

# Theoretically Based Ion Potential Models in Molecular-Based Electrolyte Equations of State for the Prediction of Solvation Energies

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Thermodynamic modelling of electrolyte solutions using a molecular-based equation of state (EOS) is challenging due to the complexity and range of the molecular forces: short-ranged repulsion; mid-ranged dispersion; directional hydrogen-bonding; and long-ranged Coulombic interactions. A thermodynamic perturbation approach, such as SAFT, is ideally suited to meet this challenge since its construction allows one to incorporate independent contributions to the free-energy expression, however the additive nature of the expression introduces many parameters. SAFT-VRE Mie is an extension for electrolytes of the SAFT-VR Mie [1] EOS. The Mie potential is used to represent the short-ranged repulsive, and dispersive (attractive) interactions. Coulombic interactions are incorporated at the unrestricted-primitive-model level, using Debye-Hückel [2] theory, or the MSA [3]. Physically sensible ion potential parameters are obtained from well-known physical quantities, incorporating literature values of ion diameters [4], ion-solvation diameters, and the polarizabilities of ions, using the approach of Hudson and McCoubrey [5]. Only a single solvent-ion interaction remains to be obtained from available fluid-mixture experimental data. This single-parameter approach retains near equal performance to the more-common three-parameter schemes. Our approach vastly simplifies the parameter space of the EOS; it also allows for the direct comparison of chemical potentials at the limit of infinite dilution through quantitative prediction of solvation energies in aqueous solutions.

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## References

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