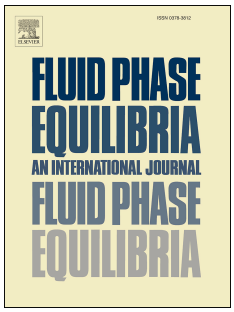

Theory of model electrolyte solutions: Assessing the short- and long-ranged contributions by molecular simulations

Florian Drunsel, Joachim Gross

PII: S0378-3812(16)30479-4

DOI: 10.1016/j.fluid.2016.09.026

Reference: FLUID 11274

To appear in: *Fluid Phase Equilibria*

Received Date: 7 April 2016

Revised Date: 22 September 2016

Accepted Date: 22 September 2016

Please cite this article as: F. Drunsel, J. Gross, Theory of model electrolyte solutions: Assessing the short- and long-ranged contributions by molecular simulations, *Fluid Phase Equilibria* (2016), doi: 10.1016/j.fluid.2016.09.026.

Theory of model electrolyte solutions: assessing the short- and long-ranged contributions by molecular simulations

Florian Drunsel[a], Joachim Gross[a,*]

[a]*Institute of Thermodynamics and Thermal Process Engineering, University of Stuttgart, Pfaffenwaldring 9, 70569 Stuttgart, Germany*

Abstract

In this work, we conduct a comprehensive simulation study on Helmholtz energies for non-primitive model electrolyte solutions in order to assess fluid theories. Simulation data is obtained with two different methods. Using a new thermodynamic integration path, we calculate Helmholtz energy contributions arising from damped, short-ranged electrostatic pair potentials. The division of the potential into a damped, short-ranged and a long-ranged part using a complementary error function corresponds to the division of a standard Ewald sum. Additionally, we applied a standard thermodynamic integration method to obtain the full electrostatic contribution to the Helmholtz energy. We evaluate the analytical long-range contribution developed by Rodgers and Weeks [J. M. Rodgers and J. D. Weeks, J. Chem. Phys. **131**, 244108 (2009)] and find excellent agreement to our simulation data for any damping parameter $\alpha^* \geq 1.5$ for liquid-like densities. Further, the simulation data is compared to a third order perturbation theory we recently presented.

*Corresponding author
Email address: gross@itt.uni-stuttgart.de (Joachim Gross)