Electronic Supplementary Information

Negative Li Transference Numbers in Li Salt/Ionic Liquid Mixtures: Does Li Drift in the "Wrong" Direction?

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A. Diffusion coefficients and expected electrophoretic mobilities

Table S1: Diffusion coefficients of ions in the ionic liquids EmimTFSI and EmimBF$_4$ and corresponding IL/Li salt mixtures, determined by PFG-NMR at 298 K. Errors are estimated to 10 %.

Anion; $c_{\text{Li salt}}$ / (mol L^{-1})	D_{cation} / (10^{-11}m^{2}s^{-1})	D_{anion} [10^{-11}m^{2}s^{-1}]	D_{Li} / (10^{-11}m^{2}s^{-1})
TFSA; 0.00	5.4 ± 0.6	3.2 ± 0.4	–
TFSA; 0.25	4.4 ± 0.4	2.4 ± 0.2	1.3 ± 0.2
TFSA; 0.50	3.6 ± 0.4	1.8 ± 0.2	1.0 ± 0.2
BF$_4$; 0.00	4.8 ± 0.6	3.9 ± 0.4	–
BF$_4$; 0.25	4.1 ± 0.4	3.0 ± 0.4	1.3 ± 0.2
BF$_4$; 0.50	3.6 ± 0.4	2.3 ± 0.2	1.0 ± 0.2

Table S2: Apparent electrophoretic mobilities estimated from the diffusion coefficients of Table S1, assuming independent ion motion, according to Equ. (4) for neat IL and binary systems at 298 K. Errors are estimated to 10 %.

Anion; $c_{\text{Li salt}}$ / (mol L^{-1})	$\mu_{D,\text{cation}}$ / (10^{-10}m^{2}V^{-1}s^{-1})	$\mu_{D,\text{anion}}$ / (10^{-10}m^{2}V^{-1}s^{-1})	$\mu_{D,\text{Li}}$ / (10^{-10}m^{2}V^{-1}s^{-1})
TFSA; 0.00	21 ± 2	-12.6 ± 1.2	–
TFSA; 0.25	17.1 ± 1.8	-9.2 ± 1.0	5.1 ± 0.6
TFSA; 0.50	13.9 ± 1.4	-6.9 ± 0.6	4.0 ± 0.4
BF$_4$; 0.00	19 ± 2	-15.2 ± 1.4	–
BF$_4$; 0.25	16 ± 1.6	-11.7 ± 1.2	4.9 ± 0.6
BF$_4$; 0.50	13.9 ± 1.4	-9.0 ± 1.0	4.0 ± 0.4

B. Exemplary raw data of phase shifts in electrophoretic experiments

Figure S1 to S4 displays exemplary experiments for different samples and nuclei at Li salt concentrations of 0.00 and 0.50 molL^{-1}, respectively. The applied voltage and drift time are given for each experiment.

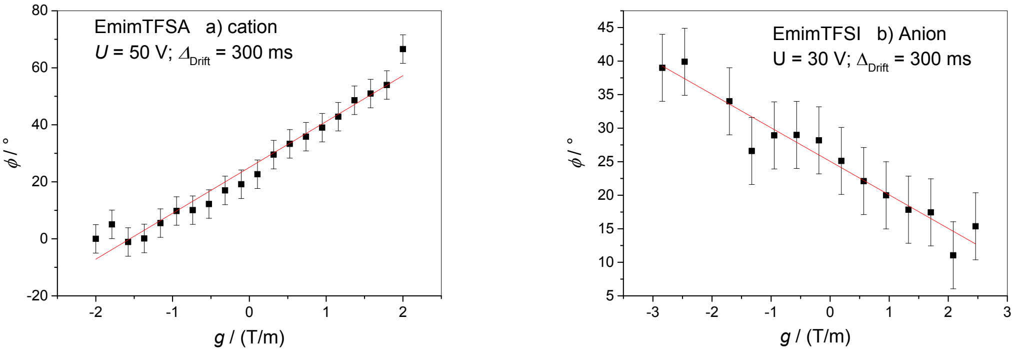

Figure S1: Phase in dependence on the gradient strength of EmimTFSA for a) cation (^{1}H) and b) anion (^{19}F).

