

# Development of methods for predicting solvation and separation for energetic materials in supercritical fluids

Christopher J. Cramer,<sup>a</sup> Jason Thompson,<sup>b</sup> and Donald G. Truhlar<sup>a</sup>  
Department of Chemistry and supercomputing Institute  
University of Minnesota  
Minneapolis, MN 55455

<sup>a</sup>principal investigator

<sup>b</sup>graduate student research assistant

The goal of the work at the University of Minnesota is to achieve a better understanding of the solubility and other properties of substances in supercritical fluids and to employ that understanding in the development of supercritical fluid technologies for recycling and reclamation of energetic materials. We plan to model solubility in supercritical fluids. This technique is proving to be a potentially useful technique for decontaminating items and soils which have been exposed to various toxic species, e. g., sulfur or amine mustards or phosphonate-derived pesticides, and it also has applications to energetic materials. We will develop accurate predictive methods and models for solvation of energetic materials in supercritical carbon dioxide, with the practical goal of providing the means to facilitate the design of practical procedures for extraction, recycling, and reusing materials. A critical component of the work will be detailed comparisons with available experimental data. We will work with ARL on an ongoing basis to transfer our findings to DoD researchers as well as to benchmark and validate the models. The end goal of this subproject will be a set of methods and computer codes that provide DoD researchers with predictive theoretical tools for predicting solvation and separation for energetic materials in supercritical fluids. Our work will include both first-principles models for predicting chemical structure, energetics, and reactivity using continuum solvation models and also theoretical linear solvation energy relationships with calculated molecular descriptors.

We have begun on work whose goal is to develop models for computing free energies of transfer of molecules from the gaseous, liquid, and solid phases into supercritical fluids. This model development effort is proceeding simultaneously from both semiempirical and first-principles standpoints because both approaches can contribute to improved understanding of the fundamental physics of solvation in a supercritical medium.

From an empirical standpoint, considerable success achieved in the past by correlating data for solubility in supercritical fluids with molecular property and/or topological descriptors; such a statistical approach is referred to as a linear free energy relationship (LFER) or a theoretical linear solvation energy relationship (TLSER). As an example of this approach we note that the solubilities of a series of 18 aromatic compounds in supercritical CO<sub>2</sub> at 308 K have been correlated with 5 TLSER descriptors derived from calculations at the highly efficient modified-neglect-of-differential-overlap (MNDO) level of semiempirical molecular orbital theory.[1] The TLSER descriptors are designed to correlate with fundamental properties of molecules, e.g., polarity, polarizability, and so forth. Given such a correlation, an analysis of descriptor *t*-scores can be used to evaluate which physical interactions govern solubility

behavior. In the above cited example, for instance, the electrostatic TLSEr terms accounted for the majority of the correlation, consistent with viewing the solute-supercritical solvent interactions as being dominated by “hard”-type interactions.

Similar observations have been made by Politzer et al.[2], who have employed a different regression formalism based on using only a single theoretical descriptor computed over the molecular surface. While examples of this approach to date have been somewhat limited in the functionality of the training sets, early successes suggest that this formalism should provide a useful starting point for empirical correlation analysis focusing more specifically on energetic materials. There is a long history of using the electrostatic potential as a guide to understanding other molecular properties,[3] and we are taking the development of a more accurate electrostatic model as the first step in our new work. In particular we are carrying out further development of the class IV generation of models for partial atomic charges. Such so called class IV charge models, originally [4,5] developed in our group, provide very accurate molecular charge distributions (and hence accurate electrostatic potentials) at very low computational cost. Further details of our current work on this first stage is provided below.

Prior to focusing exclusively on energetic materials, we think it will be worthwhile to attempt to create more general models to identify particular physical phenomena that may be operative in the supercritical phase, but not in the normal liquid solution phase, where most prior LFER and TLSEr analysis has been carried out. Thus, for instance, a special issue that arises in supercritical fluids is clustering, and special attention may be required to identify a descriptor that correlates well with a tendency for clustering to occur. Such a descriptor is likely to depend on molecular polarity, and our class IV models for partial atomic charges are likely to be of use in this regard as well.

