Determination of Fick Diffusion Coefficients in Electrolyte Systems Comprised Entirely of Ions by Dynamic Light Scattering (DLS)

Maximilian Piszko, Chathura J. Kankanamge, Michael Heinrich Rausch, Tobias Klein [C] and Andreas Paul Fröba[S]
Institute of Advanced Optical Technologies - Thermophysical Properties (AOT-TP), Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Erlangen, Bavaria, Germany
tobias.klein@fau.de

Electrolytes are relevant in many fields of chemical and energy engineering. Their applications include, for instance, energy storage and conversion. Recently, ionic liquids (ILs) have attracted considerable interest for electrolyte systems due to their unique properties comprising low volatility and low flammability. For the efficient design of processes and apparatuses using electrolyte systems, an accurate knowledge on the diffusive mass transport is essential. Until now, however, especially for electrolyte systems consisting entirely of ions, only few experimental techniques and data are reported in the literature for the Fick diffusion coefficient (D_{11}).

The present contribution demonstrates, for the first time, the applicability of dynamic light scattering (DLS) for the investigation of molecular diffusive mass transport in electrolyte systems by the determination of D_{11} at macroscopic thermodynamic equilibrium. For four binary model mixtures comprised entirely of ions, it could be evidenced that the obtained experimental signals are associated with hydrodynamic modes. These systems are based on three different ILs and a salt and always share a common ion in the mixture. Between (293 and 353) K, the influence of temperature and composition on D_{11} and its correlation with further thermophysical properties are discussed. The investigations were performed under a heterodyne detection scheme, where the lowest uncertainties for D_{11} of 3.0% were found at scattering angles of 90°. For small scattering angles, it could be shown that thermal and mutual diffusivities can be simultaneously determined. Furthermore, the presence or absence of water impurities could be resolved by an additional experimental signal. In summary, it could be demonstrated that DLS is a powerful tool for the determination of D_{11} in electrolytes comprised entirely of ions with typical expanded uncertainties between (3.0 and 15)%.