tag{1}$$

where μ_{self} and μ_{solvent} are the chemical potential of the solute compound in its pure liquid state and in solvent respectively, X is the solubility as a mole fraction, and T is the temperature. For solid compounds, a correction term for the free energy of fusion ΔG^{fus} must be added to the above equation. The solubility of solutes in their solid state can then be calculated according to the equation:

$$\log X = \frac{\mu_{\text{self}} - \mu_{\text{solvent}} - \max(0, \Delta G^{\text{fus}})}{RT \ \ln(10)} \tag{2}$$

Finally, the normalized mass-based solubility of a compound i in a mixture of water and ions (in this case, Na$^+$ and Cl$^-$) can be written as:

$$S^{\text{sol}} \ (\text{g/g}) = X_i^{\text{sol}*} \frac{MW_i}{\{X_i^{\text{sol}}*MW_i + (1 - X_i^{\text{sol}})*MW_{\text{solvent}}\}} \tag{3}$$

where MW_i denotes the molecular weight of solute i. The solvent molecular weight includes contributions from salt where appropriate, though this term is small for all salinities considered.

Herein we develop a quantitative structure-property relationship (QSPR) to estimate the term ΔG^{fus} based on a comparison of the experimental water solubilities at a specific reference temperature and the liquid-phase COSMO-RS value at the same conditions. The discrepancy between these is used to estimate the correction factor ΔG^{fus}, though with this method other corrections besides the free energy of fusion alone may be incorporated (for example, corrections to the hydrogen bonding or van der Waals energies in solution). The temperature-dependent solubility in pure water of eighteen solid explosives and byproducts were drawn from a number of experimental studies and used to create a QSPR descriptor based on molecular volume, molecular flexibility, and the chemical potentials of the explosive compounds in solution and in their liquid state. Similar descriptors were also used by Klamt and co-authors to treat the solubility of solid phase drugs and pesticides, though their specific parameters from these studies were found to be unsuitable for explosive materials [33, 34]. The general regression equation for the free energy of fusion correction factor (in kJ mol^{-1}) for explosive compounds used in our work is given by

$$\Delta G^{\text{fus}} = 19.3 \ V - 0.41\mu_{\text{solvent}} + 0.41\mu_{\text{self}} - 0.081N \tag{4}$$

where V is the cavity volume of the solute molecule which is measured by a van der Waals molecular surface in units of Å^3, the chemical potentials (in kJ mol^{-1}) are derived from COSMO-RS as discussed above and are taken at the reference temperature, and N is either the number of aromatic ring atoms as a measure of molecular rigidity or the number of rotatable bonds for non-aromatic systems. Rotatable bonds are defined as the number of single bonds

that are non-cyclic, non-terminal, and non-ring bonds. Bonds attached to hydrogen or C—N amide bonds are considered non-rotatable. Representative values of *V* and *N* for several explosive compounds are given in the Supporting Information. The correction term should in general be temperature-dependent, but proper accounting for this would require (for the free energy of fusion, at least) knowledge of the melt temperature. For estimates of new explosive molecules, this would require an additional QSPR. As the temperature range of interest for environmental fate and transport is relatively limited and the correction factor is relatively small, we assume it is temperature independent.

The calculated values of ΔG^{fus} were then used to predict the solubility of a large number of explosive compounds as a function of ionic strength and temperature, including 26 compounds not within the training set. Most organic compounds show decreased solubility (a salting-out effect) with increasing ionic strength *I*, defined as:

$$I = \tfrac{1}{2} \sum_i C_i Z_i^2 \qquad (5)$$

where C_i is the concentration of ion type *i* and Z_i is the oxidation number or valance of ion *i*. The effect of ions on the aqueous solubility is often quantified using the empirical Setschenow relation,

$$\log \left(\frac{S^{water}}{S^{ion}} \right) = K_s I \qquad (6)$$

where S^{water} is the solubility in pure water, S^{ion} is the solubility in a salt solution, *I* is the ionic strength of ions in water in units of mol L^{-1}, and K_s is the Setschenow or salting-out coefficient in unit of L mol^{-1} and may vary with ionic strength. All computational results reported herein are for water solutions with only Na^+ and Cl^- ions; the small concentrations of other relevant ions found experimentally in seawater do not have a significant effect on the calculated results. The COSMO-RS method incorporates the effect of salt in the following way. The chemical potentials of the salt anion and cation are computed at infinite dilution in the solvent, and then used to construct a new overall $\mu_{solvent}$ for the combined water, Na^+, and Cl^- system at a given salinity. The solubility of a solid explosive is then calculated in the normal way from Equation (1), including the addition of the ΔG^{fus} term derived from our QSPR. Finally, by calculating the explosive solubilities at a range of salt concentrations, we can determine the salting-out/in coefficients according to Equation (6).

