

Characterization of Fick Diffusion in Electrolyte Systems by Equilibrium Molecular Dynamics (EMD) Simulations

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Electrolyte systems are of interest in many areas of chemical and energy engineering. Applications are, for instance, separation processes, metal-ion batteries, and electrochemical double-layer capacitors. One key property required for the optimum design of corresponding processes and apparatuses is the Fick diffusivity (D_{11}). In current and planned research projects, simulations and experiments are combined to get a fundamental understanding of the influence of varying thermodynamic states including composition on the diffusive mass transport in binary electrolyte systems.

The objective of the present study is to test the capability of equilibrium molecular dynamics (EMD) simulations in predicting D_{11} in electrolyte systems. As model systems, binary mixtures consisting of the ionic liquid (IL) 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([HMIM][NTf₂]) and carbon dioxide (CO₂) as well as of the IL 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][NTf₂]) and lithium bis(trifluoromethylsulfonyl)imide ([Li][NTF₂]) were investigated at or close to vapor-liquid equilibrium. For a fundamental understanding of the influence of temperature and composition, the simulations for mixtures with CO₂ were performed for mole fractions between 0.01 and 0.8 and temperatures from (298.15 to 348.15) K. For the binary electrolyte mixture made entirely of ions, simulations were performed with a [Li][NTF₂] mole fraction of 0.073 at 298.15 K. For all investigated systems, the quantities directly accessible by EMD are the self-diffusivities of the three species and the Maxwell-Stefan (MS) diffusivities. The latter properties, resulting in an effective MS diffusivity, were combined with the thermodynamic factor obtained from EMD via different approaches to determine the Fick diffusion coefficient with typical expanded statistical uncertainties smaller than 15%. Within this value the simulated data agree well with D_{11} measured at AOT-TP by dynamic light scattering. In summary, the present work demonstrates for the first time, to the best of our knowledge, a consistent way of evaluating D_{11} for electrolyte systems using only EMD simulations.