Supporting Information for

Overdetermination Method for Accurate Dynamic Ion Correlations in Highly Concentrated Electrolytes

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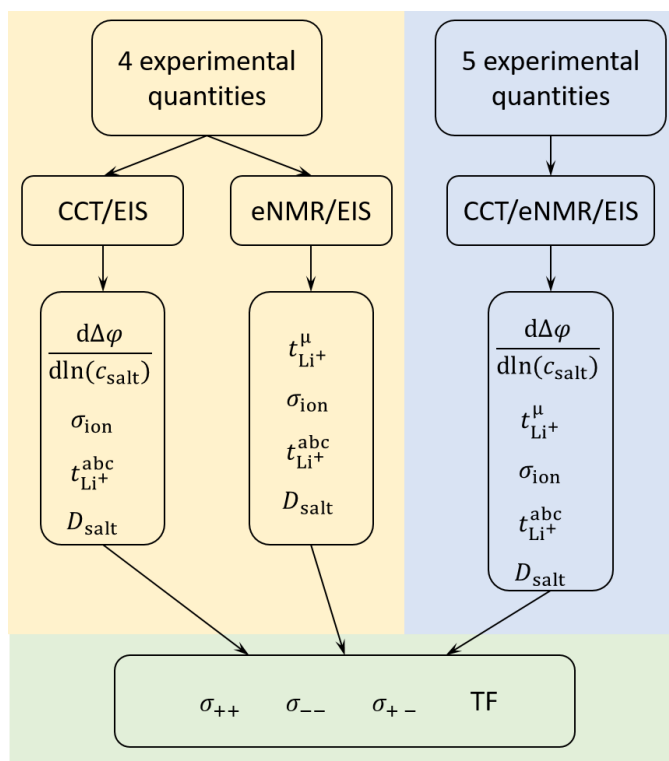
Calculation of the Onsager coefficients

Figure S1: Scheme of the three different approaches for determining the Onsager coefficients and the thermodynamic factor.

S1

Equations for calculating the auxiliary parameters A_i from experimental quantities m_i:[1,2]

$$A_1 = 1 \tag{S1}$$

$$A_2 = t_{Li+}^{abc} \tag{S2}$$

$$A_3 = \frac{D_{salt} \cdot c_{salt} \cdot F^2}{2 \cdot R \cdot T \cdot \sigma_{ion}} \tag{S3}$$

$$A_4 = \frac{d\Delta\varphi}{d\ln(c_{salt})} \cdot \frac{F}{2 \cdot R \cdot T} \tag{S4}$$

$$A_5 = t_{Li+}^{\mu} \tag{S5}$$

Equations to calculate the auxiliary parameters $A_{i,calc}$ from the target values z_i: [1,2]

$$A_1 = (\sigma_{++} + \sigma_{--} - 2 \cdot \sigma_{+-}) \cdot \frac{1}{\sigma_{ion}} \tag{S6}$$

$$A_2 = \left(\sigma_{++} - \frac{\sigma_{+-}^2}{\sigma_{--}}\right) \cdot \frac{1}{\sigma_{ion}} \tag{S7}$$

$$A_3 = (\sigma_{++} \cdot \sigma_{--} - \sigma_{+-}^2) \cdot \frac{d\ln(a_{\pm})}{d\ln(c_{salt})} \cdot \frac{1}{\sigma_{ion}^2} \tag{S8}$$

$$A_4 = (\sigma_{--} - \sigma_{+-}) \cdot \frac{d\ln(a_{\pm})}{d\ln(c_{salt})} \cdot \frac{1}{\sigma_{ion}} \tag{S9}$$