One particular limitation in applying current class IV charge models to energetic material is that available data for molecular electric multipole moments (which form the basis for parameterization of the charge models) as limited with respect to the functionality found in energetic materials (e.g., nitro groups). This challenge may be addressed by carrying out converged quantum mechanical calculations in order to compute the necessary multipole moments from first principles, and then adding these data to the parameterization set to provide improved coverage of the requisite functionality. A specific goal of our early work will be to develop such a database and mine it for new charge model development. Our recent experience suggests that hybrid Hartree-Fock-density-functional theory [6,7] will be very useful for this purpose.

While it appears that TLSEr correlation is able to predict solubility with a high degree of accuracy in some data sets, we are also working toward the development of full quantum mechanical models. This will potentially permit a much broader analysis of supercritical fluid solubility, since changes in molecular and electronic structure and how they interact with the supercritical fluid would be treated more consistently via the quantum mechanical continuum model than by simple correlation analysis. In particular, we mention as one possibility a physically reasonable treatment of clustering via a modification to our calculation of solvation free energy to include an inhomogeneous dielectric around the solute. We will explore this option. The charge model work will also be critical for the methodologies we are developing from first principles. In particular we are expanding upon our extensive body of work in the design of so-called continuum solvation models,[8-16] where our previous work has focused entirely on noncritical liquid solutions. Our previous models have been developed for use with a variety of solute models ranging from molecular mechanics [9] to semiempirical molecular

orbital theory [8,10,11,14,15] to *ab initio* MO theory [13] to density functional theory.[12] Access to this range of theoretical levels makes us well prepared to attack a broad range of molecular size in further model development. Most of the existing models depend on the accuracy of class IV charge models to predict polarization free energies in solution, so advances made in the empirical correlation work will feed directly into solvation model refinement as outlined next.

We plan to examine first the utility of existing continuum models, *i.e.*, those which do not take any special account of the supercritical nature of the surrounding condensed phase, for predicting solvation free energies of compounds in a supercritical fluid. This will be done using our generalized Born models [8-16] for the long-range electrostatics and with appropriate surface-tension terms for short-range effects; the latter will be parameterized over available training set data. Surface-tension terms capture solvation phenomena beyond electrostatics, including cavitation, dispersion, hydrogen bonding, and structural changes taking place in the first solvation shell(s), as well as local changes in the permittivity of the solvent. An alternative to the atomic surface tensions is to model the short-range contributions to solvation from separate estimates of cavitation energies, repulsion, and dispersion interactions.

From another point of view, modeling the local permittivity may be considered to be a key to modeling supercritical fluids because clustering effects can introduce spatial inhomogeneities in the surrounding medium such that the dielectric constant depends on the position in the fluid as well as the pressure and temperature.[17] Thus, we plan to simultaneously examine model systems using a supercritical fluid reaction field model first described by Luo and Tucker [18] and later refined.[19,20] In these models, the local dielectric constant is computed from its density dependence with the density  $\rho$  computed as

$$\rho = \rho_0 + \int_0^E \frac{1}{2} \epsilon_0 \rho_0^2 \kappa_T \left( \frac{\partial \epsilon}{\partial \rho} \right)_T d(E')^2$$

where  $\rho_0$  is the density at zero electric field for the particular values of pressure and temperature  $T$  employed,  $E$  is the electric field created in response to the solute charge distribution,  $\epsilon_0$  is the electric permittivity of free space, and  $\kappa_T$  is the isothermal compressibility. The various quantities in the above expression for  $\rho$  are all available from experiment, except the electric field, which is computed from the solute charge distribution. Because the field varies over space, the dielectric constant is usually solved on a grid, and that same grid is then used in solution of the Poisson equation to determine the free energy of solvation.[16] This process will be made self-consistent as part of a molecular orbital or density functional calculation in order to create a full self-consistent reaction field model.