Supporting Information (see footnote on the first page of this article): Representative values of *V* and *N* for several explosive compounds.

3 Results and Discussion

In agreement with previous work, the solubility calculations using an unmodified COSMO-RS method show good agreement with available experimental data for certain explosive compounds, including some nitroaromatics such as 2,4,6-trinitrotoluene (TNT), nitrobenzene and 4-aminodinitrotoluene (4-ADNT). However, direct COSMO-RS predictions show a large discrepancy (often 2 LU or more) for many other important explosive compounds, including HMX, CL-20, and triaminotrinitrobenzene (TATB). Thus while the average COSMO-RS error over many known explosive compounds is reasonably low, it is highly desirable to eliminate these strong discrepancies and allow this solvation model to be used as a general predictive tool for a range of energetic materials.

Table 1 shows experimental water solubilities at ambient temperature (log S^{exp}) compared with the unscaled COSMO-RS values (log S^{COSMO}) as well as those corrected for the free energy of fusion and other factors (log S^{QSPR}) using the QSPR given in Equation (4). The list in Table 1 covers a range of different classes of explosives, including nitroaromatics, nitramines, nitrate esters, and degradation products. We note that several of these compounds are liquids at ambient conditions [denoted with (l) next to the name in Table 1]; the liquids have the smallest correction factor, but do still benefit from this term since our method of correction includes more than simply a free energy of fusion.

An accuracy of 0.25 LU in the standard deviation is achieved by incorporating the free energy correction, compared to the 0.75 LU accuracy from direct COSMO-RS calculations (which we again note are for a supercooled liquid). More importantly, results for problematic compounds such as secondary nitramine high explosives are greatly improved (see Figure S1 in the Supporting Information for a graphical depiction of the calculated and experimental solubility data in Table 1). Errors are brought down close to the typical scatter in experimental measurements (often 0.1 to 0.4 LU for those explosives with multiple experimental reports). The pure-water solubility calculations for six representative explosives from this Table, corrected using the above regression equation, are shown in Figure 1. Solubilities for TNT and 2,4-DNT, the most widely studied compounds experimentally, are underpredicted by this approach, but most of the highly problematic compounds such as RDX and CL-20 are improved by orders of magnitude with the modified method.

While the temperature dependence of the solubility is generally in good agreement with the limited experimental data, there are exceptions. As can be seen in Figure 1, the temperature variation of the solubility of 2,4-DNT and 2,6-DNT is in poor agreement with experiment compared to many of the other explosive compounds. While there are likely multiple reasons for this, one important factor is that we have ignored the temperature dependence of the correction term ΔG^{fus}. As discussed above, this would likely re-

Table 1. Correction factors (ΔG^{fus}), pure water solubility computed using unmodified COSMO-RS, modified pure water solubility with ΔG^{fus}, and experimental pure water solubility of explosive compounds at 25 °C. Compounds denoted with (l) are liquids at ambient conditions. All logarithms are base 10.

Explosive structure	Structure name	CAS number	ΔG^{fus} [kJ mol^{-1}]	log S^{QSPR} [g L^{-1}]	log $S^{exp\,a)}$ [g L^{-1}]	log S^{COSMO} [g L^{-1}]	|logS^{QSPR}–log S^{exp}| [g L^{-1}]	|log S^{COSMO}–log S^{exp}| [g L^{-1}]
2-NT(l)	2-Nitrotoluene	88—72—2	2.033	−0.310	−0.187[e]	0.027	0.123	0.338
3-NT(l)	3-Nitrotoluene	99—08—1	1.657	−0.420	−0.301[e]	−0.135	0.119	0.285
4-NT	4-Nitrotoluene	99—99—0	1.979	−0.350	−0.335[e]	−0.010	0.015	0.340
2,4-DNT	2,4-Dinitrotoluene	121—14—2	3.364	−0.980	−0.553	−0.361	0.427	0.619
2,6-DNT	2,6-Dinitrotoluene	606—20—2	3.460	−0.960	−0.682	−0.321	0.278	0.639
DNB	Dinitrobenzene	99—65—0	2.356	−0.520	−0.273	−0.095	0.247	0.425
NB(l)	Nitrobenzene	98—95—3	1.046	0.1220	0.254	0.276	0.132	0.154
TNB	1,3,5-Trinitrobenzene	99—35—4	3.221	−1.300	−0.414	−0.674	0.886	0.626
TNT	2,4,6-Trinitrotoluene	118—96—7	4.376	−1.520	−0.999	−0.875	0.521	0.645
EGDN(l)	Ethyleneglycol dinitrate	628—96—6	1.184	−0.190	−0.300	0.033	0.110	0.223
NG	Nitroglycerin	55—63—0	2.870	−0.440	0.290	−0.958	0.730	0.518
PETN	Pentaerythritol tetranitrate	78—11—5	6.849	−2.340	−1.678	−1.475	0.662	0.865
2-ADNT	2-Amino-4,6-dinitrotoluene	35572—78—2	7.795	0.099	0.440[c]	0.258	0.341	0.159
4-ADNT	4-Amino-2,6-dinitrotoluene	19406—51—0	7.820	0.088	0.440[c]	0.455	0.352	0.367
RDX	Cyclotrimethylene-rinitramine	121—82—4	6.008	−0.860	−1.220	0.281	0.360	1.141
β.HMX	Cyclotetramethylene-tetranitramine	2691—41—0	13.594	−2.200	−2.10	0.407	0.100	2.607
TATB	1,3,5-Triamino-2,4,6-trinitrobenzene	3058—38—6	9.870	−1.310	−0.796	0.541	0.514	1.851
CL-20	Hexanitrohexaazaiso-wurtzitane	135285—90—4	8.502	−2.20	−2.360[d]	0.250	0.160	2.450