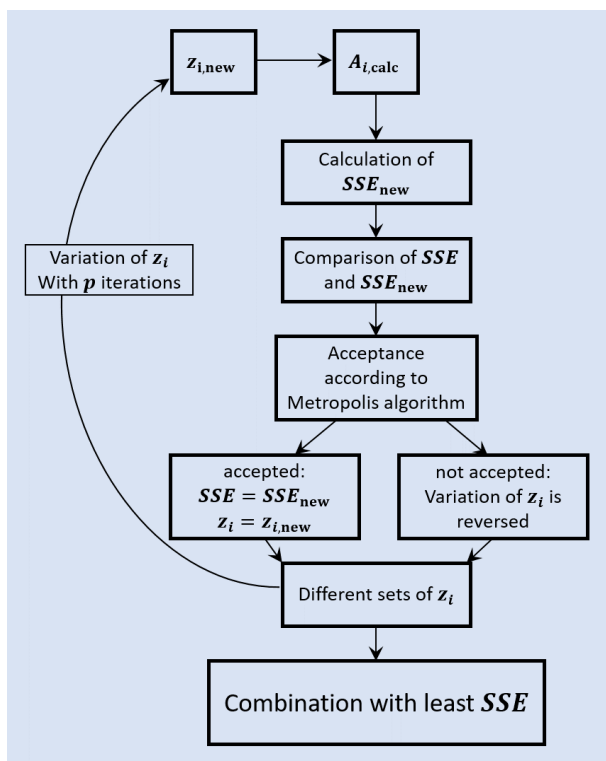$$A_5 = (\sigma_{++} - \sigma_{+-}) \cdot \frac{1}{\sigma_{ion}} \tag{S10}$$

Figure S2: Scheme of the Reverse Monte Carlo approach for determining the Onsager coefficients and the thermodynamic factor from five experimental quantities.
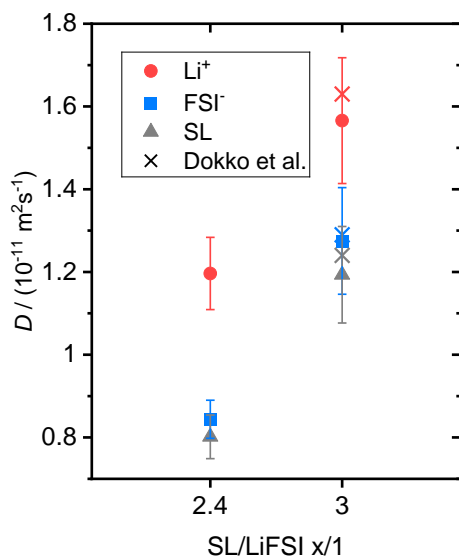
Diffusion coefficients

Figure S3: Diffusion coefficients D of SL/LiFSI = x/1 electrolytes with x = 2.4, 3 for Li$^+$ (red circles), FSI$^-$ (blue squares) and SL (grey triangles). Crosses show data from Dokko et al.[3]
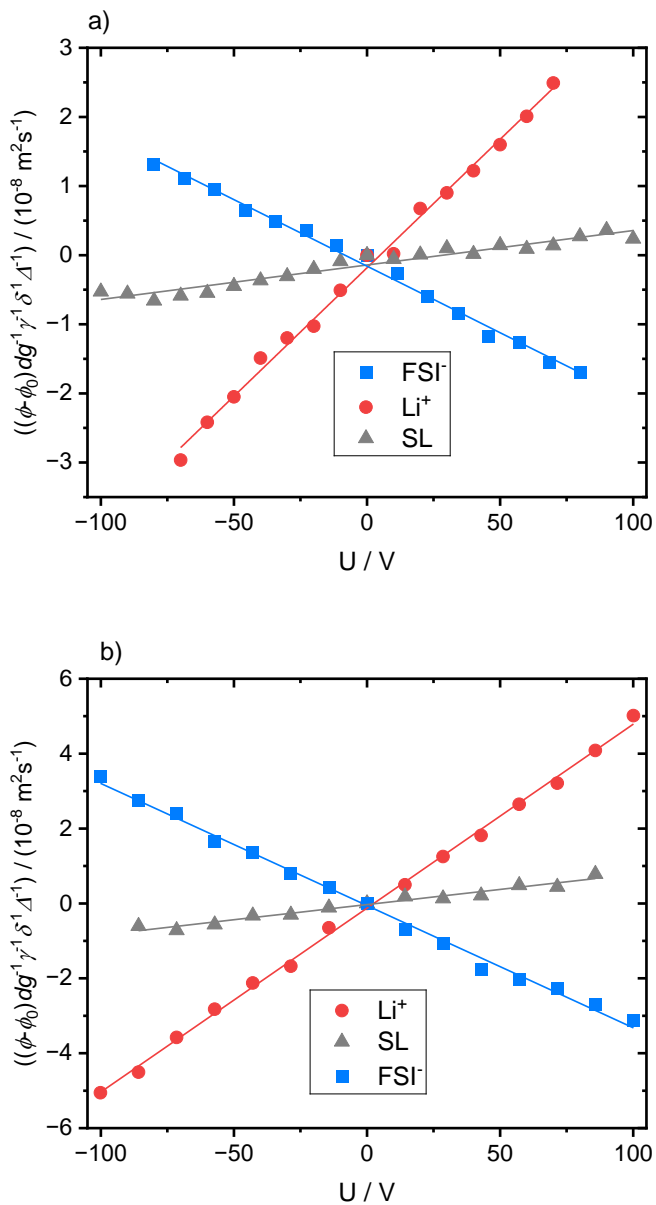
Phase shift data from eNMR

