Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPLEMENTARY MATERIAL

Electrolyte solvents for high voltage lithium ion batteries: ion correlation and specific anion effects in adiponitrile

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1 CHELPG partial charges for atoms of adiponitrile

Table 1 shows the CHELPG partial charges for atoms of adiponitrile with regard to quantum chemical calculations as described in the main article. All other parameters (bonded and non-bonded interactions) are identical to the corresponding atom types defined in the OPLS/AA force field (1).

Table 1: CHELPG partial charges for atoms of adiponitrile. All other parameters are identical to Ref. 1.

Atom types	Partial charges $q\,[e]$
N	-0.53
C(N)	0.48
C3	-0.35
C(alkyl)	0.10
H(C3)	0.13
H(alkyl)	0.02

2 Mass densities: experimental and simulation results

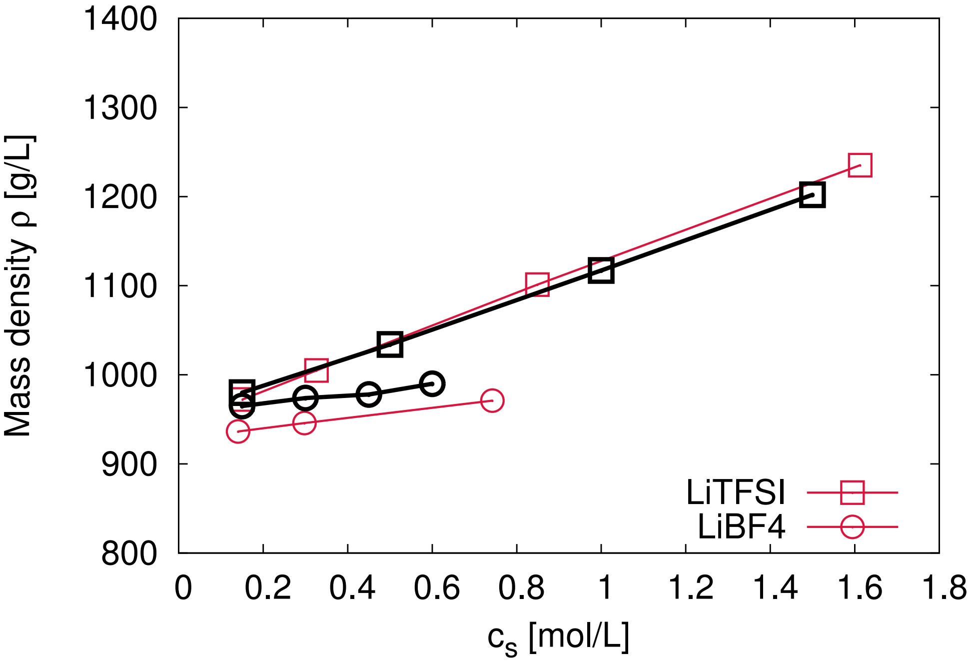

Figure 1: Mass densities of all simulated adiponitrile-lithium salt electrolyte formulations. Black symbols represent experimental results, whereas red symbols indicate simulation outcomes. The values for LiTFSI and LiBF4 electrolyte solutions with different salt concentrations c_s are marked as squares and circles, respectively.

