This article first appeared in *tce*, which is published monthly by the Institution of Chemical Engineers
Editorial: aduckett@icheme.org, Subscriptions: jcressey@icheme.org
Advertising: nigel.stephens@mainlinemedia.co.uk
www.tcetoday.com

tce

the chemical engineer | issue 824 | february 2010

future foods

coding caviar to avoid species extinction

CHEMICAL ENGINEERS WHO CHANGED THE WORLD | PROCESS SIMULATION | ARSENIC REMOVAL

Model behaviour

Mark Matzopoulos explains new physical property modelling techniques for strongly associating systems and polymers

Physical properties are at the heart of virtually every calculation performed by practising chemical engineers. The size of vessels, operating conditions, temperatures, energy requirements, safety limits and many other critical design and operating quantities all depend on the intrinsic properties – vapour pressure, density and phase partitioning, for example – of the fluids being processed.

The last 20 years have seen significant research into 'advanced molecular thermodynamic' methods aimed at improving the representation of pure component and mixture properties, making it easier to determine properties for new components and apply these within process modelling tools. Much of this effort centres on statistical associating fluid theory (SAFT).

The SAFT approach allows many different thermodynamic properties of mixtures to be determined accurately based on models of molecules and their interactions. These are much more sophisticated than those used by more well-known techniques such as the cubic equations of state. The resulting fluid model can then be used to accurately predict a wide range of properties over a range of operating conditions.

SAFT is particularly good for strongly-associating systems, such as the azeotropic hydrogen fluoride-water mixture used in the production of refrigerants, aqueous solutions of non-ionic surfactants and even strong electrolyte solutions. It also accurately quantifies the behaviour of systems involving high molecular weight components, such as polymer-gas systems – all typically poorly represented by conventional equations of state.

The development of SAFT has been given a strong focus at Imperial College London, where a team of around 25 are working on molecular systems engineering (MSE) funded by a £3.6m ($5.8m) EPSRC grant. The key focus of Imperial's SAFT group, led by George Jackson, Amparo Galindo and Claire Adjiman, is in providing thermodynamic modelling tools for industry.

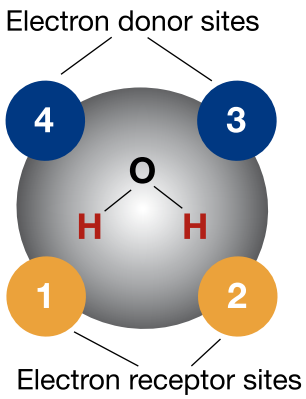
background

At its heart SAFT is an equation of state, a term likely to send shivers down the spine of any chemical engineer who endured a course in thermodynamics. SAFT embodies significant advances over the traditional van der Waals equation or cubic engineering equations such as Peng-Robinson, which are better suited to near-spherical molecules.

The main difference is that the SAFT equation is underpinned by a physically realistic representation of the molecule that includes its shape, size and the interactions between molecules – for example, hydrogen bonding within a mixture.

The major advantage over other thermodynamic methods is that because the underlying molecular model has a much more physically meaningful basis, SAFT's predictions can be extrapolated much more widely – a particular advantage for systems where there is limited experimental data in the areas of operation being studied.

Also, traditional equations of state cannot adequately represent the behaviour of systems involving complex materials such as polar solvents, hydrogen bonded fluids and polymers. SAFT's associating fluid approach – which can account for the electrostatic, polar and other association forces that need to be considered – provides an unprecedented capability for modelling such systems accurately.