Figure S4: Representative reduced phase shift data $(\phi - \phi_0)dg^{-1}\gamma^{-1}\delta^{-1}\Delta^{-1}$ from eNMR including a linear fit for Li$^+$ (red circles) FSI$^-$ (blue squares) and SL (grey triangles) of SL/LiFSI x/1 electrolytes at concentrations a) x = 2.4 and b) x = 3.

Calculation of σ_{eNMR}

The mobilities obtained from eNMR can be used to calculate the conductivity σ_{eNMR}, which is in good agreement with the results from impedance spectroscopy. Since the electrophoretic mobilities of each constituent take into account ion correlations in the electrolyte, Eqs. S11 applies:

$$\sigma_{eNMR} = \sum_i \sigma_i = \sum_i e\, z_i \mu_i N_i \tag{S11}$$

Here, z_i is the charge number, and N_i is the number density of the respective ionic constituent, which was calculated from the mass density, see Table S1 and accompanying text.
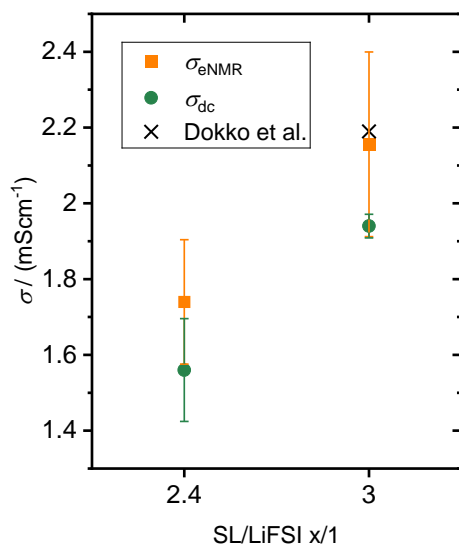

Figure S5: Comparison of conductivities σ from eNMR (orange squares), impedance spectroscopy (green circles) and literature[3] (cross) for SL/LiFSI x/1 electrolytes with x = 2.4, 3.

Density measurements

A DDM 2910 Automatic Density Meter (Rudolph Research Analytical, Lünen, Germany) was used to measure mass densities, which were subsequently used to calculate the concentrations of species in the electrolytes. Prior to use, the instrument was flushed with dry nitrogen to prevent the samples from contact with oxygen and water. The measurement temperature was set to 30 °C with a thermal equilibration time of at least 15 min.