3 Coordination number of adiponitrile molecules around lithium ions

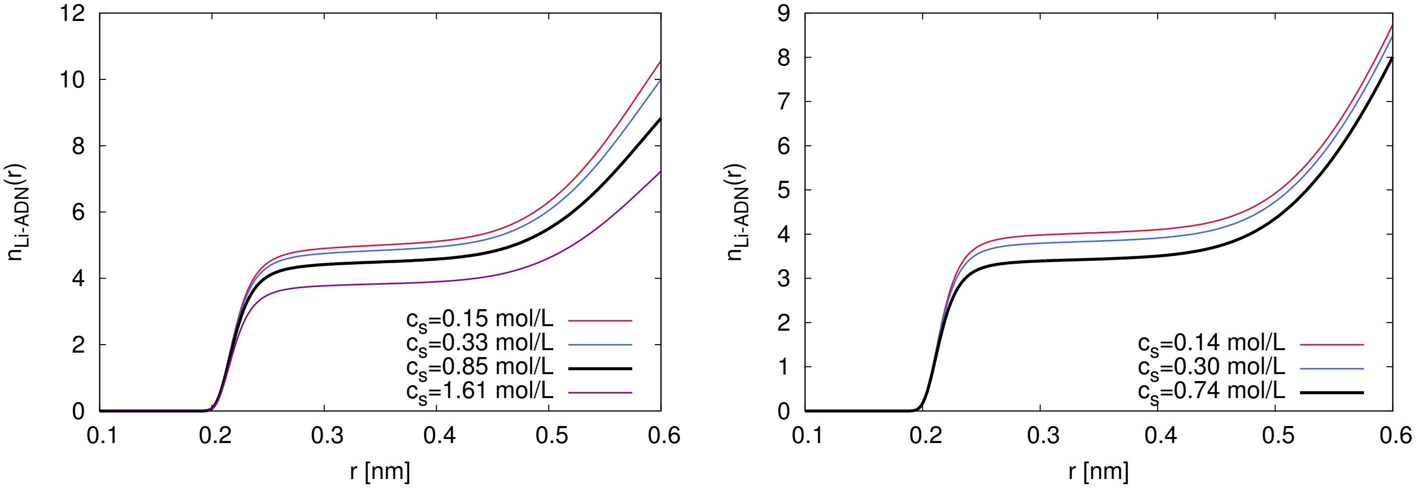

Figure 2: Left side: Coordination number of adiponitrile molecules $n_{\text{Li-ADN}}(r)$ around lithium ions for various salt concentrations of LiTFSI. Right side: Coordination number of adiponitrile molecules $n_{\text{Li-ADN}}(r)$ around lithium ions for various salt concentrations of LiBF_4.

4 Center-of-mass radial distribution functions between lithium ions and anions

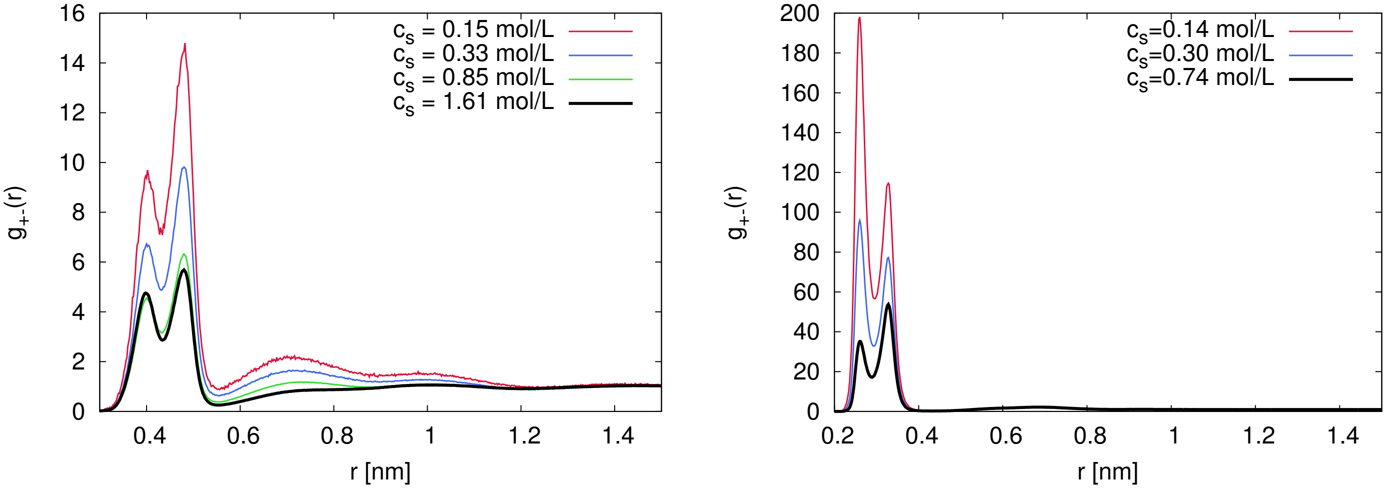

Figure 3: Left side: Center-of-mass radial distribution functions between lithium ions and TFSI anions for different salt concentrations c_s of LiTFSI in adiponitrile. Right side: Center-of-mass radial distribution functions between lithium ions and BF_4^- anions for different salt concentrations c_s of LiBF_4 in adiponitrile.

