Adsorption Isotherms and Solubility Limits in Aqueous Dilute Solutions via the Potential of Mean Force

Sabine Leroch, Rupert Tscheliessnig, Markus Vinzent, Lukas Geyrhofer, Martin Wendland [C, S] and Johann Fischer

Institute for Chemical and Energy Engineering, University for Natural Resources and Applied Life Sciences (BOKU), Vienna, Austria

Thermophysical properties of dilute solutions are very important for many technical and natural processes, but are difficult to determine by molecular simulations. E.g., a hydrophobic molecule has a low solubility in water and will be strongly adsorbed at a hydrophobic wall from an aqueous solution. In a conventional molecular dynamic (MD) simulation of the adsorption isotherm of a hydrophobic molecule from an aqueous solution at a plane hydrophobic wall, the hydrophobic solute molecules will all be found at the wall, but hardly in the aqueous bulk solution. Thus, the MD simulation will provide results for the adsorbed amount but not for the bulk concentration which are both needed for the adsorption isotherm. This is overcome by the PMF (potential of mean force) method where one solute molecule is fixed at different positions along a path from the bulk to the wall. The mean force on the fixed solute is calculated and then integrated to the PMF [1]. The density or concentration profile of the solute including the bulk concentration can be calculated easily from the PMF. If the solution is over-saturated, one can even determine the solubility limit which is very low for hydrophobic solutes in aqueous solutions [2]. The method was successfully applied for the adsorption and solubility limit of benzene from or in aqueous solutions. Also examples for some more complex solute molecules will be given.

[1] W. Billes, R. Tscheliessnig, L. Sobczak, M. Wendland, J. Fischer, J. Kolafa. Adsorption isotherms for dilute solutions from molecular simulation via potential of mean force. Mol. Sim. 33 (2007) 655-666.

[2] R. Tscheliessnig, L. Geyrhofer, M. Wendland, J. Fischer. Adsorption from oversaturated aqueous solution: Mean force molecular simulations. AIChE J. 54 (2008) 2479-2486.

.