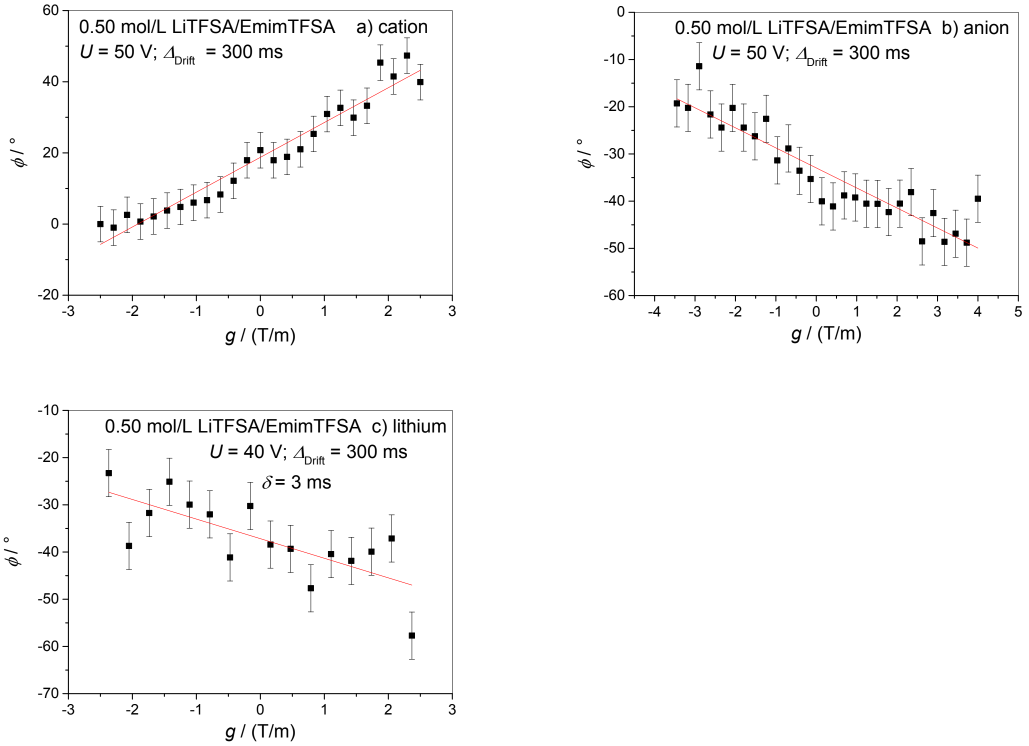

Figure S2: Phase in dependence on the gradient strength of 0.50 mol·L^{-1} LiTFSA/EmimTFSA for a) cation (^{1}H), b) anion (^{19}F) and c) lithium (^{7}Li).

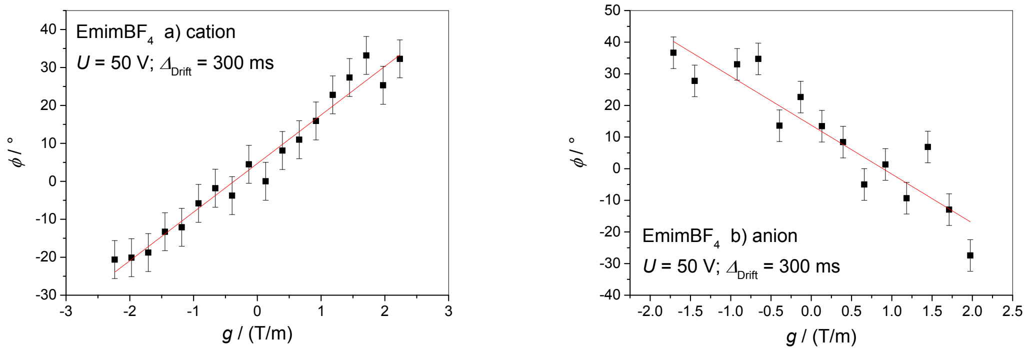

Figure S3: Phase shift in dependence on the gradient strength of EmimBF$_4$ for a) cation (^{1}H) and b) anion (^{19}F).

