

Mass diffusivities of binary mixtures of normal alkanes with dissolved gases

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Knowledge on the mutual diffusivities of gases dissolved in liquids is of increasing interest for the optimization of processes such as the Fischer-Tropsch synthesis of high valued petroleum products from synthesis gas or the separation of flue gas components. Here, mass transfer is often the rate limiting step compared to, e.g., chemical reactions and/or heat transfer. In a related research project, the benefits of experimental and modelling methods are combined to get a better understanding on how molecular diffusion is affected by the characteristics of the mixture components, which contributes to the development of reliable predictions.

In the present contribution, dynamic light scattering (DLS) experiments and molecular dynamics (MD) simulations were performed at macroscopic thermodynamic equilibrium for a first set of model systems based on liquid normal alkanes and dissolved gases. The solvents *n*-hexane and *n*-decane in their binary mixtures with the solutes hydrogen, helium, nitrogen, and carbon monoxide were studied over a broad temperature range from (298 to 423) K at gas mole fractions below 5%. With DLS, the relaxation behavior of microscopic fluctuations in the properties of state is analyzed. In the case of concentration fluctuations in binary mixtures, their mean decay time is related to the mutual diffusivity which can be accessed by DLS in an absolute way without calibration. The present measurements document that even for small gas concentrations implying weak light scattering signals, reliable mutual diffusivities with typical uncertainties below 5% ($k = 2$) can be obtained. These results serve as a database for MD simulations. Here, thermophysical properties are computed by investigating the dynamics of molecules interacting with each other. Based on suitable models for the mixture components, the self-diffusion coefficient of the gas was determined with uncertainties of about 10% ($k = 2$).

In agreement with theory, similar values for the mutual diffusivity and the self-diffusivity were found. Furthermore, no detectable influence of the solute concentration on the mass diffusivities could be found by DLS and MD simulations within the narrow investigated mole fraction range between about (1 and 5)%. The broad range of mass diffusivities of the studied gas-liquid systems covering about two orders of magnitude from about (10^{-9} to 10^{-7}) $\text{m}^2 \cdot \text{s}^{-1}$ allow for developing structure-property relationships. Here, effects of the molecular weight and polarity of the various gases as well as the varying alkyl chain length of the solvents on the mass diffusivities are discussed. To further develop the intended prediction scheme, two additional classes of alkane-based solvents featuring the hydroxyl group – namely normal alcohols – as well as bulky charged structures in the form of ionic liquids will be studied in their binary mixtures with the aforementioned gases in a next step. In the same context, the DLS data will be used to test how reliably mutual diffusivities can be computed in MD simulations for the various fluid systems by different approaches.