

## Comparison of Debye-Hückel and the Mean Spherical Approximation for Electrolyte Equations of State

Bjørn Maribo-Mogensen<sup>C, S</sup>, Georgios M. Kontogeorgis and Kaj Thomsen

*Technical University of Denmark, Department of Chemical and Biochemical Engineering, Kgs. Lyngby,*

*Denmark*

*bmm@kt.dtu.dk*

Solutions containing electrolytes are encountered in many important industrial processes, such as post-combustion CO<sub>2</sub> capture, acid gas scrubbing, purification of proteins and pharmaceuticals, and corrosion in wet gas pipelines. To describe the phase equilibrium of mixtures containing electrolytes, it is necessary to account for the long-range electrostatic forces between charged molecules. The thermodynamics of electrolyte solutions has been investigated by many scientists throughout the last century. While several theories have been presented, the most popular models for the electrostatic interactions are based on the Debye-Hückel and Mean Spherical Approximation (MSA) theories. Both models use Coulomb's law to describe the force between two charges, but the Debye-Hückel is derived from a linearization of the Poisson equation while MSA is derived from statistical mechanics. The differences between the Debye-Hückel and the MSA theories are investigated from a theoretical and a practical point of view, with emphasis on use in an equation of state. We compare the numerical results for the Helmholtz energy and its derivatives with respect to temperature, volume and composition. The investigation shows that the implicit non-restricted MSA theory performs similarly to Debye-Hückel, despite the differences in the derivation. We furthermore show that the static permittivity is a key parameter for both models and that in many cases it completely dominates the results obtained from the two models. Consequently, we conclude that the simpler Debye-Hückel theory may be used in connection with electrolyte equations of state without loss of accuracy.