238c Modelling of Strongly Polar and Polarizable Fluids and Their Mixtures

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Mixtures containing strongly polar components often exhibit a non-ideal phase behavior (e.g. azeotropes), resulting from the differences in molecular interactions. Different approaches were developed for dipolar interactions, which explicitly account for the effect of polarity to the Helmholtz energy of a mixture and therewith to an equation of state. Most of them are suitable for dipolar components of moderate dipole moments of up to 2 D as e.g. ketones, ethers and esters and their mixtures. However, so far the effect of very strong dipolar interactions could not be described satisfactorily.

To account for the non-additive dipolar induction due to the polarization of molecules, in this work the renormalized perturbation theory for polarizable polar fluids of Wertheim was applied in combination with a new dipole contribution for non-spherical molecules. A comparison to simulation data of pure polarizable dipolar fluids indicates a good agreement between the renormalized perturbation theory and the simulations.

This study illustrates the suitability of perturbation theories to model real dipolar mixtures. In particular, the framework is applied with the Perturbed-Chain SAFT equation of state to model phase equilibria of real mixtures containing strongly polar components as e.g. dimethylformamide with a dipole moment of 3.82 D. Using experimental dipole moments and polarizabilities from independent sources, no additional adjustable parameters are thereby introduced in the equation of state. It is confirmed that accounting for dipolar interactions as well as for induction effects not only reduces the value of the binary interaction parameter, but in many cases significantly improves the description of pure-component and mixture phase equilibria of real components.