**Model Performances Evaluated for Infinite Dilution Activity Coefficients Prediction At 298.15K.**

Thomas Brouwer\*, Boelo Schuur
*University of Twente, Faculty of Science and Technology, Sustainable Process Technology group, PO Box 217, 7500AE, Enschede, The Netherlands.
\*Corresponding author: t.brouwer@utwente.nl*

**Highlights**

* Eight models were evaluated for infinite dilution activity coefficient prediction.
* The most accurate model depends on each specific solute-solvent pair
* An accurate hydrogen bond description is essential for an accurate prediction
* An extended MOSCED model could be a potential approach for ionic liquids

**1. Introduction**

The global community relies on the chemical industry for the production of goods from complex raw materials, such as oil and biomass. The separation processes required in these production routes account for up to 50 % of the total energy costs in refineries[1] and improving the efficiency of separations can significantly reduce the environmental impact of the chemical industry. This can only be made by achieved by understanding the separation processes on molecular-level, which includes a good description of thermodynamic equilibria. An accurate description of these equilibria are possible with models like UNIQUAC and NRTL, but require labour intensive experimental data. Alternative predictive models can provide engineers with first estimates for molecular behaviour with less experimental data. In this manuscript, we explore different predictive models in predicting a molecular descriptor, the infinite diluted activity coefficient, $γ\_{i}^{\infty }$. This descriptor can be used in combination with predictive models to make a first estimate on the thermodynamic behavior in separation processes. Several types of models are known to be able to predict the $γ\_{i}^{\infty }$, for instance the Hildebrand parameter[2], Hansen Solubility Parameters[3], various Group Contribution Methods (UNIFAC), the Conductor like Screening Model for Real Solvents (COSMO-RS) model[4], Abraham model[5] and the Modified Separation of Cohesive Energy Density (MOSCED) model.[6] The aim of this manuscript is to compare the performance of these fundamentally different approaches in prediction the $γ\_{i}^{\infty }$ of (a)-polar solutes in (a)-polar (ionic) solvents. The relative performance of all evaluated models will be linked to the fundamental assumption incorporated in the various models.

**2. Methods**

For all $γ\_{i}^{\infty }$ predictions a systematic assessment was done at 298.15K and all model specific parameters were imported from literature sources. The overall average relative deviation (ARD) was determined both overall for all models as for specific solute-solvent combinations.

**3. Results and discussion**

A larger ARD was observed for Ionic Liquids (ILs) than for molecular solvents due to the additional ionic interactions. Overall averaged, the MOSCED model was the most accurate model for the prediction of $γ\_{i}^{\infty }$ of all solute classes in molecular solvents with an ARD of 16.2±1.35%. The UNIFAC Group Contribution Methods (GCMs), COSMO-RS and the Abraham models perform comparably with ARDs of 24.3-32.2%. Models using the Hildebrand parameter and the Hansen Solubility Parameters are significantly less accurate due to an insufficient description of intermolecular interactions such as hydrogen bonds. For predicting the $γ\_{i}^{\infty }$ in ILs, the Abraham model is overall the most accurate model with an ARD of 65.1±4.50%. The GCMs are less accurate with ARDs of 86.2-122%, while COSMO-RS is far less accurate with an ARD of 182±16.7%, due to a deficient description of long-range interactions.

Upon classification of solutes and molecular solvents, the evaluating for each of the solvent and solute classes was performed. Each model predicts most accurately, with the exception of the Hildebrand parameter and Hansen Solubility Parameters, the $γ\_{i}^{\infty }$ for specific classes of binary solute-solvent pairs. Though the accuracy decreases with the polarity of the solute. For ILs, the Abraham model is overall averaged most accurate, though several cations are more accurately described with mod. UNIFAC (Ly) or mod. UNIFAC (Do). The large ARDs from the UNIFAC models and the Abraham model are mainly due to large ARDs for bis(trifluoromethylsulfonyl)imide ([NTF2]), tetrafluoroborate ([BF4]) and the 2-(2-Methoxyethoxy)ethyl sulfate ([MDEGSO4]) anions. Hence, improving the prediction of these anions will greatly increase their overall prediction accuracy. Additionally, the most accurate model for molecular solvents, MOSCED, could not be assessed for ILs. Therefore, an extension of MOSCED towards ILs may become an accurate tool in predicting accurate $γ\_{i}^{\infty }$ in ILs.

**4. Conclusions**

Based on the evaluation results, it can be concluded that choosing the most accurate model for estimation of $γ\_{i}^{\infty }$ depends on both the solute and solvent categories under evaluation. Using a predicted $γ\_{i}^{\infty }$ for IL screening should be done with caution, as these on average easily exceed deviation of 65%.

**References**

1. Kiss, A.A., et al., *Separation technology–Making a difference in biorefineries.* Biomass and Bioenergy, 2016. **95**: p. 296-309.

2. Hildebrand, J. and R. Scott, *The solubility of nonelectrolytes, Reinhold Pub.* Co., New York, 1950. **3**.

3. Hansen, C.M., *The three dimensional solubility parameter.* J. Paint Technol, 1967. **39**: p. 105.

4. Eckert, F. and A. Klamt, *Fast solvent screening via quantum chemistry: COSMO‐RS approach.* AIChE Journal, 2002. **48**(2): p. 369-385.

5. Abraham, M.H., *Scales of solute hydrogen-bonding: their construction and application to physicochemical and biochemical processes.* Chemical Society Reviews, 1993. **22**(2): p. 73-83.

6. Thomas, E.R. and C.A. Eckert, *Prediction of limiting activity coefficients by a modified separation of cohesive energy density model and UNIFAC.* Industrial & Engineering Chemistry Process Design and Development, 1984. **23**(2): p. 194-209.