Technical Article – Physical Property Prediction

Physical Property Prediction for the Twenty-First Century: The SAFT-γ Mie Group Contribution Approach

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Thermodynamic methodologies are continuously being developed and improved in order to meet the industrial requirements for accurate property prediction in an ever expanding range of applications. An important consideration is the predictive capability of these methods, commonly perceived as the ability to predict the properties of a system for which no experimental data is available. Such predictive methods allow for application within integrated process and solvent design as fluid formulation tools. An important class of predictive thermodynamic models are group contribution (GC) approaches, where molecules are modelled based on their corresponding chemical moieties, and the molecular properties are then obtained from the contributions of these specific chemical structural groups to the thermodynamic properties.

The key assumption of GC approaches (at first level) is that these chemical moieties are described by a set of transferable group parameters, or in other words, that they give rise to the same behaviour regardless of the molecule on which they are present. In the Molecular Systems Engineering group we have recently developed the SAFT-γ Mie group contribution approach, which brings together the molecular rigour, accuracy and versatility of the SAFT formalism with the predictive capabilities intrinsic of the GC concept. More specifically, the SAFT-γ Mie GC approach has been developed on the premise of the molecular-based SAFT-VR Mie equation of state, where the intermolecular potential employed for the description of the interactions between segments is a Mie (generalised Lennard-Jonesium) potential with variable repulsive and attractive interactions. The key elements of the newly presented SAFT-γ Mie (and the SAFT-VR Mie) approaches are the significantly improved description of the fluid-phase behaviour at conditions near to the critical point, and the ability to simultaneously describe, based on a single set of group parameters, the fluid-phase behaviour and second-order thermodynamic derivative properties (e.g., the heat capacity, compressibility, thermal expansivity etc.) of a variety of pure substances and mixtures over a large region of thermodynamic conditions.

Some highlights of the performance of the SAFT-γ Mie approach are illustrated in this article. In Figure 1 the description obtained with the SAFT-γ Mie approach is compared to the experimental vapour-liquid and liquid-liquid equilibrium (VLE and LLE) data for the phase behaviour of the acetone + *n*-hexane binary mixture. An excellent agreement between the theoretical description and the experimental data is seen, and for the region of liquid-liquid immiscibility both the compositions of the two phases in coexistence, as well as the upper critical solution temperature are very well described. This is a very challenging task and is worth noting that a single set of interaction (group) parameters is employed for the description of both types of equilibrium (VLE and LLE), and is transferable to other mixtures involving acetone and hydrocarbons.

Another interesting example is shown in Figure 2 where the SAFT-γ Mie description of the composition of the two liquid phases in coexistence at pressures along the orthobaric 3-phase line (VLLE) of the binary mixture of benzene + water is compared to experimental data. It is apparent that the SAFT-γ Mie approach provides an excellent description of the fluid-phase behaviour of the system, including the very low composition of benzene in the water-rich phase, which is accurately reproduced.

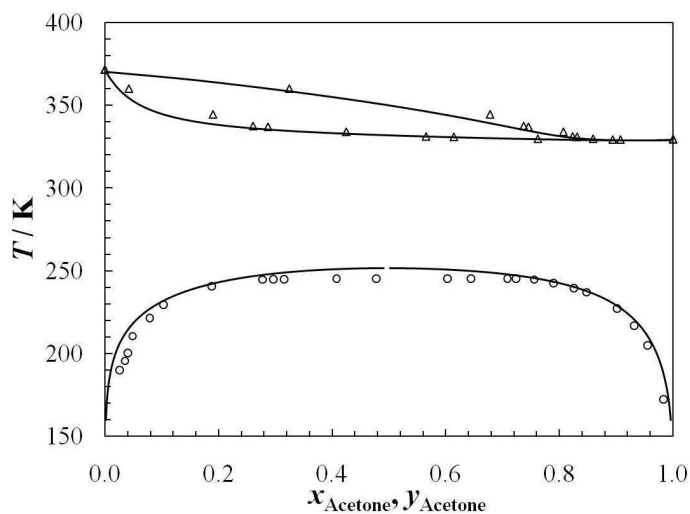## Technical Article – Physical Property Prediction

