

Why do we observe a momentum flow in eNMR measurements?

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Electrophoretic nuclear magnetic resonance (eNMR) is a powerful measurement technique to directly access ion movements in liquid electrolytes. By adding an electric field to the standard NMR setup, directional transport information in the form of drift velocities can be detected. The associated mobilities of the ionic species can be used to calculate important transport parameters like the transference number. The latter is an essential performance indicator for electrolytes used in electrochemical storage devices, e.g. batteries. Especially in highly concentrated electrolytes, like ionic liquids (ILs), the experimental determination of transference numbers is challenging. Here, eNMR together with our transport theory for highly concentrated electrolytes can help resolve recent discussions concerning their reference frame dependence (Fig. 1) [1].

Measurements on pure ILs recently showed a seeming violation of momentum conservation. However, we could show that the momentum is only locally not conserved and, thus, a different constraint governs the transport in these highly concentrated electrolytes: local volume conservation. Considering incompressibility and applying the volume-based description to eNMR measurements yields that the mobilities are better correlated to their partial molar volumes (local volume conservation) than to their molar masses (local momentum conservation) (Fig. 2) [2].

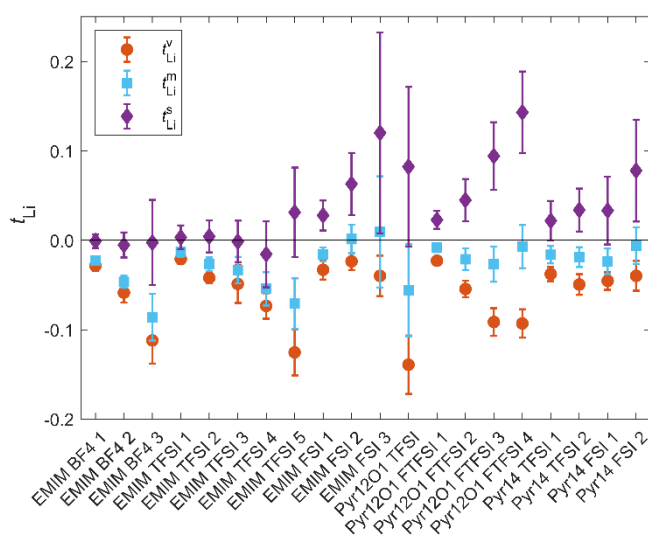


Fig. 1: Li-ion transference numbers in different reference frames derived from eNMR mobilities.

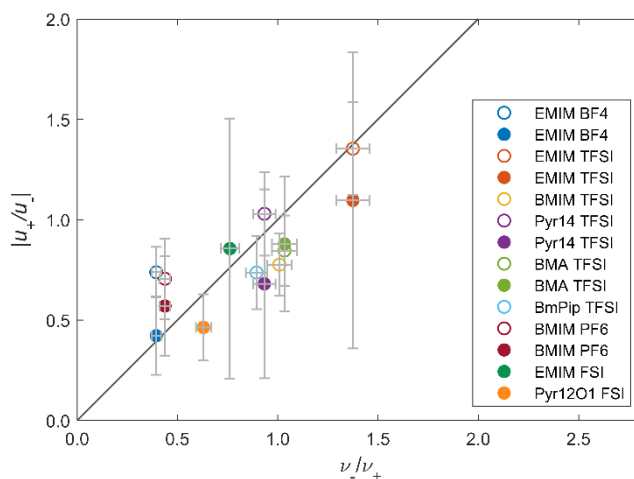


Fig. 2: Ratio of mobilities versus ratio of partial molar volumes of ionic species in pure ionic liquids.

[1] Kilchert, F. et al. *Phys. Chem. Chem. Phys.* **2023**, 25(38), 25965–25978. doi.org/10.1039/D2CP04423D

[2] Lorenz, M. et al. *J. Phys. Chem. Lett.* **2022**, 13(37), 8761–8767. doi.org/10.1021/acs.jpcllett.2c02398