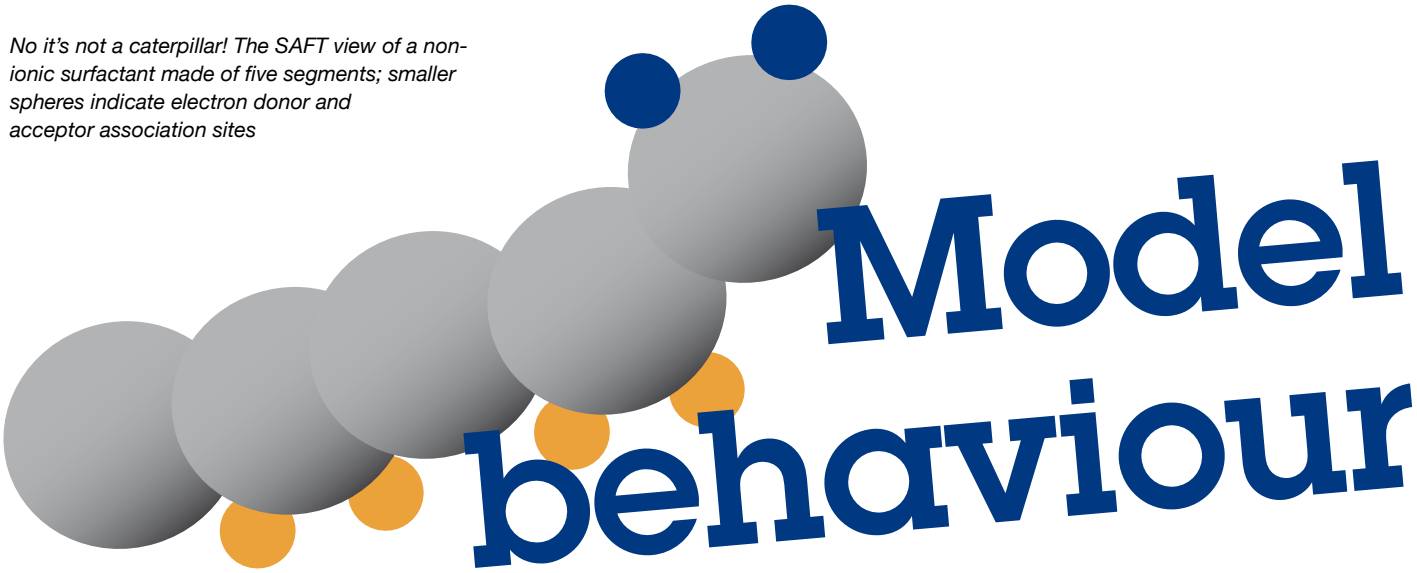


Water molecule showing association sites

One challenge that needs to be overcome is that of computational efficiency. In typical process simulations, physical properties are responsible for about 70% of computational time. The complexity of the underlying SAFT equations, which require solution of a system of non-linear equations and evaluation of its partial derivatives for every property calculation, brings additional demands as well as potential robustness issues. These are important concerns since a typical simulation will involve thousands of calls to the physical property package.

how it works

In SAFT, molecules are modelled as chains formed from spherical segments, and it's possible to add so-called association sites on the segments to treat as hydrogen bonds or



No it's not a caterpillar! The SAFT view of a non-ionic surfactant made of five segments; smaller spheres indicate electron donor and acceptor association sites

case study

The Imperial team worked with ICI and Ineos Fluor to apply SAFT-VR techniques to chemical processes for refrigerants such as the hydrofluorocarbons (HFCs) being used as replacements for the CFC refrigerants responsible for the depletion of ozone in the upper atmosphere.

HFC production involves mixtures containing hydrogen fluoride (HF) which, because of the extremely strong association between HF and water molecules, are particularly difficult to characterise with standard thermodynamic methods. SAFT-VR provides an excellent description of the vapour-liquid and liquid-liquid equilibria in these systems, which was used to design and optimise operation of the HF–water separation process.

At the other end of the molecular scale, SAFT-VR also provided an excellent description of the phase equilibria of aqueous solutions of hydrocarbons and micellar solutions of alkyl polyoxyethylene surfactants and polyethylene glycol (PEG) in work with BP Exploration, Schlumberger and ICI. These systems are key ingredients in numerous applications ranging from personal care formulations to enhanced oil recovery that can extend well lifetime by a factor of two or three.

In a recent collaboration with the Borealis Group, SAFT-VR was used to analyse phase behaviour (adsorption) in gas phase polymerisation reactions.

The analysis suggested that replacement of the inert nitrogen gas by less volatile n-pentane would significantly increase the catalytic activity of the reaction. Borealis has subsequently verified at bench scale a 30% increase in the yield of polythene compared to the conventional mixture, with no change required in the reactor conditions.

> ***"SAFT has opened up new approaches that could revolutionise the design of industrial processes"***

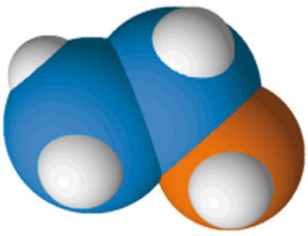
strongly polar interactions.

The basic SAFT approach starts by describing 'ideal' molecular behaviour in terms of the usual translational, rotational and vibrational kinetic energy terms. The various 'non-ideal' terms are then introduced separately: terms for the forces of attraction and repulsion between segments making up the molecules, chain bonding representing the contribution due to the formation of chains, and forces of association – for example, those resulting from hydrogen bonds in aqueous mixtures.

There are various implementations of the underlying SAFT model, which differ principally in terms of the mathematical representation of the molecule and the specific forms of the various contributions. The approach taken by the Imperial team is known as SAFT-VR, where VR stands for "variable range".

Key to the behaviour of molecules that form hydrogen bonds, such as water or the amine solvent MEA (monoethanolamine), is the definition of association sites – 'electron donors' or 'electron acceptors' – which are used to quantify hydrogen bond formation between molecules.

