

## Faraday Discussion - Carbon Capture and Storage

GJ replies

You have answered 9 specific questions.

1) 520 berend.smit@epfl.ch asks

We have now seen two methods of predicting properties of gasses and liquids: SAFT and Molecular simulations. Could each of you outline under which conditions one would like to use one approach and or the other approach? (paper 1)

Your reply

The statistical associating fluid theory (SAFT) is a molecular-based equation of state developed as a perturbation expansion from a hard-sphere reference system (e.g., see the latest incarnations of the theory based on the Mie generalized Lennard-Jones potential by T. Lafitte et al., *J. Chem. Phys.* 139, 154504 (2013)). As such SAFT approaches provide a reliable and efficient algebraic description of the thermodynamic properties and fluid-phase equilibria of complex fluids (ranging from mixtures of small polar and associating fluids to solutions of macromolecules). The group-contribution reformulations of SAFT are particularly useful for predictions based solely on a knowledge of the chemical functionality of the molecules in the system (e.g., see SAFT- $\gamma$  Mie, V. Papaioannou et al., *J. Chem. Phys.* 140, 054107 (2014)). Equations of state do not, however, directly inform on structural, interfacial, on transport properties. On the other hand molecular simulation offers a direct route to all thermodynamic, surface and dynamical properties providing one has an accurate force field for the intermolecular interactions between the chemical groups of the molecules of interest; simulation methods employ numerical algorithms to solve the statistical mechanics (Monte Carlo) or equations of motion (molecular dynamics) and hence are more computational intensive to implement than algebraic theories. There is therefore a certain synergy in the roles played by equations of state and molecular simulation: the former can be used for a rapid early assessment of the thermodynamic and phase equilibria of the system, and the latter can then provide a more detailed microscopic description of the structure and dynamics of the system. Accurate equations of state such as SAFT- $\gamma$  can also be used in the development of dependable force fields based on the Mie potential for direct use in molecular simulation extending the capability of SAFT-based approaches (C. Avendaño et al. *J. Phys. Chem. B* 115, 11154 (2011); E. A. Müller and G. Jackson, *Ann. Rev. Chem. Biomolec. Eng.* 5, 405 (2014)).

2) 504 p.styring@sheffield.ac.uk asks

The model works well for MEA, however, does it work for other systems, other amines or other sorbents where the number of interactions is different? For example 1:1 chemisorption as opposed to 1:2 chemisorption; or even physisorption? (paper 10819)

Your reply

The SAFT approach has been used to successfully describe the thermodynamics and fluid-phase behaviour of a wide range of amine systems of relevance in carbon dioxide separation and capture processes including: monoethanolamine (MEA) [N. Mac Dowell et al., *Ind. Eng. Chem. Res.*, 49, 1883

(2009); Rodriguez et al., Mol. Phys. 110, 1325, (2012)]; ammonia and 2-amino-2-methyl-1-propanol (AMP) [N. Mac Dowell et al., Computer Aided Chem. Eng. 28, 1231 (2010); Rodriguez et al., Mol. Phys. 110, 1325, (2012)]; linear alkylamines [N. Mac Dowell et al., J. Phys. Chem. B 115, 8155 (2011)]; diethanolamine (DEA) and methyldiethanolamine (MDEA) [Rodriguez et al., Mol. Phys. 110, 1325, (2012)]; poly(oxyethylene)dimethylethers (Selexol) and poly(oxymethylene)dimethylethers (OME) [J. Burger et al., AIChE J. 61, 3249 (2015)]. The group contribution version of the theory SAFT- $\gamma$  [A. Lymeriadis et al. J. Chem. Phys. 127, 234903 (2007); A. Lymeriadis et al., Fluid Phase Equil. 274, 85 (2008)] has been used predictively to assess a broad range of alkanolamine solvents and offers promise in computer aided molecular process design (CAMPD) [A. I. Papadopoulos et al., Chem. Eng. Trans. 39, 211 (2014); A. Chremos et al., Fluid Phase Equil. 407, 280 (2016); A. I. Papadopoulos, Mol. Sys. Design & Eng., in press (2016)].

