Binary Diffusion Coefficients of Liquids with Dissolved Gases as a Function of Composition by Dynamic Light Scattering and Molecular Dynamics Simulations

Tobias Klein^s, Wenchang Wu, Michael H. Rausch, Cédric Giraudet, Thomas M. Koller^c and Andreas P. Fröba Institute of Advanced Optical Technologies - Thermophysical Properties (AOT-TP), Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Erlangen, Bavaria, Germany thomas.m.koller@fau.de

Systems based on liquids containing dissolved gases are of interest in many areas of chemical and energy engineering such as separation processes or catalytic reactions. One key property required for the optimum design of corresponding processes is the mutual diffusivity. In a current research project, experimental and modeling methods are combined to get a fundamental understanding on the influence of varying compositions and thermodynamic states on the diffusive mass transport in liquids with dissolved gases.

The objective of the present study is to test the capability of molecular dynamics (MD) simulations in predicting binary diffusion coefficients of liquids with dissolved gases as a function of concentration. As model system, the solvent *n*-hexane (n-C₆H₁₄) and the solute carbon dioxide (CO₂) were investigated at temperatures from (303 to 423) K and CO₂ mole fractions between 0.01 and 0.80. From dynamic light scattering (DLS) measurements studying microscopic concentration fluctuations at macroscopic thermodynamic equilibrium, the Fick diffusivity could be accessed with typical expanded uncertainties smaller than 5 %. These results provide a database to validate equilibrium MD simulations. The quantities directly accessible by the simulations are the self-diffusivities of both components and the Maxwell-Stefan (MS) diffusivity. The latter property was combined with the thermodynamic factor obtained from the simulations or equations of state to determine the Fick diffusivity with typical expanded uncertainties. Both MD simulations and DLS show an increase for the binary diffusion coefficients with increasing temperature and by trend a decrease with increasing CO₂ concentration. Besides providing a reliable approach for calculating mass diffusivities of liquids with dissolved gases by MD simulations, the benefit of the present contribution is to probe how molecular diffusion is affected by intermolecular and structural effects in the mixtures.