

# Transport mechanisms in stoichiometric and non-stoichiometric protic ionic liquids

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Protic ionic liquids (PILs) are a subset of ionic liquids, synthesized by a neutralization reaction of a Brønsted acid and a Brønsted base. They are promising candidates as electrolyte components since they offer an available proton for proton conduction, a high electrochemical and thermal stability and are low in cost [1]. In this work, triethylamine-based PILs are used in stoichiometric (1:1) and non-stoichiometric (1:x) mixtures with trifluoroacetic acid (TFAH) and trifluoromethanesulfonic acid (TfOH). Among these are non-stoichiometric PILs with an excess of acid and therefore with an additional hydroxyl group. The mobilities of the different species as well as the charge transport mechanism and the influence of the acid excess are investigated.

Various NMR methods are employed to characterize the PILs, of which the Pulsed Field Gradient NMR (PFG NMR) provides the diffusion coefficients. Additional impedance spectroscopy (EIS) enables calculating the inverse Haven ratio also referred to as ionicity. From <sup>1</sup>H and <sup>19</sup>F electrophoretic NMR (eNMR) measurements, mobilities of the individual species can be determined and thus their drift direction and velocity in an electric field. Herewith the effective charge can be quantified, which can be considered as a species-specific ionicity [2].

1D NMR experiments revealed a separate signal for the hydroxyl group implying that at least minor amounts of the neutral acid are also present in the two stoichiometric PILs TEAH TFA and TEAH TfO. In addition, a non-negligible mobility with a movement in the direction of the positive electrode was observed for the neutral acid. The conductivity, calculated from the mobilities, indicates that the neutral acid also participates in the charge transport. Furthermore, it was found that the ionicity as well as the effective charges of the anion and the cation of TEA TFAH 1:x increase with a increasing excess of acid, while these quantities remain constant for TEA TfOH 1:x.

In summary, it can be stated that the proton of the amine group is transported by the cation TEAH<sup>+</sup> in a vehicular mechanism without additional structural H<sup>+</sup> transport. On the other hand, the mobility of the proton of the hydroxyl group indicates a separate proton conduction mechanism or, more likely, cluster formation for example between the anion and the acid. Further research is currently being conducted, particularly with regard to ion correlations.

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## References:

- [1] C. Karlsson, C. Strietzel, H. Huang; M. Sjödin and P. Jannasch. *ACS Appl. Energy Mater.* 1 (2018), 6451 – 6462.
- [2] M. Gouverneur, J. Kopp, L. van Wüllen, M. Schönhoff. *Phys. Chem. Chem. Phys.* 17 (2015), 30680-30686.