Extension of association models to complex chemicals

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Summary of "Extension of association models to complex chemicals". Ph.D. thesis by Ane Søgaard Avlund The subject of this thesis is application of SAFT type equations of state (EoS). Accurate and predictive thermodynamic models are important in many industries including the petroleum industry. The SAFT EoS was developed 20 years ago, and a large number of papers on the subject has been published since, but many issues still remain unsolved. These issues are both theoretical and practical. The SAFT theory does not account for intramolecular association, it can only treat flexible chains, and does not account for steric self-hindrance for tree-like structures. An important practical problem is how to obtain optimal and consistent parameters. Moreover, multifunctional associating molecules represent a special challenge. In this work two equations of state using the SAFT theory for association are used; CPA and sPC-SAFT. Phase equilibrium and monomer fraction calculations with sPC-SAFT for methanol are used in the thesis to illustrate the importance of parameter estimation when using SAFT. Different parameter sets give similar pure component vapor pressure and liquid density results, whereas very different mixture results are obtained. The performance of the theory, therefore depends significantly on the parameter estimation, and this is important to consider if different theories (or association schemes) are compared. The CPA EoS has been applied for alkanolamines, as a continuation of a previous study, were only the simple 2 (1:1) and 4 (2:2) association schemes were investigated. It is in this work investigated for MEA (monoethanolamine) how the results with CPA is effected if a more advanced association scheme is used, where different association parameters are used for the different functional groups. It is also tested whether increasing the number of sites for DEA (diethanolamine) improves the results. It can be shown from experimental data that intramolecular association is dominating compared to intermolecular association in certain systems, and that the intramolecular association can significantly alter the phase behavior of a mixture. Lattice theories have earlier on been extended to include intramolecular association for polyethoxyalcohols, while SAFT has only been extended to intramolecular association for chains with 2 associating sites. A general theory for intramolecular association is presented in the thesis, and compared to the corresponding lattice theory. The theory for intramolecular association is then applied in connection with sPC-SAFT for mixtures containing glycol ethers. Calculations with sPC-SAFT (without intramolecular association) are presented for comparison, and the results with sPC-SAFT are moreover compared to results with CPA and SAFT-HS. The comparisons show that while the improved theory does improve the predictive performance of the model, the choice of association scheme and the parameter estimation are at least as important. In general it is found in this project that the parameter estimation is very important for the performance of a SAFT EoS, and that emphasis should be put on that area as well as on improving the theory.

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