**Technical Article – Molecular Systems Engineering**

# Expanding the applicability of the SAFT-g group contribution equation of state

Claire Adjiman

The group contribution reformulation of the statistical associating fluid theory (SAFT) equation of state, referred to as SAFT-γ, is one of the key developments to have emerged from CPSE and its Molecular Systems Engineering group in the area of molecular thermodynamics. In this short article, we describe recent developments and future efforts in extending the types of compounds and mixtures that can be modelled with SAFT-γ. For further details of the background to the SAFT and SAFT-γ family of equations, the reader is referred to our previous technical article[i] and references therein.

The process of recasting the SAFT equation of state as a group contribution equation[ii,iii,iii] has greatly expanded the range of compounds and mixtures for which the phase behaviour and thermodynamic properties can be *predicted* with SAFT, even in the absence of experimental data. SAFT-γ has been developed in two forms: one based on a square-well (SW) intermolecular potential; and one on a Mie potential. While the Mie potential offers improved accuracy, especially with respect to caloric properties, the SW version allows for fast prototyping of new concepts. In recent years, several members of the Molecular Systems Engineering team have collaborated with industrial partners to address a variety of applications and increase the size of the chemical space that can be modelled with SAFT-γ.

## The group parameter table

The group parameter table lies at the heart of the SAFT- γ concept and determines which mixtures can be modelled. Recent effort has been devoted to: i) expanding the table; and ii) improving the methods by which the group parameters are derived, to achieve improved predictive accuracy and shorter development times. While the group parameters are being developed as part of projects that are focused on different industries, the parameters can be transferred from project to project, so that our partners are able to derive benefits from research carried out in different, non-competitive, industrial contexts. Recent focus has, for example, included the oil and gas sector, the power generation industry, pharmaceuticals and consumer products. There exists significant overlap between the basic chemical functionality in these industries: the alkyl, alkenyl, phenyl or benzyl groups, of course, but also hydroxyl, ether or carboxyl groups, and their interaction with water and other key molecules (carbon dioxide, acetone).

Working with different sectors has also helped us to develop an increasingly reliable representation of the contribution a chemical group makes to the thermophysical properties, across multiple applications. It has led us to expand the range of data considered in developing group parameters. For example, an accurate prediction of the mutual solubilities of alkanes and water, which span several orders of magnitude, is of most direct relevance to the oil and gas industry. In addition, we have shown that accurate water-alkane solubilities are also key to achieving reliable predictions for the partitioning of pharmaceutical molecules in octanol and water.

In the remainder of this article, we highlight recent developments in the parameter table and applicability of SAFT-γ.

## The SAFT-γ Mie parameter table

The most recent version of the SAFT-γ Mie parameter table in use by CPSE is shown in Figure 1. In addition to the groups shown here, other groups have been the subject of recent research, including $(CH_3)$-O- and $(CH_2)$-O- for ethers (and their interactions with methane and carbon dioxide) and $CH_2OH$. Representative highlights of the predictive accuracy achieved with the available parameters are shown in Figures 2 to 4, including the vapour-liquid and liquid-liquid equilibria of acetone + *n*heptane (Figure 2[iv]) the mutual solubilities of water and *n*-alkanes (Figure 3), and the solid-liquid phase equilibria of ibuprofen and ketoprofen in acetone (Figure 4). For the latter mixtures, we note that solubility data for ketoprofen and ibuprofen was not used in obtaining the relevant group parameters, highlighting the predictive capabilities of the SAFT-γ Mie framework.

## Technical Article – Molecular Systems Engineering

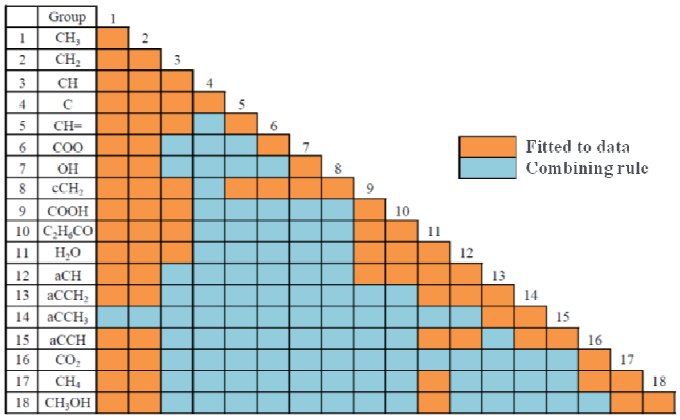


**Figure 1.** The current SAFT-γ Mie group parameter table, showing in orange groups that have been estimated from experimental data and in blue groups that can be calculated using combining rules.