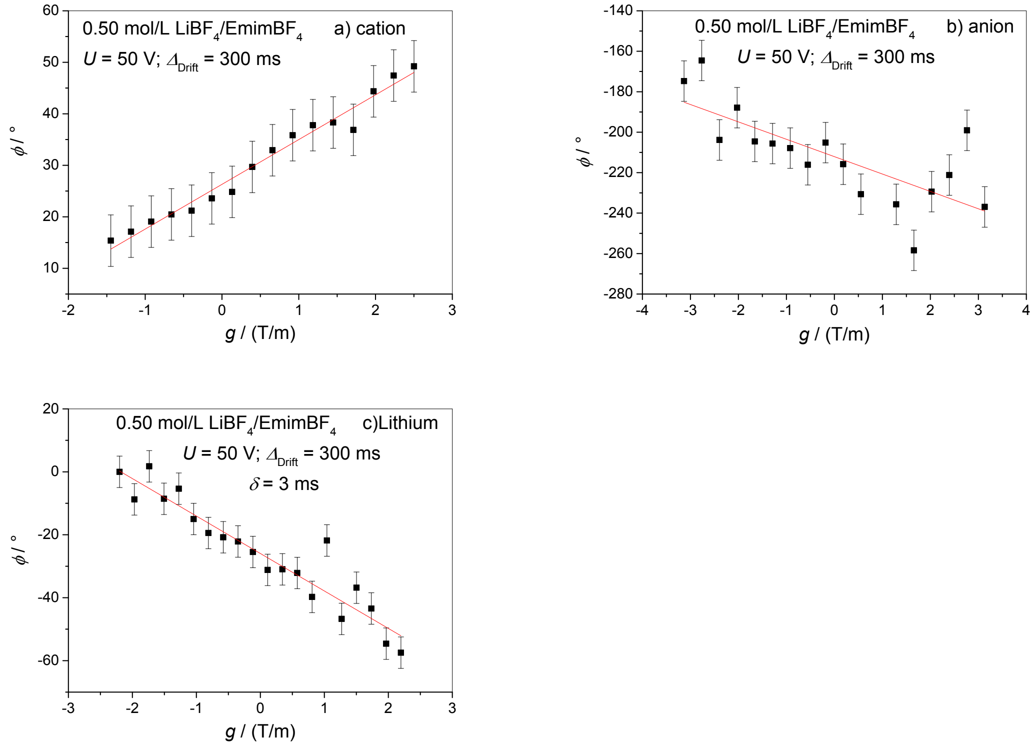

Figure S4: Phase shift in dependence on the gradient strength of 0.50 mol·L^{-1} LiBF$_4$/EmimBF$_4$ for a) cation (^{1}H), b) anion (^{19}F) and c) lithium (^{7}Li).

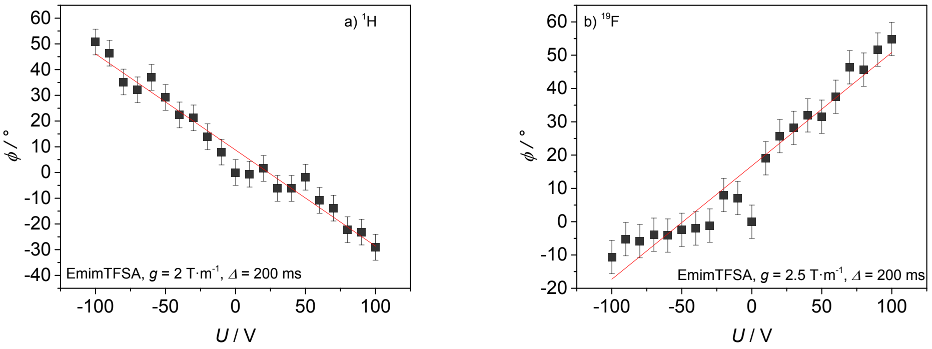

Figure S5: Phase in dependence of the applied cell voltage in EmimTFSA for a) cation (^{1}H) and b) anion (^{19}F). The linearity is proving the absence of voltage dependent artefacts, such as convective flow or electroosmosis.

C. Comparison with conductivities from impedance spectroscopy

The values of the electrophoretic mobilities can be controlled by comparing the conductivity σ_{eNMR} from the sum of the electrophoretic mobilities with the conductivities σ_{dc} from impedance spectroscopy. The conductivities from electrophoretic mobilities are calculated

$$\sigma_{eNMR} = \sum_i F\, c_i z_i \mu_i$$

where F is the Faraday constant and z_i the ion charge. The conductivities are displayed in Figure S5. The conductivities calculated from electrophoretic NMR, σ_{eNMR}, are in excellent agreement with σ_{dc}, which validates the determined electrophoretic mobilities.

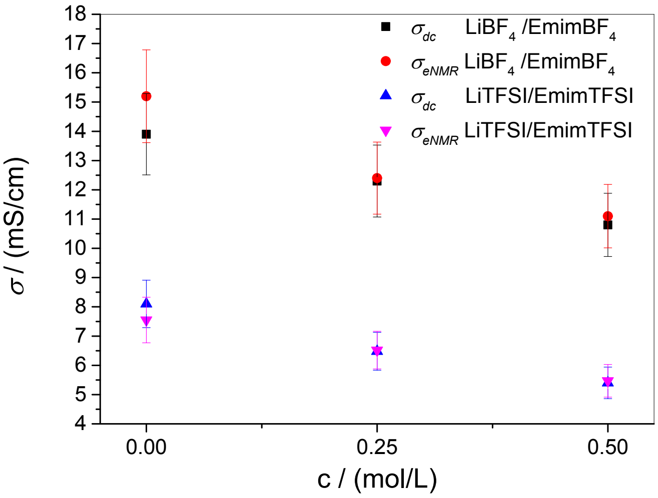

Figure S6: Conductivity σ_{eNMR} determined by electrophoretic mobility compared to conductivity σ_{dc} from impedance spectroscopy. The errors are determined from the standard deviation (σ_{eNMR}) and error propagation (σ_{dc}).