Figure 1. SAFT-g Mie description of the fluid-phase behaviour (vapour-liquid and liquid-liquid) of the binary mixture of acetone + *n*-heptane as a temperature-composition (*T*-x) slice at *p* = 0.10132 MPa. The open triangles represent the experimental data for the vapour-liquid coexistence and the open
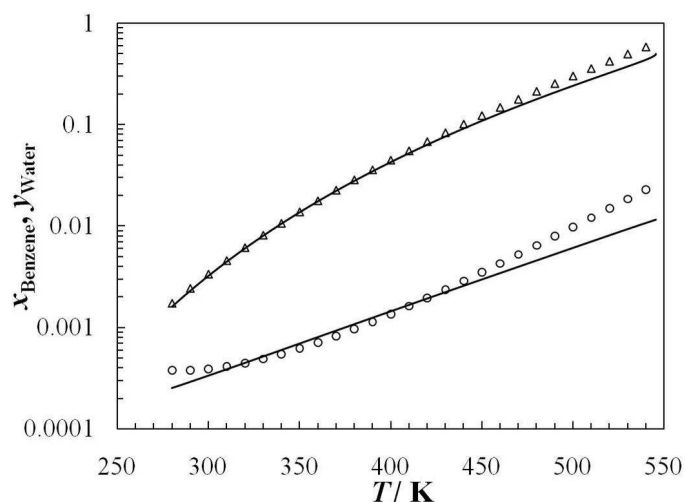

Figure 2. SAFT-g Mie description of the fluid-phase behaviour (liquid-liquid equilibrium) of the binary mixture of benzene + water as a temperature-composition (*T*-x) projection at pressures along the orthobaric line of vapour-liquid-liquid equilibrium. The open triangles represent the experimental data for the composition of water in the benzene-rich (liquid) phase and the open circles for the composition of benzene in the water-rich (liquid) phase.

An exciting application of such predictive approaches is in the description of the solubility of complex molecules, such as active pharmaceutical ingredients (APIs), in solvents and solvent mixtures. The advantage of a predictive approach in this case is that the parameters required for the solubility prediction can be developed from experimental data for simple systems. Hence, the solubility of a given API is obtained in a

fully predictive manner, without the requirement for API-specific experimental data for the parameterisation of the model. The potential of the SAFT-γ Mie approach in predicting the solubility of APIs in organic solvents is illustrated by the example depicted on Figure 3, where the solubility of ibuprofen in a range of organic solvents obtained with the theory (based on preliminary group parameters) are compared to the corresponding experimental data. Good agreement between the predictions of the theory and the experimental data is seen, and the correct ranking of the solvents is successfully reproduced.

These examples offer an insight into the accuracy and predictive capabilities of the SAFT-g Mie GC approach for the simultaneous description of vapour-liquid, liquid-liquid and solid-liquid equilibria in complex mixtures.
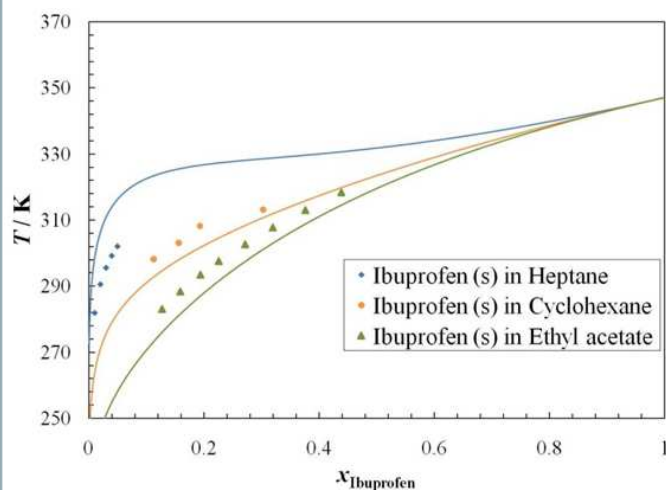

Figure 3. Description of the solubility (solid-liquid equilibrium) of ibuprofen in a range of organic solvent as a temperature-composition (*T*-x) projection at *p* = 0.10132 MPa. The symbols represent the experimental data: blue for the solubility in *n*-heptane, orange for the solubility in cyclohexane, and green for the solubility in ethyl acetate, and the corresponding continuous curves the predictions of the SAFT-g Mie GC approach.

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V.Papaioannou, T. Lafitte, C. Avendaño, C.S. Adjiman, G. Jackson, E. A. Müller, and A. Galindo, *J. Chem. Phys.* **140**, p. 054107, (2014).

T. Lafitte, A. Apostolakou, C. Avendaño, A. Galindo, C.S. Adjiman, E. A. Müller, and G. Jackson, *J. Chem. Phys.* **139**, p. 154504, (2013).