a,b) Refs. [35, 36]. c) Ref. [37]. d) Ref. [38]. e) Refs. [23, 39].

quire an additional QSPR and more experimental data than currently exists; thus, in order to keep our method valid as a general prediction tool, we have kept this term as a constant.

The salting-out coefficients (at ambient temperature) of all compounds in the training set are shown in Table 2. Experimental data from Luning-Prak and O'Sullivan on a number of nitrotoluenes is also presented, along with previous COSMO-RS predictions by Kholod et al. in which the free energy of fusion was estimated from experimental enthalpies of sublimation and melt temperatures [22, 23]. Systematic data on other explosive compounds besides these nitroaromatics is extremely limited, but based on this available data we do see a significant improvement in Setschenow coefficients with the method described in this paper. Luning Prak and O'Sullivan found that the experimental salting-out coefficient of 2,4-DNT varied between 0.1 to 0.13 L mol^{-1} over a temperature range 4 to 40 °C, and for TNT values varied between 0.09 to 0.15 L mol^{-1} as shown in Figure 2 [39, 41]. We note that small concentrations of other trace ions (such as Mg^{2+}) were also present in these experiments, in contrast to the pure Na$^+$/Cl$^-$ solvents considered here. Hashimoto et al. reported Setschenow coefficients in the ranged of 0.136 to 0.163 L mol^{-1} for nitrophenols and nitrotoluene in straight sodium chloride solutions [2]. Our predicted values for these compounds fall in the range of 0.22 to 0.28, above these previous reports but in reasonable agreement considering the paucity of data on explosive compounds beyond the nitroaromatics. Full temperature-dependent salting out coefficients for

all compounds calculated in this work is given in the Supporting Information.

Figure 3 shows representative plots of the solubility of several explosive compounds as a function of temperature and salt concentration; full plots for all materials can be found in the Supporting Information. For most explosives and related compounds, the solubility increases with temperature (as would be expected if the dissolution reaction is endothermic) and decreases with increasing salt concentration (the traditional salting-out effect). These are consistent with previous experimental work. For the common materials shown in Figure 3, the solubility increases roughly 0.2 to 0.4 LU between pure water and 100 % seawater (corresponding to a concentration of roughly 4 g salt per 100 g water). Several compounds do show more complex trends with temperature and salt concentration; these are discussed in greater detail below.