5 Radial distribution functions for LiTFSI: lithium ions and nitrogen atoms of TFSI$^-$ and adiponitrile

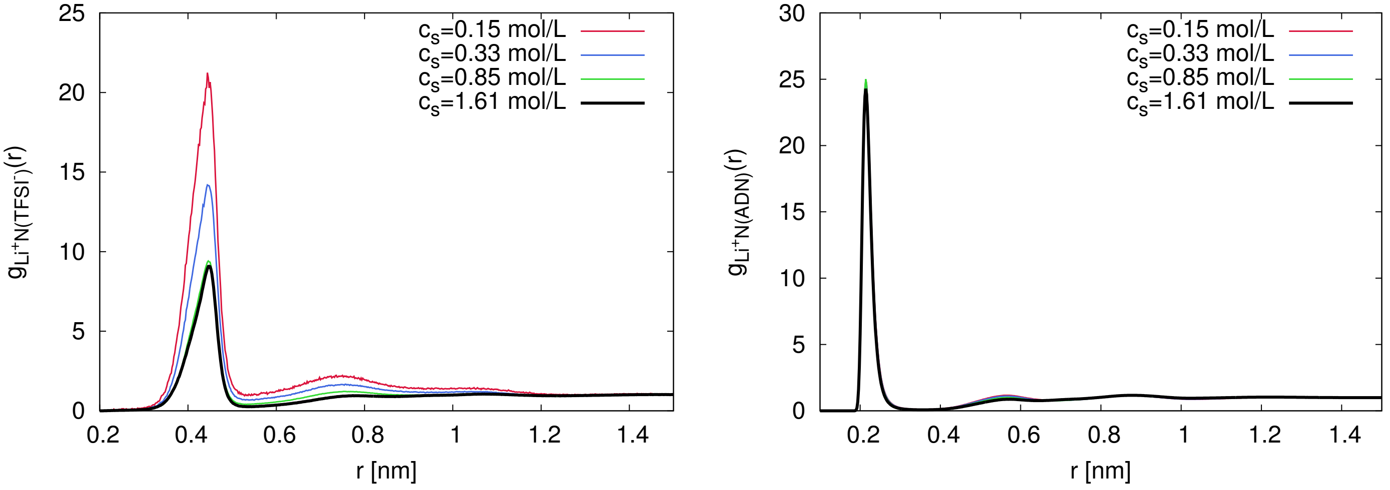

Figure 4: Left side: Atomic radial distribution functions between lithium ions and nitrogen atoms of TFSI anions for different salt concentrations c_s of LiTFSI in adiponitrile. Right side: Atomic radial distribution functions between lithium ions and nitrogen atoms of adiponitrile for different salt concentrations c_s of LiTFSI in adiponitrile.

6 Radial distribution functions for LiBF$_4$: lithium ions and fluorine atoms of BF$_4^-$ and nitrogen atoms of adiponitrile

