Calculation of Solubilities

The solubilities ("34Solubility (Henry Coefficient)" in the MoDeNa workflow) are passed from "4WP1 Thermo Tools (US)" to "6WP2 Bubble Growth Tool".

The final call to the model will have temperature and a variable specifying for which component the Henry coefficient should be returned as input parameters and this Henry coefficient as output.

Because the PC-SAFT parameters of the actual PU polymer have not been determined yet, a model system is studied here containing a polyethylene with a molecular mass of $1000 g/mol$ as well as pentane and carbon dioxide as examples of a physical and a chemical blowing agent, respectively.

Furthermore, as it is still undecided how to identify components, the call as of now only has temperature as input and the Henry coefficient of pentane as output.

The value of pressure is set to $p = 1.013$bar in all simulations.

Detailed Model

As the detailed model the PC-SAFT equation of state is used. Please see [1], [2] and [3] for the underlying theory and comparisons to experimental results.

The code reads the temperature at which to calculate the solubilities from the file *in.txt*. It then calculates the phase equilibrium at this temperature and a pressure of $p = 1.013$bar.
From Henry's Law

$$y_i \cdot p = x_i \cdot H_i$$

Henry coefficients are determined as:

$$H_i = \frac{y_i \cdot p}{x_i}$$

where x_i and y_i are the mole fractions of a given component in the liquid and vapour phase, respectively and p denotes the pressure.
The value of H_i (in Pascal) is then written to the output file *out.txt*.

Surrogate Model

As the surrogate model the van't Hoff equation is used. It describes the temperature dependence of Henry coefficients:

$$H_i(T) = H_i(T_0) \cdot exp\left(C(1/T - 1/T_0)\right)$$

where $H_i(T_0)$ denotes the value of the Henry coefficient at a reference temperature T_0, C is a fittable parameter and T is the temperature in Kelvin.

However, in this form the model was not capable of describing the temperature dependence of the Henry coefficient of carbon dioxide satisfactorily.
Therefore, the model is slightly modified and T_0 and $H_i(T_0)$ are treated as additional fittable parameters.
Thus the surrogate model reads:

$$H_i(T) = A \cdot exp\,(B(1/T - 1/C))$$

with the fittable parameters A, B and C.

Figures 1 and 2 show Henry coefficients for pentane and carbon dioxide calculated with the PC-SAFT equation of state for different temperatures which were used to fit the surrogate model and the results of the surrogate model.
From the figures it is apparent that for pentane the surrogate model fits the results of the PC-SAFT eqution of state very well while for carbon dioxide the agreement is not as good but still satisfactory.