We next use the same modified COSMO-RS method to generate temperature-dependent solubility in pure and saline water for compounds outside the test set, including a number of military, homemade, and "green" explosives. Table 3 shows a list of these compounds' solubility at room temperature in pure water. The first four compounds in Table 3 are materials that were not included for the fitting set but which do have limited experimental solubility data. The above correction improves predicted results considerably from the bare COSMO-RS values; values for FOX-7 and nitroguanidine are improved by 1.28 and 1.91 LU, respectively.
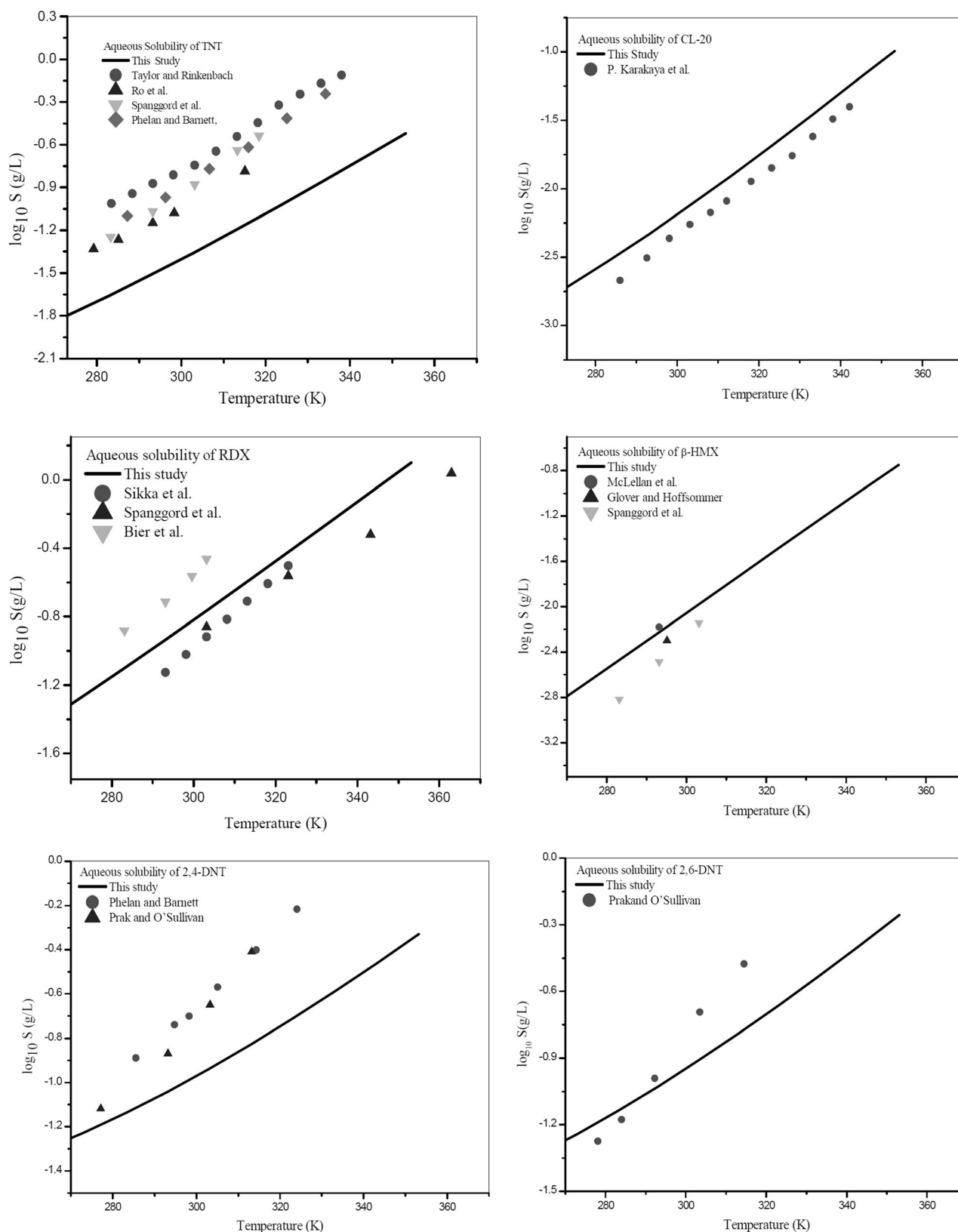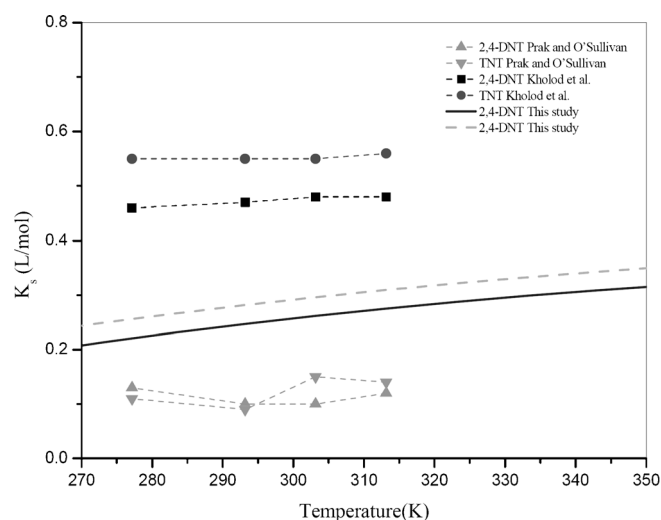
Figure 1. Aqueous solubility of TNT, 2,4-DNT, 2,6-DNT, RDX, β-HMX, and CL-20 as a function of temperature.

Table 2. Predicted salting-out coefficients compared to experimental and previous theoretical predictions.

Compound	K^{QSPR} [L mol^{-1}]	$K^{exp\ a)}$ [L mol^{-1}]	K^{Theo} [L mol^{-1}]
2-NT	0.22	0.14	0.42
3-NT	0.26	0.14	0.42
4-NT	0.25	0.15, 0.163$^{c)}$	0.41
2,4-DNT	0.25	0.11	0.47
2,6-DNT	0.25	0.12	0.47
NB	0.22	0.12	0.37
TNB	0.26	0.09	0.52
TNT	0.28	0.12	0.55
DNB	0.22		
EGDN	0.25		
NG	0.37		
PETN	0.41		
2-ADNT	0.22		
4-ADNT	0.21		
RDX	0.19		
β-HMX	0.13		
TATB	0.24		
CL-20	0.36		

a) Refs. [39–41]. b) Ref. [23]. c) Ref. [2].

