

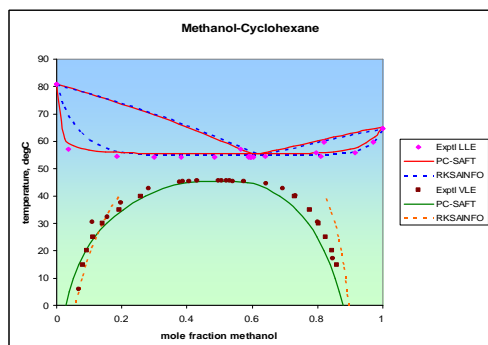
Multiflash: PC-SAFT Model

Introduction

Equations of state have traditionally been applied to systems involving relatively simple fluids such as those involving light gases and hydrocarbons. The introduction of non-standard mixing rules to cubic equations of state does extend their use for some non-ideal mixtures but the development of the Perturbed Chain Statistical Associating Fluid, PC-SAFT, equation of state has produced a model that can be applied to complex and macromolecular compounds. Many papers in the literature have detailed its application to highly asymmetric and associating mixtures. However a major application must be its ability to handle polymeric systems. Due to the large difference in the molecular sizes of polymers and solvents the excess Gibbs free energy models fail to predict the phase and volumetric behaviour.

Associating Systems

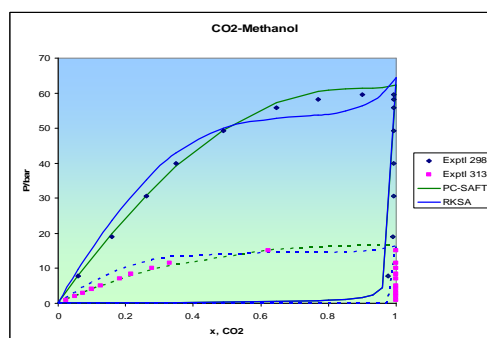
Modelling phase equilibria and thermodynamic properties of mixtures in which molecules associate is a challenging problem for the chemical industry. The Infochem implementation of PC-SAFT includes the Wertheim chemical association term. The phase behaviour of a system with one associating substance, methanol-cyclohexane, is shown. This system exhibits an azeotropic vapour-liquid equilibrium at higher temperatures and a liquid-liquid equilibrium at lower temperatures. In addition to the pure component PC-SAFT parameters, and the parameters to allow for the self-association of methanol, a single k_{ij} has been fitted to the binary liquid-liquid data.



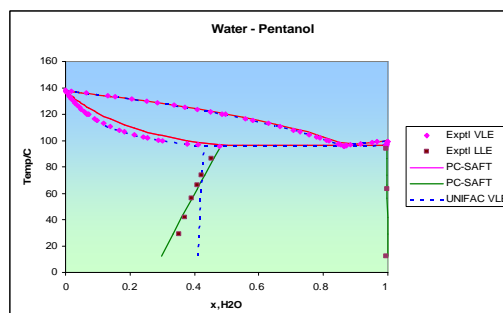
The behavior of the system, particularly the LLE, is much better represented with PC-SAFT than with a cubic equation of state with an excess G^E style mixing rule, RKSAINFO.

The PC-SAFT model requires several pure component parameters, particularly for associating components. Infochem take these from published academic research, mainly from papers by Sadowski et al., who have covered a range of components. The k_{ij} , if required, can be fitted to data as for most models.

For the following system, CO₂-methanol, the pure component SAFT parameters were already stored in Multiflash but the k_{ij} was generated by fitting. The shape of the curve agrees better with the data than that generated by standard cubic equations of state.



The modelling of mixtures where associating interactions occur between different substances is even more demanding. The phase behaviour of water-pentanol is shown below. This system has a liquid-liquid equilibrium at lower temperatures and a heteroazeotropic vapour-liquid equilibrium. The PC-SAFT model reproduces both types of behaviour with a single k_{ij} fitted to the LLE data. The comparison to the results from the UNIFAC VLE model show that the VLE data are reproduced but not the LLE data. Using the UNIFAC LLE variant, with different parameters, doesn't improve either LLE or VLE.



