Inclusion of Physical Terms in a Simultaneously Optimized Equation of State for the Description of Associating Fluids

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Recently, a new class of generalized equations of state for the thermodynamic properties of pure fluids has been proposed [1-4]. This kind of equation contains a restricted number of substance specific coefficients, allowing it to also be used on fluids with a scarce data base. Two up to date forms have been developed, respectively, for the two general categories 'non-polar fluids' and 'polar fluids'.

Aiming at an extension of this concept to strongly polar and associating fluids, a new approach has been tested, which combines a simultaneously optimized empirical form [1-4] with a physical term from the SAFT theory [5]. This physical term was directly formulated in the form of the Helmoltz energy-like modern multiparameter equations of state, so that the combination between these two approaches in a common mathematical framework could be achieved in a relatively straightforward way. The physical term and the simultaneously optimized empirical form contain 3 and 12 fluid specific fitting parameters respectively.

In a first step, two alcohols and one carboxylic acid have been selected as target fluids. As many fluids in the process and chemical industry, these fluids are affected by surface adsorption and chemical decomposition in different ranges of their thermodynamic states, which makes their experimental measurement particularly difficult. On the other hand, association makes their thermodynamic modeling particularly challenging.

A detailed comparison of the obtained equations with experimental data is presented showing advantages and limitations of the present approach. This contribution is part of an on-going project dedicated to the thermodynamic modeling of associating fluids like alcohols, carboxylic acids, inorganic acids, amines, and ethers with multiparameter equations of state.

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