Figure 2. Salting-out coefficient of TNT and 2,4-DNT compared to available experimental data and previous theoretical predictions.

Included in Table 3 are a number of environmentally important nitroso derivatives of RDX such as MNX, DNX, and TNX as well as common homemade explosive compounds such as TATP and HMTD. The former set is a group of degradation products found when RDX is destabilized due to reduction reactions under anaerobic conditions, and the latter set are volatile explosives widely used in improvised

Table 3. Salting-in/out coefficient, correction factors (ΔG^{fus}), pure water solubility computed using unmodified COSMO-RS, modified pure water solubility with ΔG^{fus}, and experimental pure water solubility of some explosive compounds at 25 °C. Compounds denoted with (l) are liquids at ambient conditions. All logarithms are base 10.

Explosive structure	Chemical name	ΔG^{fus} [kJ mol^{-1}]	log S^{QSPR} [g L^{-1}]	Ks^{QSPR} [L mol^{-1}]	log S^{exp} [g L^{-1}]	log S^{COSMO} [g L^{-1}]
FOX-7	1,1-Diamino-2,2-dinitroethylene	6.242	0.66	0.19	0.79$^{a)}$	2.08
DDNP	4,6-Dinitro-2-diazophenol	5.916	−0.77	0.16	−0.20$^{b)}$	0.35
DMNB	2,3-Dimethyl-2,3-dinitrobutane	5.690	−1.64	0.26	−1.10$^{c)}$	−0.29
NQ	Nitroguanidine	8.498	1.840	−0.02	0.95$^{d)}$	3.75
TATP	Triacetone triperoxide	8.071	−2.260	0.42		
TNA	2,4,6-Trinitroaniline	5.104	−1.140	0.21		
DADP	Diacetone diperoxide	3.891	−0.519	0.23		
PETRIN	Pentaerythritoltrinitrate	7.552	−2.04	0.37		
MNX	Hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine	5.544	−0.65	0.18		
TNX	Hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine	6.088	0.172	0.15		
DNX	Hexahydro-1,3,5-trinitroso-1,3,5-triazine	5.757	−0.27	0.17		
DINA	Diethanolnitraminedinitrate	5.485	−2.05	0.30		
TEGDN	Triethyleneglycoldinitrate	4.573	−2.36	0.44		
HP(l)	Hydrogen peroxide	3.360	2.81	−0.008		
IPN	Isopropylnitrate	1.322	−0.38	0.23		
NM(l)	Nitromethane	1.565	1.34	0.073		
ONC	Octanitrocubane	10.205	−6.06	0.60		
TNM(l)	Tetranitromethane	0.288	−1.23	0.34		
TACOT	Tetranitro-2,3,5,6-dibenzo-1,3a,4,6a-tetraazapentalene	7.866	−3.81	0.34		
HNS	Hexanitrostilbene	3.221	−5.61	0.44		
δ-HMX	δ-Cyclotetramethylen-etetranitramine	2.882	−1.40	0.07		
HMTD	Hexamethylene-triperoxidediamine	2.382	0.86	0.24		
BTATZ	3,6-Bis(1H-1,2,3,4-tetrazol-5-ylamino)-s-tetrazine	3.68	3.63	0.005		
DAAT	Diamino-azobis-tetrazine	3.43	0.33	0.130		
LAX-112	3,6-Diamino-1,2,4,5-tetrazine-1,4-dioxide	1.90	1.93	0.052		
DNAF	4,4-Dinitro-3,3′-diazenofuroxan	1.67	−3.26	0.310		

