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Lithium Transference in Electrolytes with Star-Shaped Multivalent Anions Measured by Electrophoretic NMR

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Calculation of the fraction of fully dissociated ion, f

From the discussion surrounding Equation 17 in the main text, we know that

$$v_+ = f v_{f+} + (1-f) v_-$$

where f is the fraction of fully dissociated ions moving freely under the electric field in the $+x$ direction with a velocity of v_{f+}, while the remainder are tightly coordinated with the anions and migrate with anions in the $-x$ direction with velocity v_-.

Thus, assuming the solvent velocity v_0 to be zero, which is a reasonable assumption for the present system, t_+^0 can be written as

$$t_+^0 = \frac{f v_{f+} + (1-f) v_-}{f v_{f+} + (1-f) v_- - v_-}$$

Rearranging the above equation we obtain

$$v_{f+} = \frac{t_+^0 + \left(\frac{1-f}{f}\right)}{t_+^0 - 1} v_- \quad (19)$$

Thus, $v_{f+} > 0$ defines an upper bound for f, i.e., we arrange Equation 19 to obtain the inequality $f_{thresh} < \frac{1}{1-t_+^0}$. The value of f_{thresh} provides the maximum possible fraction of fully dissociated ions assuming the present model.

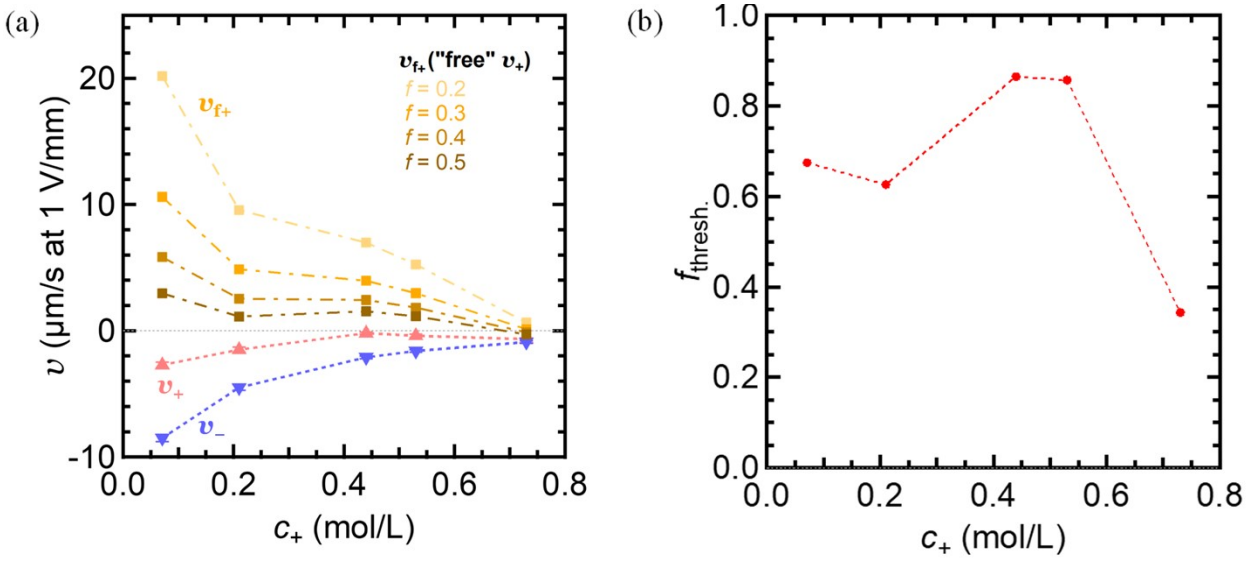

Figure S1. (a) Using ν_- and t_+^0 from eNMR and assuming different values of f, values of ν_{f+} (represented by orange squares) are calculated. For instance, at all concentrations (except the most highly concentrated sample), even if only 50% of cations are fully dissociated, values of ν_{f+} remain positive, as expected. (b) f_{thresh} plotted against c_+. f_{thresh} is a weak function of c_+, but is found to decrease with c_+ at the highest salt concentration. For example, at 0.4 M, $f_{thresh} =$ 0.86 implies that our model is consistent with 14% or more of the cations being tightly coordinated with the anions. In other words, in principle only a small fraction (~15%) of the cations need to be coordinated with anions to obtain a negative ν_+.