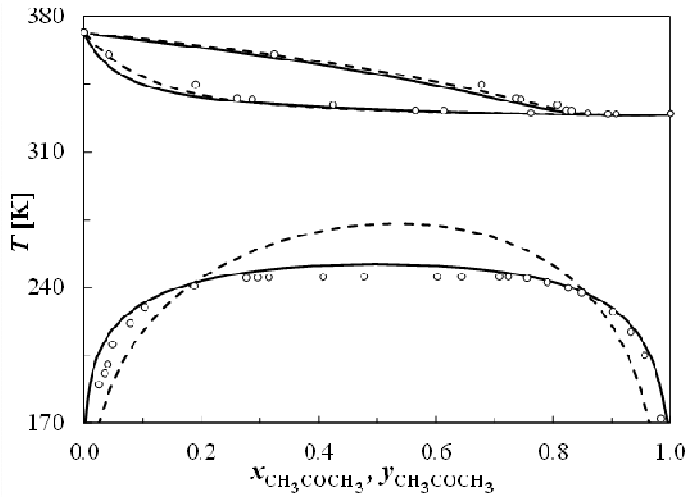


**Figure 2 -** Isobaric temperature-mole fraction (*T*-*x*) phase diagram of acetone + n-heptane at constant pressure of *P* = 101 kPa[v]. The symbols represent the experimental data, and the dashed and continuous curves the description with modified UNIFAC approach and SAFT-γ Mie method.

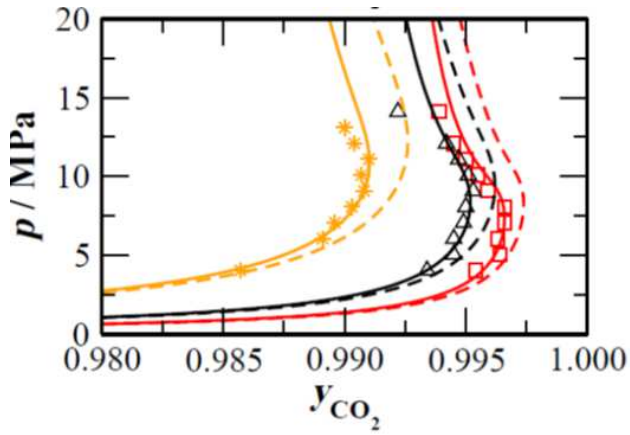


Figure 3 - Isothermal pressure-mole fraction (p-y) of the vapour-liquid and liquid-liquid equilibria of water + carbon dioxide, showing the carbon dioxide-rich phase. The symbols represent the experimental data[vi] at temperatures of T = 323 K (red squares), T = 333 K (black triangles), and T = 353 K (gold asterisks), while the continuous curves represent the description with the SAFT-ã Mie approach and the dashed curves the description with the PR76 equation of state.

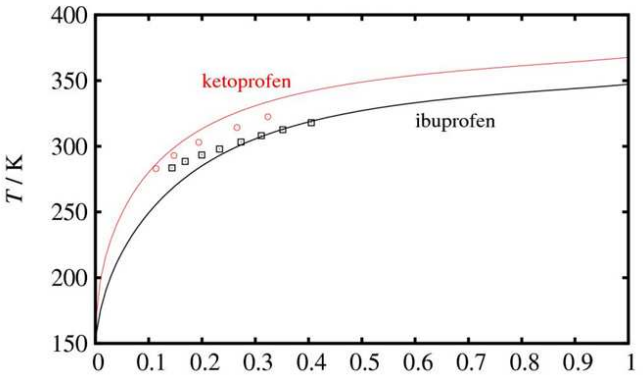


**Figure 4** – Solid-liquid equilibria of ibuprofen (black) and ketoprofen (red) in acetone as a function of temperature *T*, and at a pressure of *P* = 101 kPa. The continuous curves are SAFT-γ Mie predictions and the symbols are experimental data[vii]. $x_{API}$ denotes the mole fraction of the drug (active pharmaceutical ingredient, API).

### Current and future focus of parameter development

Priority chemical groups for the future include *heterocycles* and *amine* functionality. In addition, *charged and reacting systems* are the focus of a significant effort within the Molecular Systems Engineering group. These include:

- predictive group contribution capability for alkanolamine + carbon dioxide + water mixtures, for use in carbon capture. This concept has been demonstrated successfully with the SAFT-γ SW equation of state (cf Figure 5[viii]), and is under development for SAFT-γ Mie. It is expected this will lead to improved predictions of the heat of absorption in different solvents;
- extending the successful modelling of strong electrolytes (e.g., brines) to weak electrolytes, with applications to charged surfactants (e.g., SDS) and multifunctional molecules (e.g., drug molecules), and to alkanolamine carbon dioxide capture mixtures. This will include the effect of pH on thermodynamic properties;

## Technical Article – Molecular Systems Engineering

- extending the range of solvents and additives that can be modelled, to enhance the use of SAFT-γ Mie in molecular design, formulation design and integrated molecular and process design[i x].