Table S1. Densities ρ of sulfolane-based electrolytes at 30 °C

sample	ρ / (gcm^{-3})
SL/LiFSI 2.4/1	1.492
SL/LiFSI 3/1	1.458

Volume flux

It was shown that local molar volume conservation is the constraint governing the transport properties of concentrated, incompressible electrolytes.[4] The net volume flux must be zero, denoting that the flux of a species in one direction must be counteracted by a net flux of a constituent in the opposite direction. Experimentally this can be evidenced by means of eNMR, as the total molar volume flux J_V can be calculated from the mobilities μ_i and the molar volume v_i of the involved species. The ratio of J_V and the sum of the absolute individual volume fluxes is $J_{V,\text{tot}}$, is evaluated as a measure for the magnitude of a net volume flux. As SL has a slightly positive mobility (see Figure 3a)) it also contributes to the volume flux, and is taken into account with x accounting for the ratio SL to LiFSI in Eqs. S12.

$$\frac{J_V}{J_{V,\text{tot}}} = \frac{\mu_+ v_+ + \mu_- v_- + x\,\mu_{SL}\,v_{SL}}{|\mu_+ v_+| + |\mu_- v_-| + |x\,\mu_{SL}\,v_{SL}|} \tag{S12}$$

This ratio is zero for the electrolytes investigated here, see Fig S6.

In an analogous manner, the mass flux J_M can be calculated with the molecular weight of the constituents, which results in a non-zero ratio of the net mass flux J_M and the absolute total mass flux $J_{M,\text{tot}}$.[4]
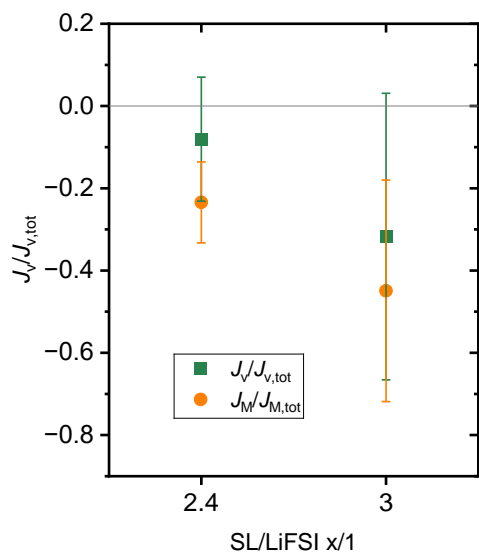
Figure S6: Ratio of the molar volume flux $J_V/J_{v,tot}$ (green squares) in comparison with mass flux $J_M/J_{M,tot}$