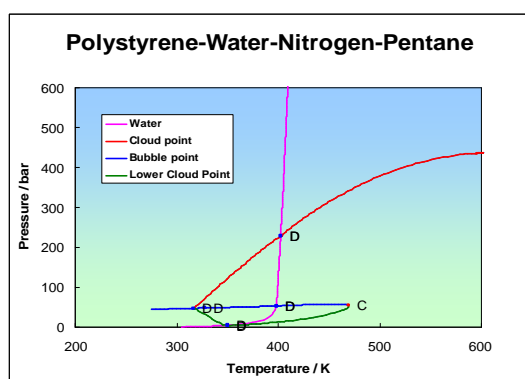
Polymer Systems

PC-SAFT has been successfully applied to a range of polar and non-polar substances but one of the most important areas of application is polymers. Polymers are not well defined chemical compounds but rather a distribution of chain molecules of varying molecular weight. In Multiflash, polymers are represented by one or more components which are set up as user-defined compounds.

A polymer can be represented by several components, each of which represents the same polymer structure but which are of different lengths—similar to pseudo components for an oil. Each sub-polymer is composed of a different number of segments and has a different molecular weight, allowing for poly dispersity.

If the polymer is a homo-polymer, and each segment is the same, then certain of the SAFT pure component parameters must be the same. One parameter, which relates to the number of segments in the chain can be calculated from the molecular weight and the bond fraction. The user can define association parameters if the polymer forms hydrogen bonds

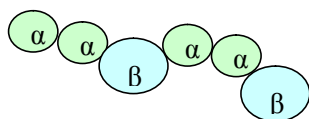
The figure shows the phase boundaries for a mixture of polystyrene, water, nitrogen and pentane. The red line is the cloud point.



PC-SAFT has been successfully applied in areas of industrial interest, including modelling of the safety aspects of the styrene polymerization process such as runaway reactions.

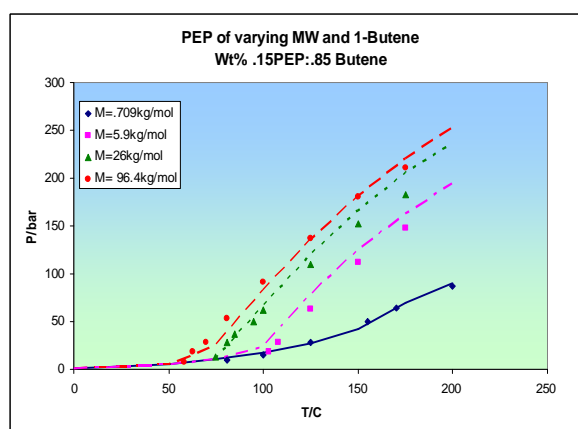
Copolymer Systems

In practice most industrially produced polymers are not homo-polymers but copolymers, composed of different types of repeat units.



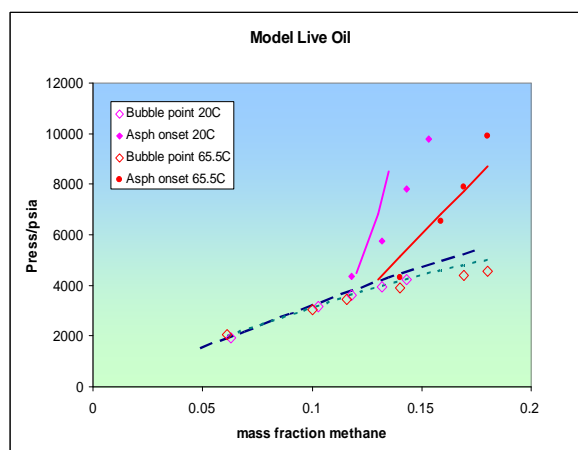
The repeat units may be arranged alternately or in a random fashion. The Multiflash implementation allows the user to define up to four different polymer segments.

The liquid-liquid equilibrium of an alternating ethylene-propylene co-polymer (PEP) of varying chain length in a mixture with 1-butene is shown below. The experimental cloud points are compared to calculations using PC-SAFT.



Other Applications

An interesting application of PC-SAFT to the prediction of asphaltene precipitation is being investigated by Rice university using their own and the Multiflash implementation. In-fochem's own Asphaltene model, and the Firoozabadi model based on PC-SAFT, assume that solvation of asphaltene by resins is the primary driving force in asphaltene precipitation. However, Rice assume that molecular size and non-polar van der Waals interactions dominate asphaltene phase behaviour in crude oil, i.e. asphaltenes exhibit poly dispersity analogous to that shown by polymer systems.



Initial calculations for a "Model oil" of asphaltene, toluene and varying amounts of methane show promise.

Another research group aims to extend the PC-SAFT equation of state to account for ion-ion, ion-dipole and dipole-dipole interactions to describe electrolyte systems from aqueous electrolytes up to polyelectrolytes.

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