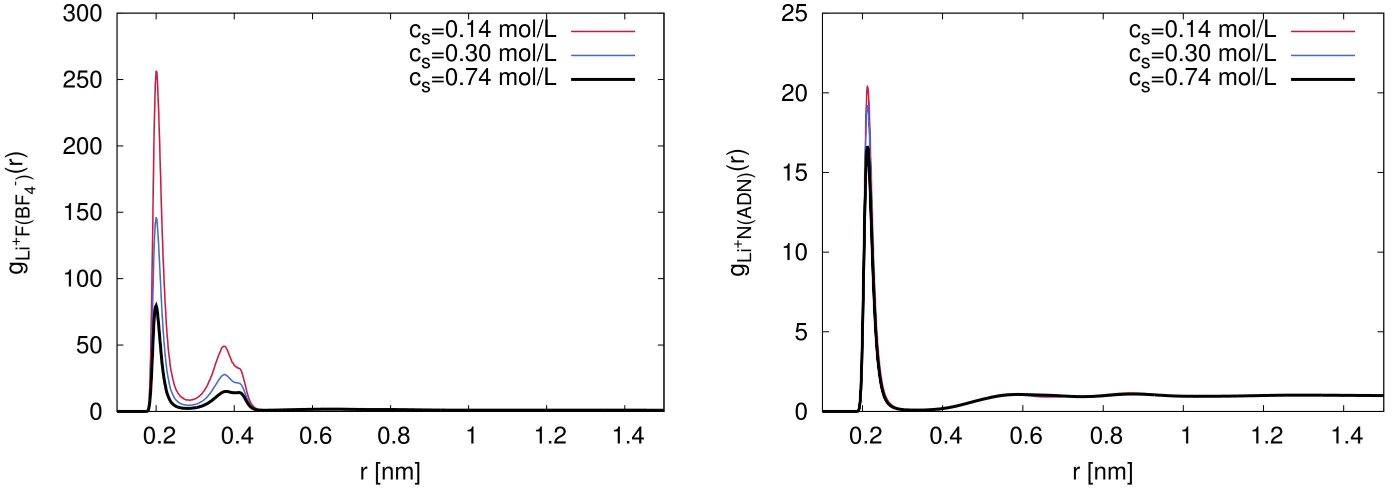

Figure 5: Left side: Atomic radial distribution functions between lithium ions and fluorine atoms of BF$_4^-$ anions for different salt concentrations c_s of LiBF$_4$ in adiponitrile. Right side: Atomic radial distribution functions between lithium ions and nitrogen atoms of adiponitrile for different salt concentrations c_s of LiBF$_4$ in adiponitrile.

7 Relative coordination numbers in LiBF$_4$-ADN mixtures: local environment around lithium and BF$_4^-$ ions

The relative coordination number around lithium and BF$_4^-$ ions is defined as $n_{(+/-)j}(r) = n_j(r)/n_{\text{tot}}(r)$, where $n_{\text{tot}}(r)$ denotes the total coordination number of all species around the corresponding reference ions. The results for LiBF$_4$ are shown in Fig. 6.

