Fick diffusion coefficients in binary fluid mixtures consisting of methane, propane, or carbon dioxide by theoretical and optical methods

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Fluid mixtures containing natural gas components such as methane, propane, and carbon dioxide are important in many areas of process and energy engineering. For the optimum design of apparatuses and processes related to such systems, the exact knowledge of mass diffusivities as a function of temperature, pressure, and composition including the specification of their uncertainties is necessary. For this, experimental techniques and theoretical approaches including molecular dynamics (MD) simulations are needed to provide a reliable database. Although theoretical approaches have to be normally validated with experimental data, they are helpful to understand macroscopic properties as mass diffusivities from a molecular perspective. Within an ongoing research project at AOT-TP, Fick diffusion coefficients in binary fluid mixtures consisting of methane, propane, or carbon dioxide should be accurately determined over a wide region of thermodynamic states ranging from the superheated vapor over the gas state and supercritical region up to the compressed liquid state by theoretical and optical methods.

With holographic interferometry applied for a Loschmidt cell (HILC), the instationary diffusion process observable in binary fluid mixtures subjected to a defined initial macroscopic concentration gradient is investigated. From the analysis of the temporal change in the partial molar density in both half cells applying two interferometers, the concentration dependency of the Fick diffusion coefficient D_{11} was accessed in the superheated vapor and gaseous state at pressures between 0.05 MPa and 0.5 MPa and at temperatures of 293 K and 313 K [1]. With dynamic light scattering (DLS) experiments in macroscopic thermodynamic equilibrium, the dynamics of microscopic fluctuations in composition is studied by the temporal analysis of the scattered light intensity. In this way, absolute D_{11} data were accessible as a function of concentration in the supercritical and compressed liquid state around the two-phase boundary at pressures between 9 MPa and 12 MPa and temperatures between 283 K and 363 K. The measurement results obtained by HILC and DLS with expanded uncertainties of about 5% served as reference for equilibrium MD simulations calculating thermophysical properties from the analysis of the statistical motion of molecules. Based on a simultaneous consideration of kinetic and thermodynamic contributions, D_{11} values were calculated by MD simulations over the entire concentration range at pressures between 0.1 MPa and 12 MPa with statistical expanded uncertainties of about 10%. For these calculations, besides molecular models or force fields from literature, newly developed ones derived from *ab initio* calculations for the pure fluids in the limit of zero density [2] were employed as alternatives. For the investigated range of thermodynamic states including temperatures between 293 K and 353 K, the simulated D_{11} values obtained with the new *ab initio*-based models are in better agreement with the experimental results.

References

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