Diffusivities in Electrolyte Systems from Dynamic Light Scattering (DLS)

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Liquid electrolyte systems are characterized by the presence of charge carriers in the form of mobile anions and cations and are relevant in many areas of chemical and energy engineering including energy storage and conversion processes. One key property required for the optimum design of corresponding processes and apparatuses is the Fick diffusion coefficient D. In ongoing research at AOT-TP, the influence of molecular characteristics as well as temperature and composition on D in electrolyte systems is investigated. For this, dynamic light scattering (DLS) experiments and molecular dynamics simulations are utilized to access D at temperatures ranging from (293 to 423) K. The binary mixtures being in the focus of this contribution consist of lithium bis(trifluoromethylsulfonyl)imide dissolved in either a non-electrolytic solvent, such as diethyl carbonate, or an ionic liquid sharing a common ion with the salt, such as 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. Although these systems involve three distinct species, the diffusive mass transport is characterized through a single diffusion coefficient, namely D_{11} , due to the electroneutrality condition. The DLS experiments presented here are performed in macroscopic thermodynamic equilibrium and give access to D_{11} with typical expanded uncertainties between (3.0 and 15)% (coverage factor k=2).

The results of the present investigations have shown that the viscosity of the solvent is strongly connected with D_{11} , as a higher viscosity leads to slower dynamics within the fluid and, thus, to smaller D_{11} values. Furthermore, the dissociation of solute molecules into anions and cations has been identified as a significant factor influencing D_{11} in electrolyte mixtures. When the dissociation of electrolytic solutes is limited, which is indicated by a low dielectric constant, the formation of large ion clusters can result in a decrease in D_{11} . The present results form the basis of further studies on D in ternary and multicomponent electrolyte systems.