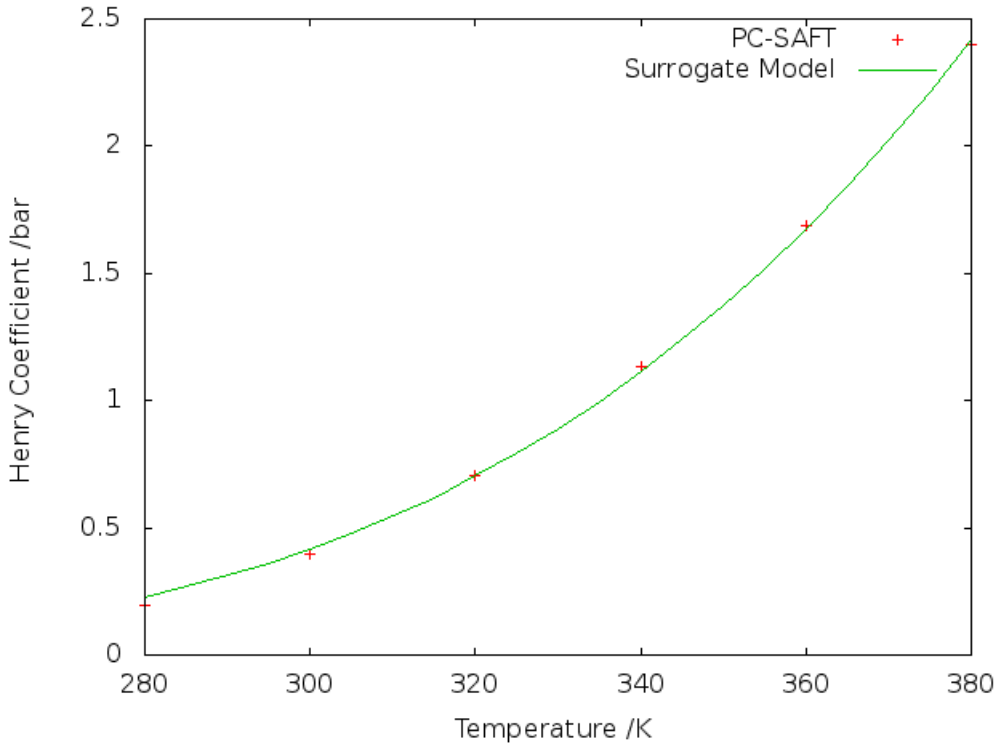

Figure 1: Henry coefficients of pentane calculated with the PC-SAFT equation of state and with the surrogate model.

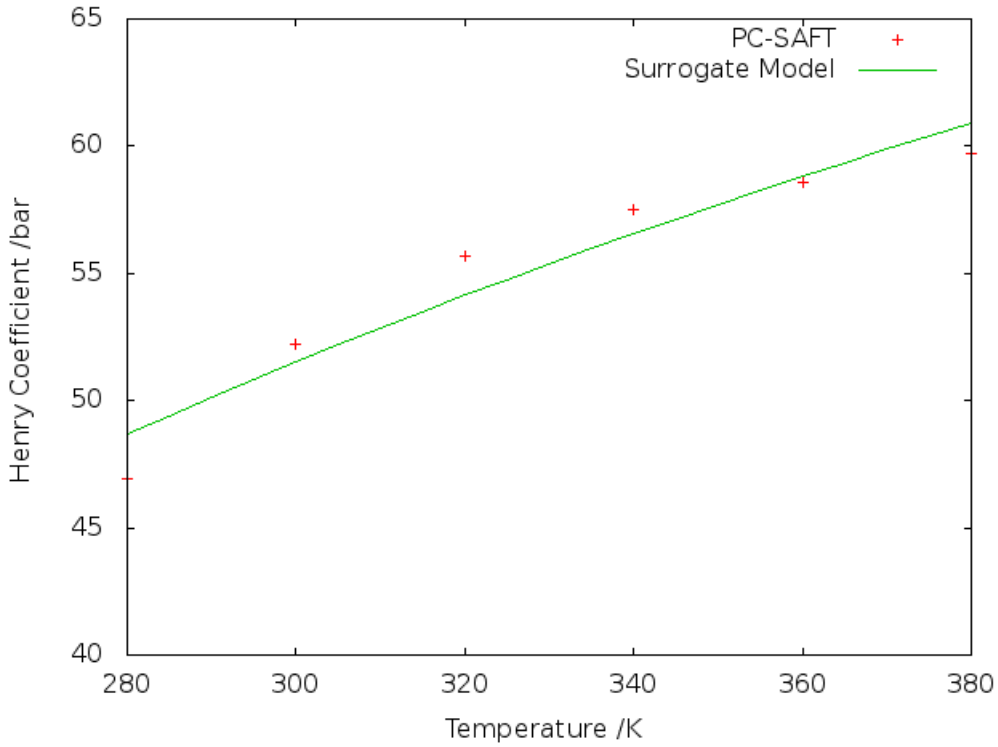

Figure 2: Henry coefficients of carbon dioxide calculated with the PC-SAFT equation of state and with the surrogate model.

Design of experiments

As soon as the surrogate model is called to evaluate the Henry coefficient for a temperature value outside the temperature range it was fitted for, the detailed model is called to provide a new data point. This new data point is chosen to be 10% larger (smaller) than the requested value if this requested value is above (below) the current temperature intervall that was used to fit the parameters of the surrogate model.

Bibliography

[1] J. Gross and G. Sadowski, "Perturbed-chain saft: an equation of state based on a perturbation theory for chain molecules," *Industrial & Engineering Chemistry Research*, vol. 40, no. 4, pp. 1244–1260, 2001.

[2] J. Gross and G. Sadowski, "Application of the perturbed-chain saft equation of state to associating systems," *Industrial & Engineering Chemistry Research*, vol. 41, no. 22, pp. 5510–5515, 2002.

[3] J. Gross and J. Vrabec, "An equation-of-state contribution for polar components: Dipolar molecules," *AIChE Journal*, vol. 52, no. 3, pp. 1194–1204, 2006.