The Molecular Systems Engineering group also has extensive experience of modelling mixtures containing polymers, refrigerants and fluorinated compounds, and is therefore keen to expand the parameter table to include groups relevant to these systems.

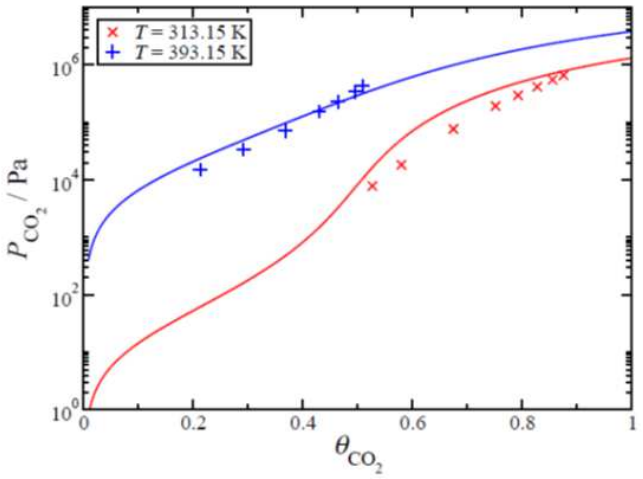


**Figure 5** - Solubility of carbon dioxide in a 30 wt% (by mass) monopropanolamine (MPA) aqueous solution at $T$ = 313.15 K (red crosses), and 393.15 K (blue pluses) as a function of the partial pressure of $CO_2$ at vapor-liquid equilibrium for the ternary mixture of MPA + $H_2O$ + $CO_2$. The solubility is represented as $CO_2$ loading $\theta_{CO2}$, defined as the number of moles of $CO_2$ absorbed in the liquid phase per mole of amine in the liquid. The symbols correspond to the experimental data[x] and the curves correspond to the SAFT-γ SW calculations.

### Can you model "my" mixture?

Making our research relevant and available to industry is a cornerstone of CPSE. This perspective pervades our research and has motivated us to make advances in thermodynamic modelling available to industry, by transferring our codes to PSE[x]. These have been incorporated into the gSAFT technology, available since 2014, and we continue to collaborate with PSE to improve this powerful thermodynamic tool. We are confident that this will provide a significant benefit to our research partners, who can quickly deploy our research findings in their own work.

Because the group parameter table is central to the predictive capabilities of SAFT-γ, every SAFT based project we undertake contains elements of parameter estimation, ensuring that the table is constantly expanding. The Molecular Systems Engineering group welcomes the opportunity to work with partner companies in order to focus on particular chemical groups. Depending on the nature of the project and its objectives, this may be carried out in conjunction with theoretical developments, involving PhD students and postdoctoral researchers as appropriate. In such cases, the SAFT-γ group parameters are normally obtained based on published experimental data and become part of CPSE publications and student theses. In other cases, it may be more appropriate to undertake parameter development as a consulting project, using proprietary data or focusing on a proprietary application; this may be carried out in conjunction with PSE as appropriate. In such a case, the parameters become the property of the industrial partner. In all cases, the SAFT-γ group parameters can be made accessible to users of gSAFT, as a public or access-restricted databank of parameters, ensuring that the research carried out in CPSE is quickly accessible to industry.

***The CPSE Newsletter comes with technical articles. Consortium Members are encouraged to suggest specific areas/topics that interested them. Please email Miss Senait Selassie: s.selassie@imperial.ac.uk***

**References**

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).

Lymperiadis, A., Adjiman, C.S., Galindo, A., Jackson, G., Journal of Chemical Physics, 127 (2007) 234903.

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

Sadeqzadeh, M., Papaioannou, V., Dufal, S., Adjiman, C.S., Jackson, G., Galindo, A., Fluid Phase Equilibria, invited special issue. Submitted (2015)

W. Wolff and K. Bernstorff, Z. Phys. Chem., 14 (1958)208; A. Zacharias, D. Srinivasan, and M.G.S. Rau, Indian J. Technol., 14 (1976) 162.

Bamberger, A., Sieder, G., Maurer, G., J. Supercrit. Fluids, 17 (2000) 97.

Espitalier, F., Biscans,B., Laguerie, C., J. Chem. Eng. Data, 40 (1995); Wang, S., Song, Z., Wang, J., Dong, Y., Wu, M., J. Chem. Eng. Data, 55 (2010).

Chremos, A., Forte, E., Papaioannou, V., Galindo, A., Jackson, G., Adjiman, C.S., Fluid Phase Equilibria, invited special issue. Submitted (2015)

Burger, J., Papaioannou, V., Gopinath, S., Jackson, G., Galindo, A., Adjiman, C.S., AIChE Journal, doi: 10.1002/aic.14838 (2015)

L. Dong, J. Chen, G. Gao, J. Chem. Eng. Data 55 (2010) 1030.

http://www.psenterprise.com/gsaft.html