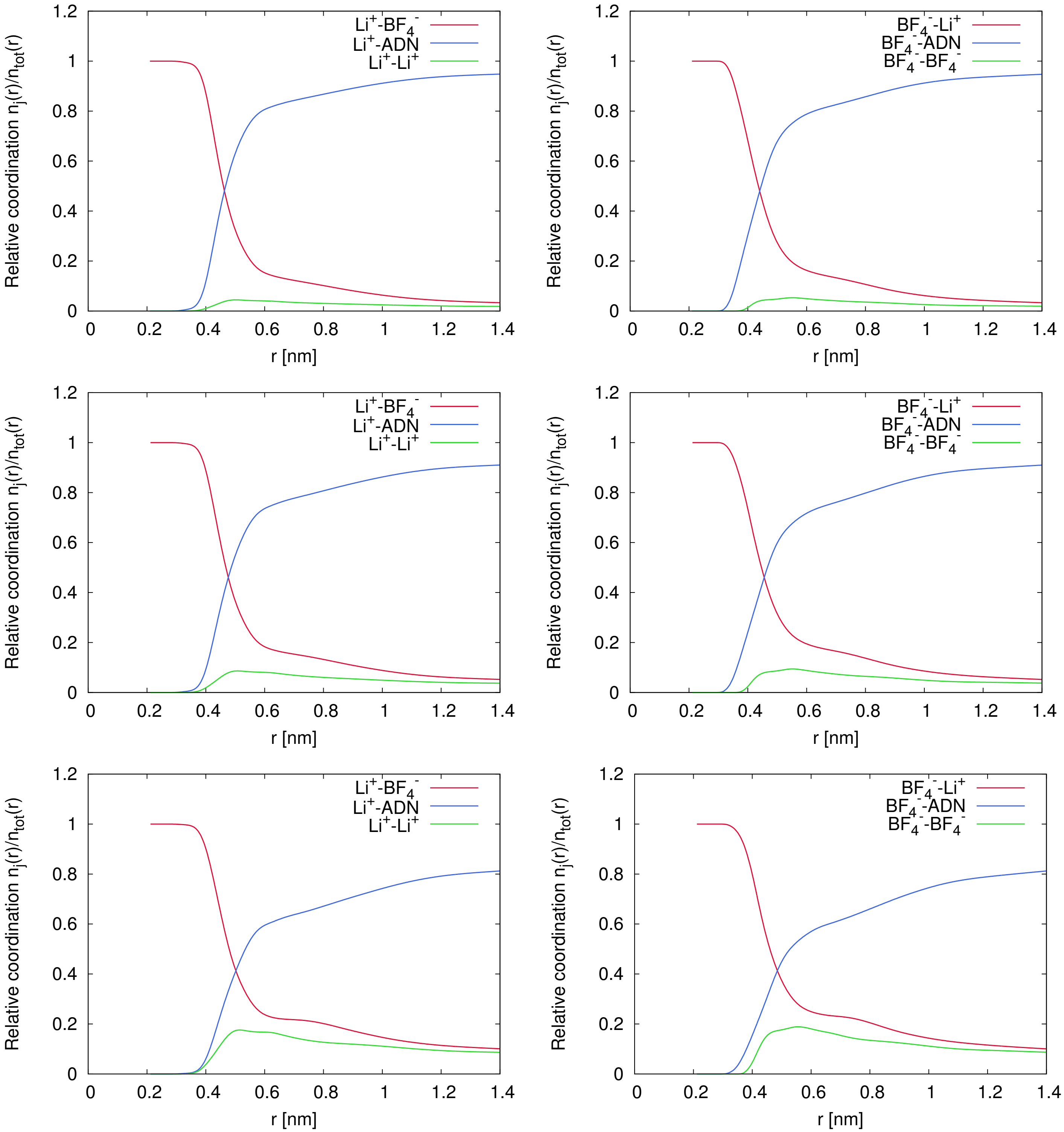

Figure 6: Relative coordination number for species $n_j(r)/n_{\text{tot}}(r)$ as denoted in the legend for different LiBF4 concentrations of $c_s = 0.14$ mol/L (top), $c_s = 0.30$ mol/L (middle), and $c_s = 0.74$ mol/L (bottom) around lithium (left side) and BF_4^- ions (right side).

8 Relative coordination numbers in LiTFSI-ADN mixtures: local environment around lithium and TFSI$^-$ ions

The relative coordination number around lithium and TFIS$^-$ ions is defined as $n_{+/-}(r) = n_j(r)/n_{\text{tot}}(r)$, where $n_{\text{tot}}(r)$ denotes the total coordination number of all species around the correspondng reference ions. The results for LiTFSI are shown in Fig. 7.