3) 507 gtr@che.utexas.edu asks

Data for the heat capacity of amine solvents are generally not accurate enough to determine the partial heat capacity of the total CO<sub>2</sub>. Therefore the enrtl representation also has difficulty getting a reasonable Cp. Where does SAFT model account for the... (paper 10819)

Your reply

The SAFT equation of state is formulated in terms of the Helmholtz free energy and all thermal thermodynamic properties (including the heat capacity, enthalpy, entropy etc.) are obtained as appropriate temperature derivatives of the free energy. In physical approaches to reactive systems, such as the Wertheim treatment of association at the heart of the SAFT approach, the heat of reaction is treated at the level of an association energy between the various reacting/associating species. In the case of the reaction of carbon dioxide in aqueous solutions of monoethanolamine (MEA) there are two association/bonding energies in the model corresponding to the 2:1 stoichiometry of the reaction: the heat of reaction is therefore treated implicitly in this type of approach. The fact that the SAFT treatment provides an accurate representation of the concentrations of the various species (protonated amine, bicarbonate, carbamate etc.) the equilibrium constant (and its temperature dependence) is also well capture. Because the slope of the (natural) logarithm of the equilibrium constant as a function of the inverse (absolute) temperature is the enthalpy of reaction, this means that the heat of reaction is also obtained in an implicit manner.

4) 500 gtr@che.utexas.edu asks

Have you attempted to use the implicit speciation of SAFT to model mass transfer with fast reaction in the boundary layer using kinetics? (paper 10819)

Your reply

No, we have not used the SAFT treatment to describe mass transfer in the boundary layer using kinetics. This is an interesting proposition which we will certainly be looking into in the near future.

5) 501 m.trusler@imperial.ac.uk commented

It appears that the parameter  $\tau$  that you use to modify the effective diffusion coefficient plays a very strong role in the overall performance of the model. I think it would be interesting to model a solvent system which has simpler chemistry in CO<sub>2</sub> c... (paper 10819)

Your reply

This would certainly be a very good way of testing the nature of our modelling approach to the effective diffusion of carbon dioxide in a reactive amine solvent. Which particularly solvent system did you have in mind?

6) 502 m.trusler@imperial.ac.uk commented

In the paper, you describe obtaining the diffusion coefficient of CO<sub>2</sub> and N<sub>2</sub> in water from a 'predictive' empirical model. My comment is that these diffusion coefficients are available experimentally and one could eliminate the (possibly large) uncertainty... (paper 10819)

Your reply

We feel that the issue is not so much determining the diffusion coefficients of carbon dioxide or nitrogen in neat water (for which there are extensive experimental data and reliable correlations), but the availability of such data for carbon dioxide in the reactive amine solvent. It would be extremely useful to have reliable experimental data of the diffusion coefficients (and other transport thermophysical properties) for the various reaction species including the unreacted carbon dioxide, the carbamate, the bicarbonate and the protonated amine.

7) 505 gtr@che.utexas.edu asks

I suggest that you attempt to represent the data by Dugas (dissertation) on the absorption of CO<sub>2</sub> into Mea and into PZ. Frailie (dissertation) has also modeled the PZ data by aspen/enrtl. (paper 10819)

Your reply

This is a good suggestion thank you. Could you please provide full details of the references?

8) 506 m.bui@imperial.ac.uk asks

Pilot plant data tends to be have variations due to amine degradation and heat loss. The degree of influence from these effects can vary from one set of pilot plant data to another. How does your model compensate for data uncertainty due these effects? (paper 10819)

Your reply

At this stage our process model does not account for the degradation of the amine solvent. In our paper we assessed one set of pilot plant data [P. Tontiwachwuthikul et al., Chem. Eng. Sci., 47, 381

(1992)] and we have not in this case found the need to compensate for the solvent degradation, though of course this may be taken into account in an effective manner with our model of the speciation equilibrium. It would be possible to account for the degradation of the amine but one would need to specify the degradation species and obtain intermolecular interaction models for the key products.

9) 503 yuezhang1992@utexas.edu asks

To match the pilot plant data, you chose to vary the single diffusivity parameter based on the sensitivity analysis. Have you tried to regress multiple adjustable parameters simultaneously to get a better fit? (paper 10819)

Your reply

The key goal of our approach is to minimize the number of adjustable parameters to describe the system retaining as much of the predictive capability of the model as possible. By varying more of the parameters in the model (to better describe the diffusivity, viscosity, enthalpies, surface tensions etc.) one could in principle achieve a better overall description of the process. We are aiming however to develop a tractable predictive platform for integrated computer aided molecular and process design (CAMD) for broad ranges of solvents including amines, ethers, and multifunctional alkanolamines for which very limited (or no) experimental data are available. The fact that the diffusivity parameter is found to be transferable to different pilot plant runs and conditions is a clear advantage in this regard. We are planning to assess the transferability of the parameter to other carbon capture solvents in the near future.

You have no unanswered questions. See below for questions addressed to all participants.