

An Examination of the Excess Thermodynamic Properties of Flexible Molecules from a Molecular Modelling Perspective

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Excess thermodynamic properties provide fundamental information on the intermolecular interactions between the species forming binary and multicomponent systems. However, phase equilibria data is normally used to test the accuracy of a theory or molecular model in predicting the thermodynamic behaviour of a given mixture. Although this approach is valid and adequate in a number of cases, some situations require stronger tests to truly determine whether a model and/or theory can predict a particular system. Excess properties serve as a valuable tool for this purpose because they are generally more sensitive to the molecular details than are phase equilibria. The goal of this work is to show how simple models, with a number of molecular parameters, are able to predict accurately excess thermodynamic properties. We concentrate on binary mixtures formed by different models of flexible molecules. In particular, we focus on two general models: the fully flexible tangentially bonded Lennard-Jones chains model and the family of united-atom realistic models for alkanes. Whereas the first model has neither bending nor torsional potentials between the monomers in the chains and bond length equal to the monomer sizes, the second one incorporates more realistic microscopic features, including bending and torsional intramolecular interactions, among others. The Statistical Associating Fluid Theory for potentials of variable range (SAFT-VR) [1] and Monte Carlo and Molecular Dynamics simulation are used to predict the phase behaviour and excess thermodynamic properties of the models considered. Although some molecular models are relatively simple [2], they are able to describe most of the important microscopic features of real chainlike molecules. The predictions obtained from theory and simulation are compared with experimental data available in the literature. The agreement between the experiments and predictions is good for a wide range of thermodynamic conditions. In addition to the vapor-liquid equilibria, the theory is able to characterize the most salient features of two important excess thermodynamic properties: the excess volume and heat.

[1] Gil-Villegas, A.; Galindo, A.; Whitehead, P. J.; Mills, S. J.; Jackson, G. and Burgess, A. N. *Journal Of Chemical Physics*, 1997, 106, 4168.

[2] McCabe, C.; Jackson, G. *Physical Chemistry Chemical Physics*, 1999, 1, 2057.