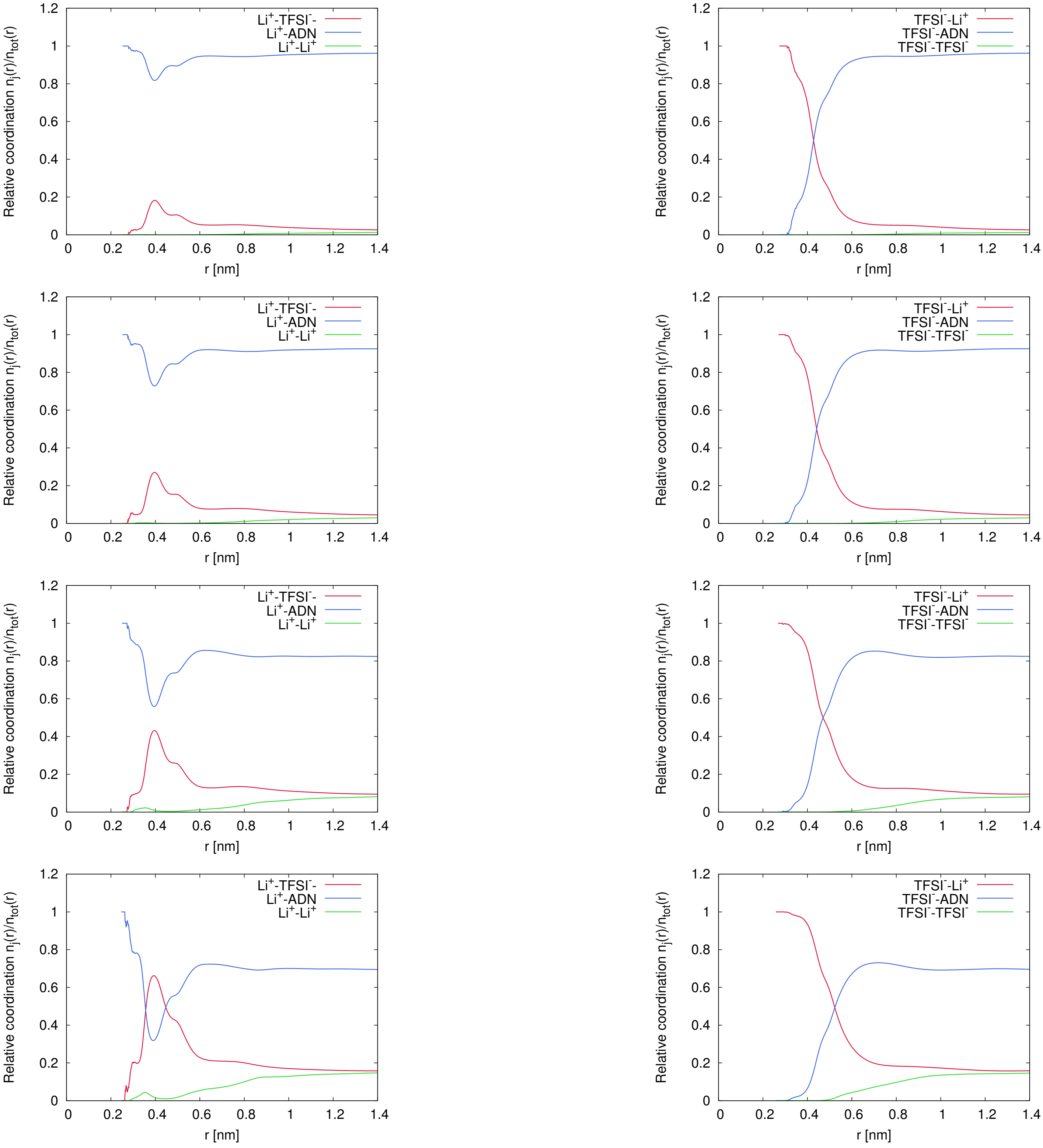

Figure 7: Relative coordination numbers for species $n_j(r)/n_{\text{tot}}(r)$ as denoted in the legend for different LiTFSI concentrations from top to bottom with $c_s = 0.15$ mol/L, $c_s = 0.33$ mol/L, $c_s = 0.85$ mol/L, and $c_s = 1.61$ mol/L around lithium (left side) and BF_4^- ions (right side)

9 Potentials of mean force between ions

Potentials of mean force (PMF) between the lithium ions and the corresponding anions were calculated in accordance with

$$\Delta_{\mathrm{PMF}} = -k_B T \ln g_{+-}(r) \tag{1}$$

where $g_{+-}(r)$ denotes the radial distribution function between Li^+ and anions (Ref. (2)).