It's these association sites that provide SAFT's unique capability in dealing with aqueous solutions, surfactants and other strongly-associating components, allowing engineers to design and optimise processes that have never been able to benefit from the application of modern model-based engineering techniques before.

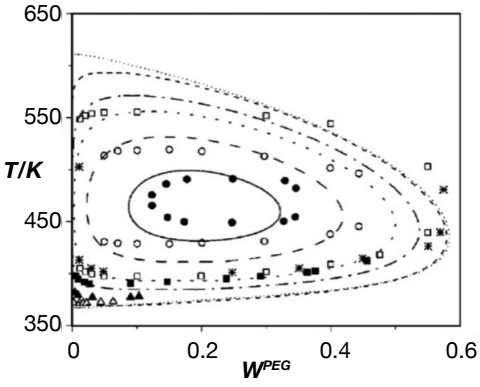


SAFT ethanol

Parameters defining all the relevant quantities that define the model for a given molecule – for example, the number and diameters of spherical segments, the number and type of association sites – are estimated from experimental data. Typically this data includes saturated vapour pressure and density measurements at different temperatures. Where available, mixture data is also used. One of the Imperial team's main activities is to build the growing databank of pure component and mixture parameters.

other key advantages

There are other advantages. For example, it's possible to transfer parameters from one molecule to another within the same class (for example, from n-alkanes to polyethylene), thus reducing or eliminating the need for measurement – although, says Galindo, "good experimental data always helps."



Above: Closed loop regions of immiscibility of aqueous solutions of PEG of molecular weight from 2180 g/mol (smallest loop) to 1,020,000 g/mol (largest loop)

For mixtures, predictions based on data fitted in one area of operation remain valid over a wide range of operating states. For example, liquid-liquid equilibrium behaviour can be predicted accurately using parameters fitted solely against vapour-liquid data, decreasing the need for complicated and often-unreliable laboratory LLE measurements.

"This is the closest that we have come to a truly universal tool for predicting pure component and mixture properties", says Jackson. "What is more it predicts phase equilibrium properties within a few percent for a vast array of complex systems."

integrated approach

Not only does SAFT simplify standard engineering design problems, it has opened up new approaches that could revolutionise the design of industrial processes. Because properties models can be closely integrated with process models it's possible to incorporate molecular-level decisions (including molecular architecture, microstructure, solvent selection, mixture formulation and so on) within the process design procedure and take decisions simultaneously rather than sequentially.

"A new approach is to design molecules and processes hand-in-hand, so that the whole system is optimal – a significant challenge because of the complexity of the physical description and the wide range of length-time scales involved," says Adjiman.

The integrated approach is exemplified by Imperial's work on the development of efficient and cost-effective solutions for CO_2 capture – a key component of most practical carbon abatement systems – through simultaneous optimisation of process and solvent design. Traditionally, decisions on

solvents are taken first then the process is designed around the 'constraints' posed by the solvent choice, potentially resulting in seriously sub-optimal performance.

commercialisation

Imperial has licensed the software to Process Systems Enterprise (PSE), which has very close links with the chemical engineering community at Imperial (the company was an early spin-out of the college), and has a significant chemical industry user base and an already-large number of academic users of its software . SAFT-VR is already interfaced with PSE's gPROMS suite, and the company is offering free trials of the capability to selected gPROMS industrial users in the chemical and polymers sectors.

reducing reliance on experimental data

Work at Imperial continues in a number of promising directions. Most of the research is related to refining the underlying molecular model, to make it as easy as possible to predict properties for existing and new molecules, and to make those properties as accurate as possible.

One major area of research relates to a new approach known as SAFT- ɣ , a group contribution method that embodies the concepts of the original UNIFAC approach developed by Fredenslund, Prausnitz and co-workers in the 1970s and 80s, but applying the 'molecular model' principles of SAFT. SAFT- ɣ is immensely powerful in terms of property prediction; once the basic functional groups defining a molecule have been characterised, pure component and mixture behaviour can be predicted very accurately with no need for experimental data-fitting whatsoever.

"It's early days for SAFT- ɣ ", says Jackson, "but initial results are very promising. We can predict mixture properties over a wide range of conditions without any data. This will significantly reduce the time and effort required to ensure accurate physical property calculations in a wide range of industrial process design projects in the future."

The MSE group has just won a £150,000 Research Excellence award from Imperial that will be used to accelerate technology transfer to industry. **tce**

Mark Matzopoulos (m.matzopoulos@psenterprise.com) is coo of London-based process modelling software supplier PSE

> *"This is a tool that will significantly reduce the time and effort required to ensure accurate physical property calculations"*