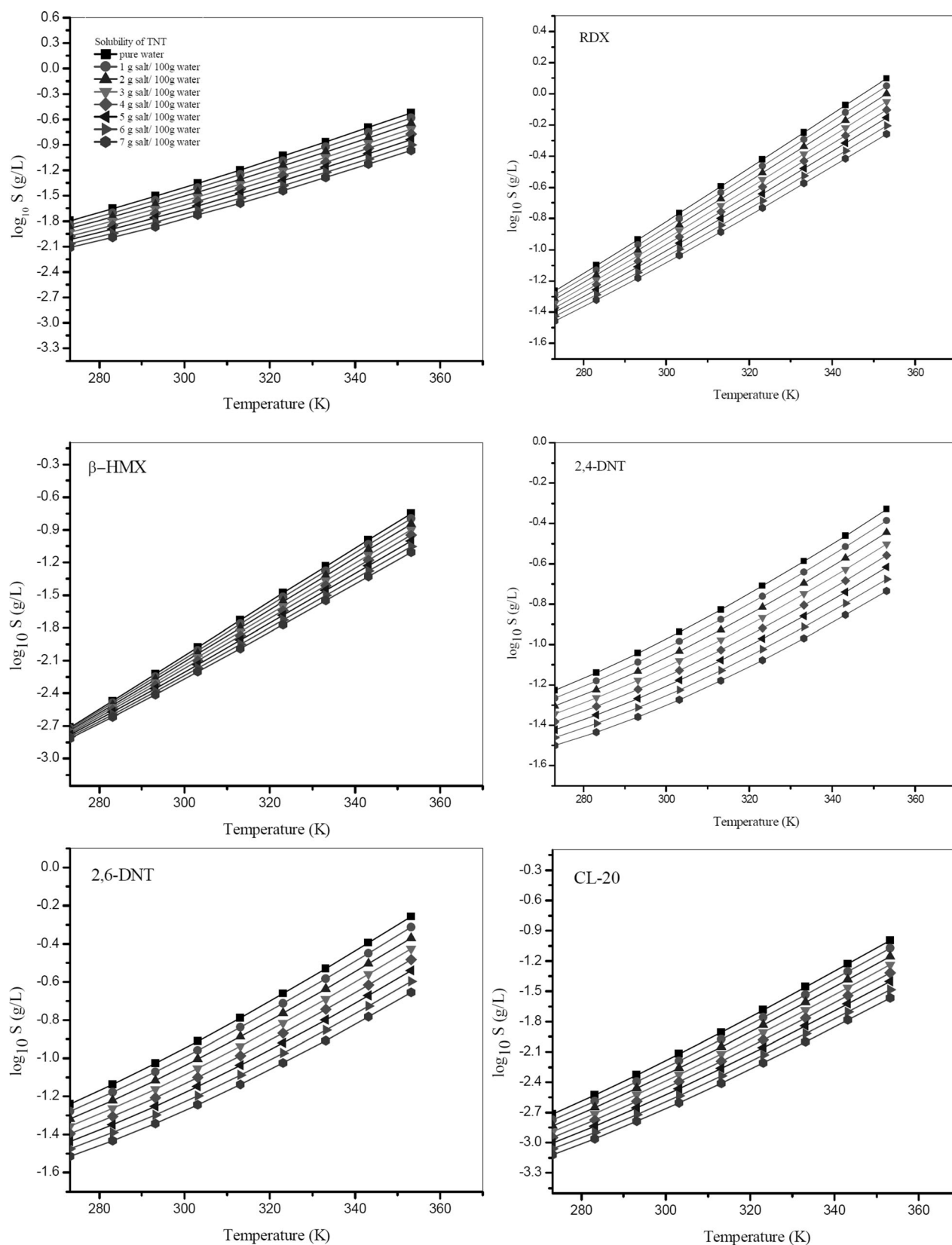a) Ref. [42]. b) Ref. [43]. c) Ref. [44]. d) Refs. [45,46].

Figure 3. Solubility of TNT, 2,4-DNT, 2,6-DNT, RDX, β-HMX, and CL-20 as a function of temperature and salt concentration.
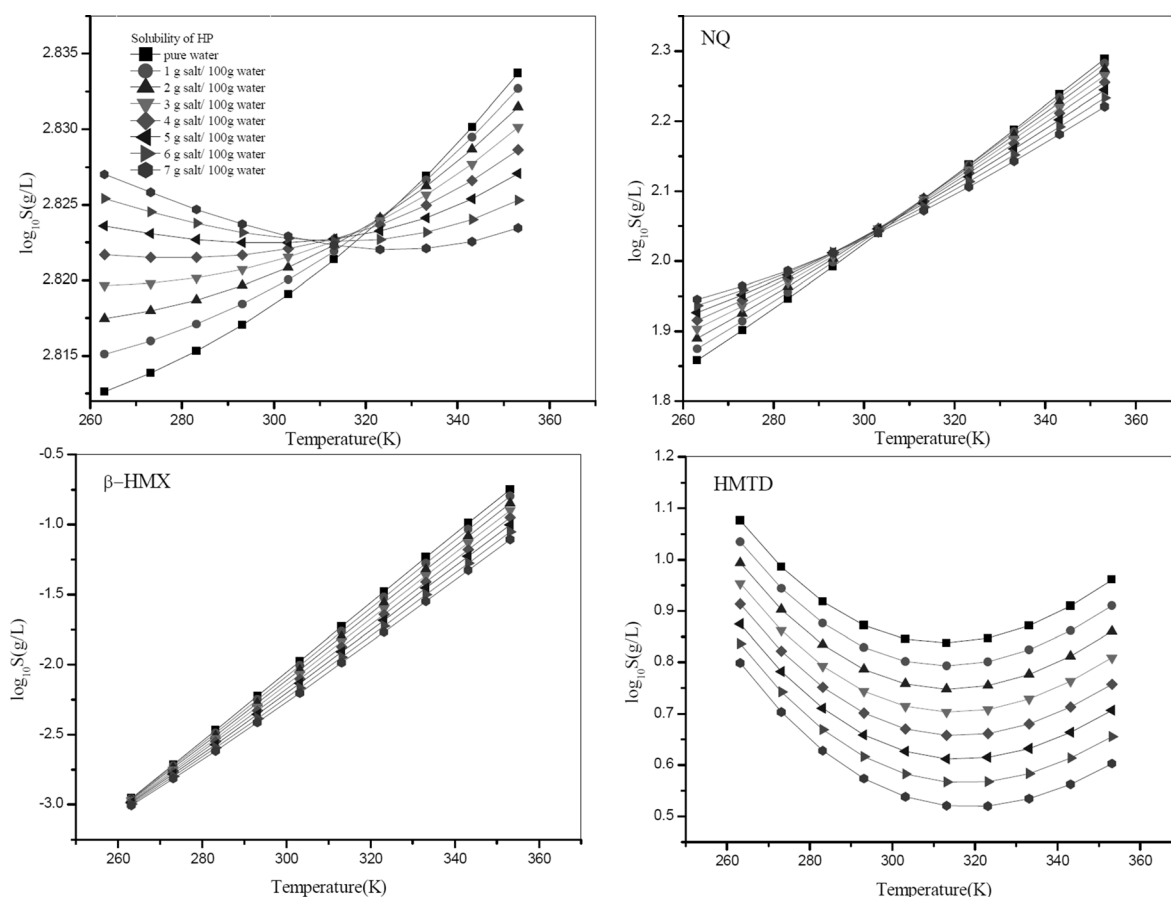
Figure 4. Solubility of HP, NQ, β-HMX, and HMTD as a function of temperature and ionic strength.

