Fick diffusion coefficients in binary liquid mixtures of *n*-alkanes or 1-alcohols with dissolved gases investigated by molecular dynamics simulations and dynamic light scattering

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Systems based on liquids containing dissolved gases are of interest in many areas of chemical and energy engineering such as separation processes, catalysis, and hydrogen storage by liquid organic hydrogen carriers. One key property required for the optimum design of corresponding processes is the diffusion coefficient. In a current research project, the benefits of experimental and modeling methods are combined to get a fundamental understanding on the influence of varying molecular species and thermodynamic state on the diffusive mass transport in liquids with dissolved gases.

The objective of the present study is to characterize the molecular diffusion in binary systems consisting of liquids and dissolved gases via the study of the Fick diffusion coefficient. For this, the strategy was to combine the benefits of dynamic light scattering (DLS) experiments and molecular dynamics (MD) simulations. To account for variations in the polarity of the solvents and the size of the solutes, binary mixtures of the solvents *n*-hexane (*n*-C_6H_{14}) or 1-hexanol (1-$C_6H_{14}O$) with the dissolved gases hydrogen (H_2), helium (He), carbon monoxide (CO), nitrogen (N_2), and carbon dioxide (CO_2) were investigated at temperatures between (303 and 423) K. While for the gases H_2, He, CO, and N_2, which show low solubilities in the solvents, investigations were limited to relatively small mole fractions below 0.05, the entire concentration range was studied for mixtures with CO_2 at mole fractions between 0.01 and 0.95. From DLS measurements studying microscopic concentration fluctuations at macroscopic thermodynamic equilibrium, the Fick diffusion coefficient 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-diffusion coefficients of both components and the Maxwell-Stefan diffusion coefficient. The latter property was combined with the thermodynamic factor obtained from the simulations or equations of state to determine the Fick diffusion coefficient with typical expanded statistical uncertainties of 10%.

The main findings of the present study may be summarized as follows. At conditions approaching infinite dilution of the dissolved gas, the self-diffusion coefficient of the gas and the Fick diffusion coefficient of the mixtures were found to be equal [1], which is in agreement with theory. For a given gas and temperature, the mass diffusivities in *n*-C_6H_{14} and in 1-$C_6H_{14}O$ correlate with the behavior of the solvent viscosities. While the matching mass diffusivities for systems containing CO and N_2 follow the expected trend, the larger values for the systems containing the heavier He in comparison with those containing the lighter H_2 could be related to the smaller size of He. It could be shown that the MD simulations can also represent the non-ideal concentration dependency of the Fick diffusion coefficient obtained by DLS for the CO_2-based mixtures [2]. Radial distribution functions and hydrogen-bonding statistics calculated by the MD simulations show that the slowing-down of the Fickian diffusion with increasing CO_2 mole fraction is caused by a distinct structural organization in the binary mixtures. An indication for this behavior could also be received by Raman spectroscopy performed simultaneously with the DLS measurements.

References

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