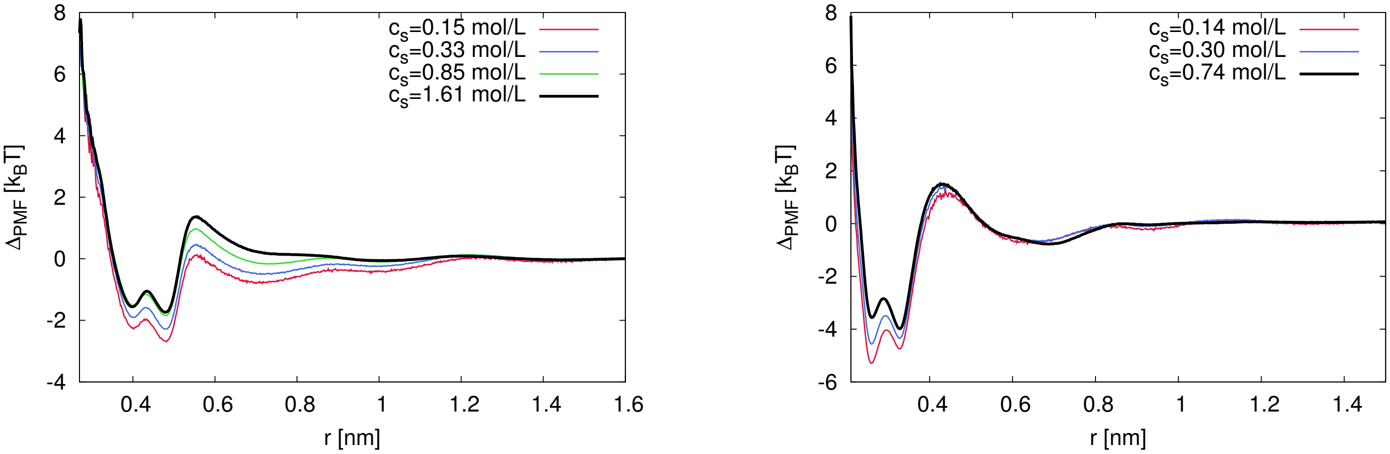

Figure 8: PMF values Δ_{PMF} between lithium ions and anions for different concentrations c_s of LiTFSI (left side) and LiBF_4 (right side).

10 Ion self-diffusion coefficients

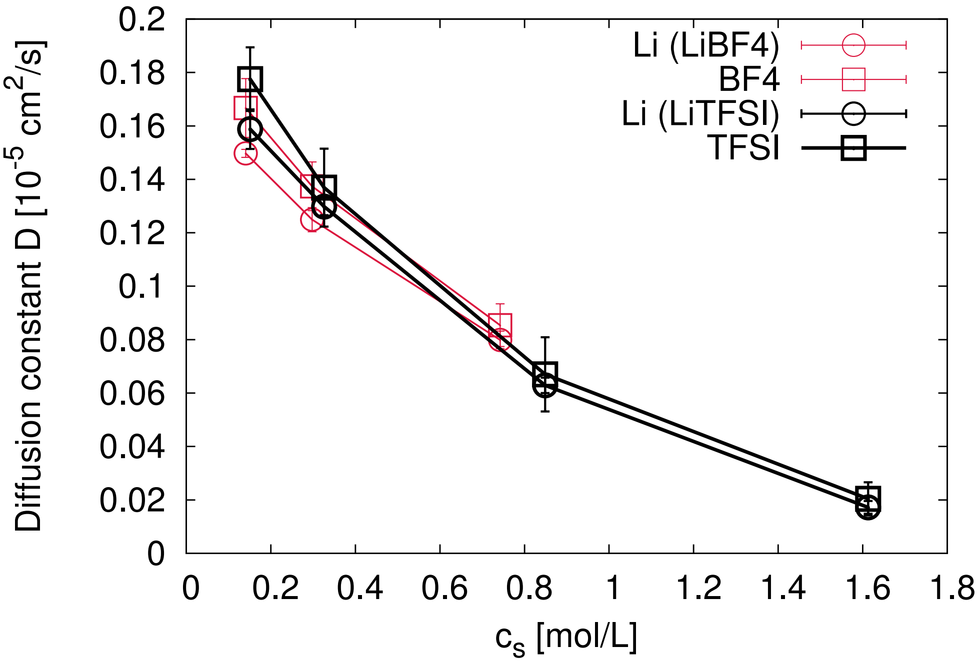

Figure 9: Self-diffusion coefficients for all ions at various salt concentrations c_s. The values for lithium ions are shown as circles (red color for lithium ions of LiTFSI and black color for lithium ions of LiBF_4). The corresponding results for the anions are shown as squares. The lines are just guides for the eye.

11 Correlation between relaxation time scales

The relaxation times τ_{TST} for ion species are calculated in accordance with Eqn. 29 in the main text (values from Fig. 4). The ion relaxation times are calculated according to the values shown in Tab. 3 in the main text. All values are shown in Tab. 2.

