Development of New Molecular Models for Applications in Process Engineering on the Basis of Quantum Chemical Calculations

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Molecular modeling and simulation opens new perspectives in process engineering, e.g., in thermo-physical fluid property modeling. With a comparable number of parameters molecular models give far better predictions of the properties of real fluids than phenomenological models [1-4]. In our group new molecular models of real fluids are systematically developed, that show excellent predictive power in a wide range of applications at relatively low computational cost [5,6]. A consistent model class, multi-center Lennard-Jones plus partial charges, point dipoles and point quadrupoles, is used, so that the pure component models can easily combined in mixtures [6,7].

In previous work, the parameterization of these models was done solely by adjustment to experimental VLE data. This procedure is limited to small and simple molecular models with only a few parameters. For more complex molecules only a part of the parameters can reasonably be derived from adjustment on thermo-physical data. In the present work a substantial part of the model parameters is determined from quantum chemical ab-initio calculations. Geometric parameters and electrostatics are directly used from quantum chemical computations at HF/6-31G and MP2/6-311 G* levels, respectively. For electrostatics, calculations are carried out in a dielectric cavity (similar to the COSMO method) to simulate the liquid state. Dispersive and repulsive interactions are modeled by Lennard-Jones potentials. These were adjusted to experimental VLE data, as here a quantum chemical calculation is very expensive and the accuracy would be questionable.

The above described procedure was used to parameterize molecular models of different technical interesting real fluids, e.g., ammonia, ethanol, acetone, dimethyl ether and cyclohexane. In the presentation the parameterization method will be discussed and results both for pure component and mixture properties will be shown.

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