Finally, we will use the results from the grid-based approach to evaluate whether the generalized Born formalism, which is computationally more efficient than solution of the Poisson equation, can be modified to incorporate dielectric inhomogeneities. Such a development would have broad fundamental utility, since it would open the door to better predicting partitioning behavior in general, as well as possibly extending to solutions where finite electrolyte concentrations affect dielectric behavior as well.

The initial stage of our work under the funding of this MURI grant has been to make our models more stable for calculations employing diffuse basis functions. This is motivated from two directions. First of all, we plan to use hybrid density functional theory [6,7,21,22], and recent work has demonstrated that this kind of molecular orbital theory delivers much better performance when diffuse basis functions are used. [23] Second, we note that negative groups

such as nitro groups are very important for many of the target compounds, and diffuse basis functions tend to be especially important for an even handed description of negative functional groups and lone pairs. However, in previous work we had noticed that conventional methods for population analysis, which is the first step in the calculation of class IV charges, tend to be unstable when diffuse functions are included in the basis set. Therefore we developed [24] a method that alleviates some of the sensitivity to the inclusion of diffuse basis functions when calculating partial atomic charges from a Löwdin population analysis. This new method locally redistributes that part of the Löwdin population that comes from diffuse basis functions so that the final charges closely resemble those calculated without diffuse functions. We call this method the redistributed Löwdin population analysis (RLPA) method. The method contains one parameter for each atomic number, and we optimized the parameter for the 6-31+G(d) basis set. The method has been tested on compounds that contain H, Li, C, N, O, F, Si, P, S, Cl, and Br. For a test set of 398 compounds with experimental and high-level theoretical dipole moments, the dipole moments derived from the charges obtained by standard Löwdin population analysis have errors 35% larger than those obtained by the corresponding RLPA analysis using the same basis set. In judging the quality of the RLPA method with respect to the test set of dipole moments, we have also found that dipole moments derived from Mulliken population analysis have errors 120% larger than those derived from RLPA analysis for the same basis set. The new method is particularly successful for the 207 systems containing only first row atoms (H, C, N, O, F) for which the errors in the dipole moments computed from the partial atomic charges obtained by standard Löwdin and Mulliken analysis are respectively 115% and 419% larger than those obtained by RLPA.

In subsequent work [25], this RLPA method was incorporated into a new class IV charge model called charge model 3 (CM3), which is designed to obtain accurate partial atomic charges from hybrid density functional theory or Hartree-Fock calculations with or without diffuse basis functions. The model maps partial atomic charges obtained from Löwdin population analysis or RLPA into improved (class IV) charges that reproduce accurate charge-dependent observables for molecules containing H, Li, C, N, O, F, Si, S, P, Cl, and Br. Dipole moments computed from CM3 charges have mean unsigned errors in the range 0.19-0.28 Debyes when compared to experiment. These CM3 charges will be used in the solvation models to be developed for supercritical fluids.

An important point in the computation of solubility that arises for solid solutes is accounting for the free energy of fusion in the crystal. In the absence of crystal structural information, this is a very difficult problem, and we will examine whether continuum approaches that treat the crystal as a homogeneous medium can be of any use in estimating fusion free energies. In cases where structural data *are* available, we will examine the extent to which modeling the crystal using class IV charges at atomic lattice positions may be useful in computing fusion free energies. In both cases, some accounting will also have to be taken of non-electrostatic terms, but this seems much more likely to be amenable to treatment via a surface-tension-like approach, such as that already used in the continuum models.

Validation and benchmarking against experiment is a very important part of this proposal. For validating charge models we have developed a training set of accurate dipole moments for 369 small polar molecules with diverse functionality [24,25]. The data are mainly experimental, but in a few cases we use well reliable, high-quality theoretical data. For parameterizing solvation models we have developed a database of 2315 experimental free energies of transfer for over 300 solutes in over 90 solvents.[15] In addition to these general

databases, we intend to compare our results to experimental data and molecular simulations for specific explosive molecules.[26-28]

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