Diffusivities in Electrolyte Systems from Equilibrium Molecular Dynamics Simulations

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Electrolyte systems consisting of a salt dissolved in a solvent which can be a pure fluid or a fluid mixture are working fluids in many areas in chemical and energy engineering, where a prominent example is energy storage in metal-ion batteries. To achieve an optimum design of such applications, Fick diffusion coefficients are required to describe diffusive mass transport. Current research at AOT-TP aims at improving the understanding of how the molecular characteristics of the components of systematically selected electrolyte systems influence the Fick diffusion coefficients. For this, both dynamic light scattering (DLS) experiments and equilibrium molecular dynamics (EMD) simulations are used.

The present contribution focuses on the study of the influences of solvent and solute characteristics on the diffusive mass transport in binary electrolyte systems using EMD simulations. The selected binary systems consist of the solute $[Li][NTf_2]$ in the solvents acetonitrile, dimethyl sulfoxide, diethyl carbonate, dimethyl carbonate, $[EMIm][NTf_2]$, $[HMIm][NTf_2]$ or $[BPyr][NTf_2]$ and the solute $[EMIm][NTf_2]$ in the solvents $[EMIm][EtSO_4]$ or $[EMIm][TFO]$. The systems are investigated at temperatures between (293.15 and 398.15) K and a solute mole fraction of about 0.05. To obtain the Fick diffusion coefficient D_{11} by EMD simulations, the Maxwell-Stefan diffusion coefficient and the thermodynamic factor are accessed and combined.

This work demonstrates that non-polarizable force fields (FFs) can be used to determine D_{11} in mixtures involving non-electrolytic solvents if the FFs of the pure solvents are adjusted to accurately predict their liquid dielectric constant and viscosity. Furthermore, the so-called solvation number associated with ion dissociation, which also influences D_{11}, could be determined by EMD simulations. This helps to explain the results from EMD simulations and DLS experiments which show that D_{11} for $[Li][NTf_2]$ in diethyl carbonate is by a factor of five smaller than that in acetonitrile despite clearly smaller differences in the solvent viscosity.