Distribution of Onsager coefficients and of the thermodynamic factor for SL/LiFSI 2.4/1
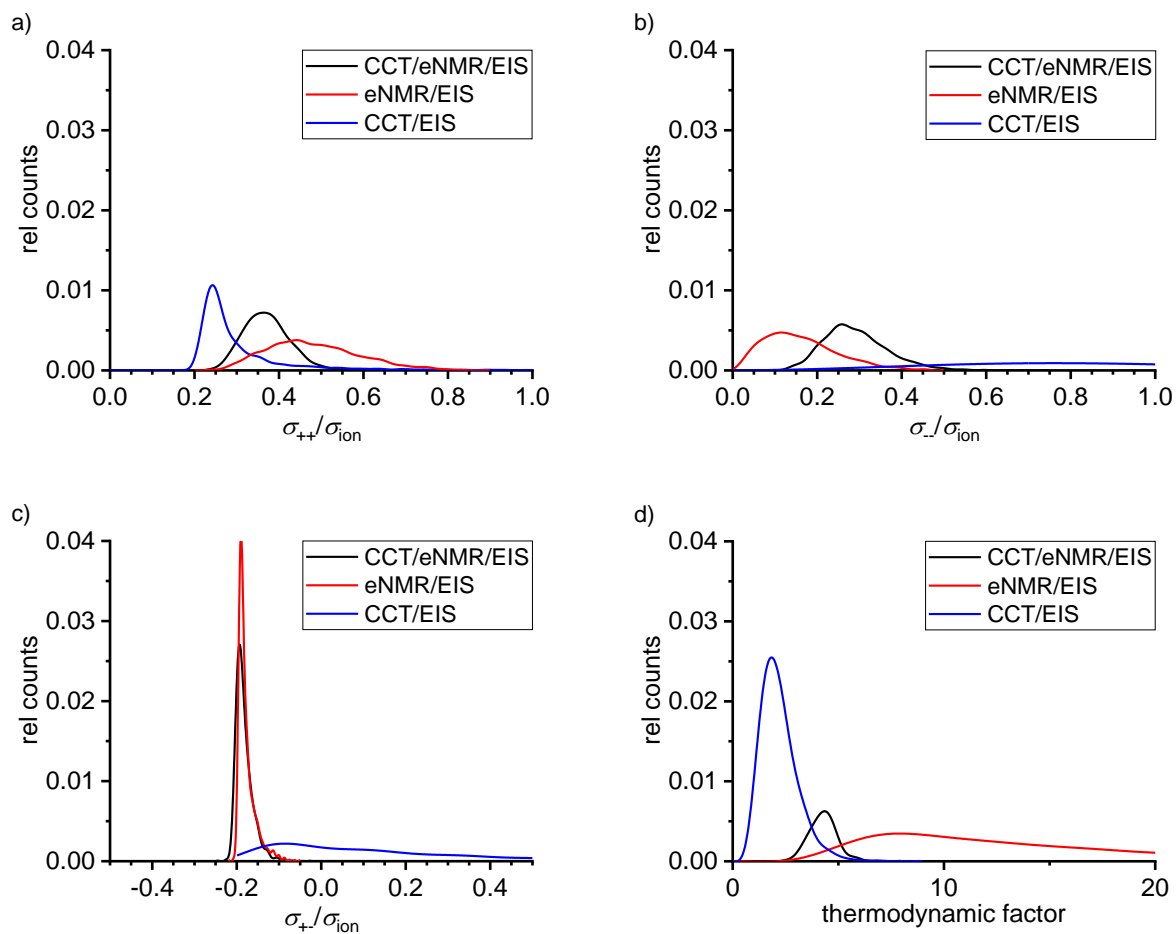

Figure S7: Calculated distributions of the normalized Onsager coefficients a) σ_{++}/σ_{ion}, b) σ_{--}/σ_{ion}, c) σ_{+-}/σ_{ion} and d) the thermodynamic factor for the SL/LiFSI 2.4/1 electrolyte.

Table S2: Normalized distinct parts of σ_{++} and σ_{--} for both electrolytes.

SL/LiFSI	$\sigma_{++}^{distinct}/\sigma_{ion}$	$\sigma_{--}^{distinct}/\sigma_{ion}$
2.4/1	-0.5 ± 0.2	-0.4 ± 0.1
3/1	-0.4 ± 0.1	-0.37 ± 0.09

References:

1. D. Dong, F. Sälzer, B. Roling and D. Bedrov, *Phys. Chem. Chem. Phys.*, 2018, **20**(46), 29174.

2. S. Pfeifer, F. Ackermann, F. Sälzer, M. Schönhoff and B. Roling, *Phys. Chem. Chem. Phys.*, 2021, **23**(1), 628.

3. K. Dokko, D. Watanabe, Y. Ugata, M.L. Thomas, S. Tsuzuki, W. Shinoda, K. Hashimoto, K. Ueno, Y. Umebayashi and M. Watanabe, *J. Phys. Chem. B*, 2018, **122**(47), 10736.

4. M. Lorenz, F. Kilchert, P. Nürnberg, M. Schammer, A. Latz, B. Horstmann and M. Schönhoff, *J. Phys. Chem. Lett.*, 2022, **13**(37), 8761.