1. PRF#: 56896-UNI6

2. Project Title: Using Ionic Liquid Mixtures for the Extraction of Organosulfur Compounds from Petroleum Streams

3. P.I. Name, Affiliation: Andrew S. Paluch, Miami University

Overview

The ultimate goal of the present study is to use molecular simulation to parameterize established thermodynamic models. While molecular simulation is predictive and can give molecular-level insight, the calculations are typically time consuming. On the otherhand, many analytic models (i.e., excess Gibbs free energy models) exist to model phase behavior for process design applications. However, these models are not truly predictive in that reference data must first be available to obtain parameters for novel systems before predictions may be made. Here we seek to combine the predictive nature of molecular simulation with the efficiency of analytical expressions. Specifically, we focus on the use of MOSCED wherein the parameters are related to molecular descriptors.

This project is focused on the design of mixtures of ionic liquids as novel solvents to extract organosulfur compounds from petroleum streams. There are a large number of ionic liquids that have previously been synthesized, and an even larger number of potential ionic liquids and ionic liquid mixtures. The use of molecular simulation alone would be impracticle. By using molecular simulation to parameters MOSCED, we obtain a predictive method suitable for early stage processes design applicaitons that additional sheds insight into the underlying molecular level details.

Much of the past calendear year has been spent understanding the strengths and limitations of MOSCED, which has resulted in four peer reviewed publications with undergraduate students. Many additional publications are being prepared.

1 Establishing MOSCED as predictive tool

MOSCED takes the general form:

$$\ln \gamma_2^\infty = \frac{v_2}{RT}\left[(\lambda_1 - \lambda_2)^2 + \frac{q_1^2 q_2^2 \left(\tau_1^{(T)} - \tau_2^{(T)} \right)^2}{\psi_1} + \frac{\left(\alpha_1^{(T)} - \alpha_2^{(T)} \right)\left(\beta_1^{(T)} - \beta_2^{(T)} \right)}{\xi_1} \right] + d_{12} \tag{1}$$

$$d_{12} = \ln \left(\frac{v_2}{v_1} \right)^{aa} + 1 - \left(\frac{v_2}{v_1} \right)^{aa}$$

where γ_2^∞ is the limiting activity coefficient of the solute (2) in a solvent (1), and the first three terms result from comparing solute and solvent intermolecular interactions. A limitation of MOSCED is it can only predict limiting activity coefficients. In order to predict composition dependent activity coefficients which may be necessary for phase-equilibria calculations, MOSCED must be used to parameterize an excess Gibbs free energy model. The model is optimized for limiting activity coefficient because this captures the maximum deviations from ideality, can be related directly to solute-solvent intermolecular interactions, and can in turn be used to parameterize an excess Gibbs free energy model to compute composition dependent values. Our first publication focused on an evauation of using limiting activity coefficients to parameterize an excess Gibbs free energy model, and the resulting accuracy to predict phase-equilibria. The result were very promising, and motivated our continued studies. At that point the test set was limited to the conventional solvents for which MOSCED parameters currently exist.

The parameters all have physical significance: λ_i, τ_i, α_i, and β_i correspond to dispersion, polar, and the hydrogen bond donating and accepting ability of a compound, respectively. Additionally, MOSCED is based on the concept of separation of cohesive energy density. With this, we published a pair of papers discussing novel methods to predict MOSCED parameters devoid of experimental data. First, we developed a group contribution method. The group contribution framework allows us to model a wider range of compounds using more limited data. At this stage the method was not applied to ionic liquids, but to conventional solvents for which data was readily available for comparison. We then took this a step futher to use molecular simulation and electronic structure calculation to directly predict MOSCED parameters. This study was limited to the series of 1,n-alkanediols; they were chosen because MOSCED parameters did not exist, but sufficient reference data was available for comparison.

Last, during this process we discovered that MOSCED performed poorly when modeling water. We realized that this was the result of an oversight in the original parameterization of MOSCED. We re-parameterized MOSCED for water, and published the improved results.

2 Predicting MOSCED paramters

Having demonstrated the ability of MOSCED to model mixtures of conventional solvents, and our ability to predict parameters using group contribution methods, molecular simulation and electronic structure calculations, we next turned our attention to ionic liquids. This work has resulted in a series of four publications that are being prepared for publication.

First, a team of undergraduate students surveyed the literature, and tabulated a database of reference limiting activity coefficients for solutes in ionic liquids. The database was then screened for suspect data. With this in hand, we regressed parmaters for approximately 200 ionic liquids. This set of MOSCED parameters serves as our reference set.

Next, we worked to extend our developed group contriution, molecular simulation, and electronic structure methods to ionic liquids. We started by predicting parameters for the compounds in our reference set, allowing us to refine and improve these methods for ionic liquids.

The ultimate goal of this work is to use MOSCED to parameterize an excess Gibbs free energy model to model the phase behavior of mixtures involving ionic liquids. We therefore spent a great deal of time understanding the ability to do this. This mainly involved modeling the use of ionic liquids as entrainers in extraction distillation processes, as reference data was readily available. In doing so, we are preparing a publication in which we describe best practices with detailed examples.

3 Impact

This completes the second year of this project. We have accomplished a tremendous amount, and I expect to spend another year writing manuscripts based on this work.

In the two years working on this project, four undergraduates have been directly supported by this PRF grant, along with two MS students. The undergraduates were supported during summer and winter breaks. During the academic year, approximately 15 undergraduate students worked on this project, and received academic credit or funding from university resources. The undergraduate students over the summer were additional supported by the Undergraduate Summer Scholars Program from the Miami University Office of Undergraduate Research with additional support from the Miami University College of Engineering and Computing.

The experience afforded the students the opportunity to use state-of-the-art computational methods and additionally to use a physical based model for process design applications. Additionally, the students have had the opportunity to write-up research articles with the guidance of the PI, and to additionally present their work as poster and oral presentations at professional meetings.

The undergraduate students have made poster and oral presentations at the 2017 and 2018 AIChE North Central Student Regional Conference, the Ohio Supercomputing Center Statewide User Group bi-annual conference during Fall 2017 and Spring 2018, and the 2017 and 2018 Midwest Thermodynamics and Statistical Mechanics Conference.

The positive impact of the work has led to three undergraduate students pursuing the combined BS/MS program here at Miami University. One of the three completed the program this past year supported by the PRF grant, and the other two will complete a thesis next year. Additionally, one undergraduate student is currently applying for PhD programs in Chemical Engineering beginning next year.