explosive devices and roadside bombs. The majority of these compounds show similar trends with temperature and ionic strength as the common military high explosives and nitroaromatics; namely, a modest increase in solubility with temperature and a solubility reduction of 0.2–0.4 LU between pure water and seawater.

Not all explosive compounds follow this same trend; Figure 4 shows four exceptions. Three explosives in this list with higher solubility in water [hydrogen peroxide (HP), nitroguanidine (NQ) and hexamethylene triperoxidediamine (HMTD)] are predicted to have more complex variations with temperature and ionic strength, though these variations are relatively small compared to the magnitude of their room temperature solubility. As shown in Figure 4, HP and NQ are predicted to have negative Setschenow coefficients in sodium chloride solutions (a salting-in effect) above temperatures of 323 K and 313 K, respectively. HMTD, a volatile homemade explosive, shows an unusual temperature dependence, in which solubility is predicted to decrease with increasing temperature below 315 K (consistent with an exothermic dissolution process), and resumes the regular temperature dependence above this point. The behavior remains even in saline solutions. Previous work by Oxley and co-authors has suggested HMTD

has low solubility in water, [47,48] but we know of no systematic data on this compound. The predicted temperature dependence of HMTD should be straightforward to evaluate experimentally. Finally, β-HMX, the most common polymorph of the high explosive HMX, is shown in Figure 4 as an example of a compound with a nontrivial variation in Setschenow coefficient with temperature. K_s increases from approximately 0.08 near 273 K up to 0.23 at 333 K. A number of other explosive compounds also show a nontrivial variation in salting-out coefficients with temperature (full details are in the Supporting Information), but systematic salting-out experimental data is only available for the small number of nitroaromatics discussed above.

Finally, we consider four high-nitrogen "green" explosives that are being considered as environmentally friendly replacements for common nitramines such as RDX and HMX. These systems, still largely at the laboratory stage, tend to have very high nitrogen content, high positive enthalpies of formation, and ideally should readily biodegrade in the environment into non-toxic products. The modified COSMO-RS method allows for estimation of solubilities and salting-out behavior for these materials with reasonable confidence. In this paper we examine four molecules (LAX-112, BTATZ, DAAT, and DNAF) that have recently received
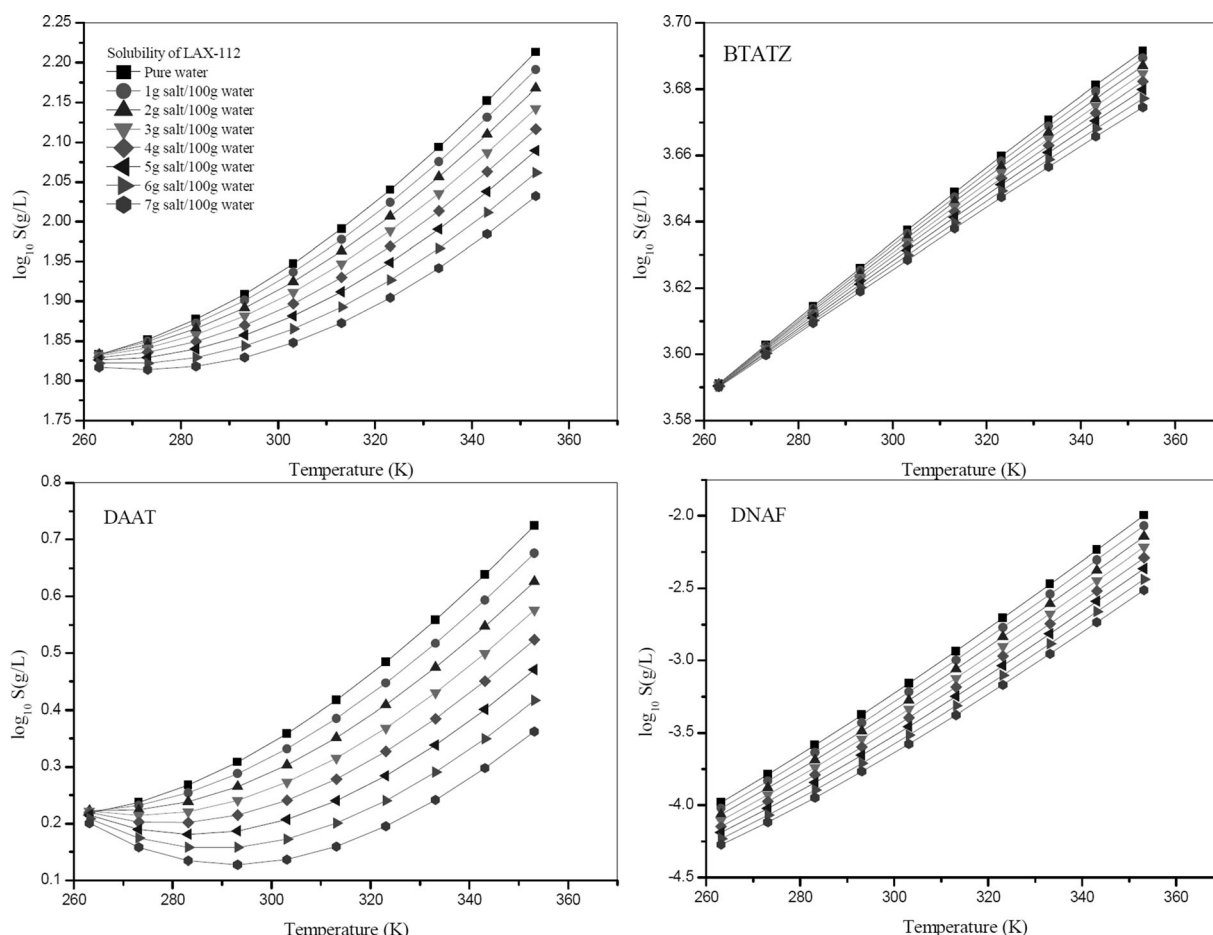
Figure 5. Solubility of BTATZ, LAX-112, DAAT, and DNAF as a function of temperature and ionic strength.

attention as explosives or gun propellants. Equation (4) was used to calculate the correction and determine the solubility in pure and saline water for these compounds; the estimated correction factor, aqueous solubility, and salting-in/out coefficients at room temperature for these compounds are shown at the bottom of Table 3.

The solubilities of BTATZ, DAAT, and LAX-112 are high compared to military explosives such as RDX and HMX. DNAF has among the lowest solubility of any compound considered here. The solubility as a function of temperature and ionic strength are shown in Figure 5 below.

4 Conclusions

Pure and saline water solubility is a critical property for understanding and remediating explosives in the environment, and has application in toxicological studies as well as for sensing landmines and improvised explosive devices. In this work we have modified the COSMO-RS solvation model with a QSPR-based correction for the free energy of fusion and other factors, allowing the technique to be used

for quantitative predictions of new explosives or systems with limited experimental data. This QSPR correction brings the predicted water solubility to within 0.25 log units of the most reliable experimental data, and greatly improves COSMO-RS results for important explosive compounds such as nitramines. Salting-out coefficients are considerably improved compared to previous COSMO-RS results, but are overestimated compared to the limited data that exists for nitroaromatic compounds. The solubility of most explosives increases slightly with temperature and decreases with salt concentration, but a number of higher solubility materials (such as the homemade explosive HMTD) are predicted to have more complex behavior. The salting-out coefficients for most explosives vary slowly with temperature over the range relevant for toxicology and detection, but a number of materials such as the nitramine β-HMX show a nontrivial increase in the salting out effect with temperature. The use of this correction factor allows the COSMO-RS method to be used for solubility predictions of new proposed compounds, such as "green" propellants and energetics that may have reduced toxicity in the environment.

Acknowledgments

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