Table 2: Relaxation τ_{TST} and corresponding ion correlation times τ for distinct concentrations c_s of LiTFSI and LiBF$_4$ in adiponitrile.

Salt	Concentration c_s [mol/L]	τ_{TST} [ns]	τ [ns]
LiTFSI	0.15	0.005	0.319
LiTFSI	0.33	0.003	0.454
LiTFSI	0.85	0.001	2.169
LiTFSI	1.61	0.001	80.002
LiBF$_4$	0.14	0.036	6.653
LiBF$_4$	0.30	0.101	6.653
LiBF$_4$	0.74	6.292	24.644

12 Comparison of ideal ionic conductivities with results from NVE simulations

In order to study the influence of the barostat and the thermostat coupling times, we also performed NVE simulations in absence of any barostat or thermostat. We thus used preequilibrated structures from the NpT simulations (LiTFSI and LiBF4 in adiponitrile) with the corresponding salt concentrations, and radomly attributed velocities to the atoms in order to achieve a Maxwellian velocity distribution centered at 300 K. The simulations were run for 10 ns in order to keep the numerical error low. In order to increase the statistical accuracy, we only focused on salt concentrations above $c_s > 0.3$ mol/L. The corresponding results for the ideal ionic conductivity are shown in Fig. 10. As can be seen, the values between the NVE and NpT simulations differ by a factor of 4.5, but a linear relationship becomes evident. Hence, the presence of the barostat and the thermostat impose a constant factor to the ionic conductivities.

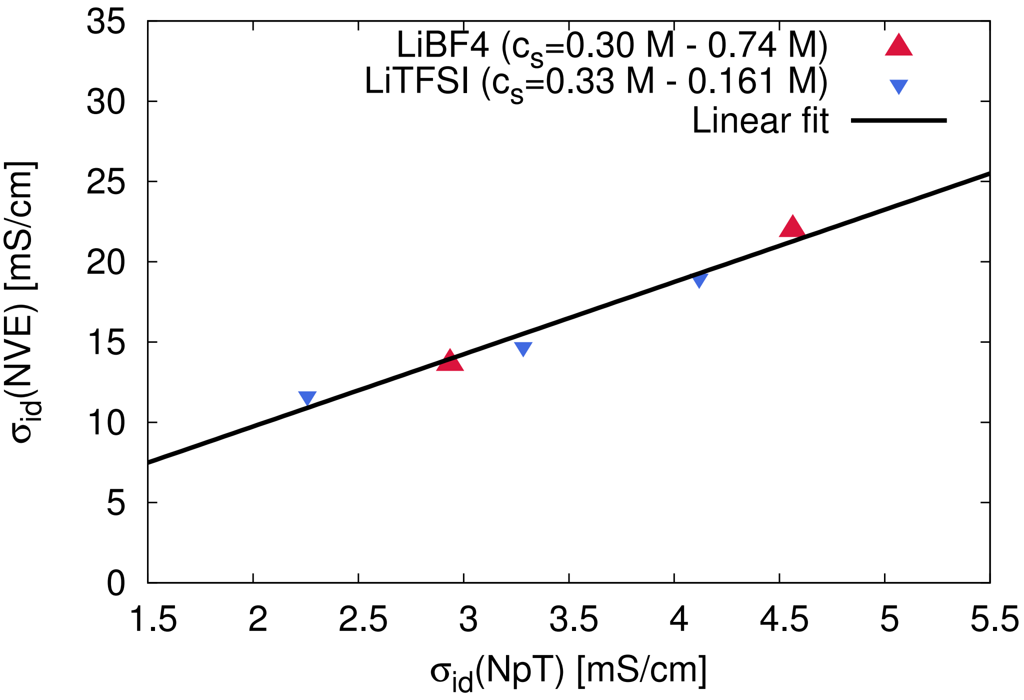

Figure 10: Values for the ideal ionic conductivities from NpT and NVE simulations with the corresponding salt concentrations as mentioned in the legend. The black solid lins corresponds to a linear fit function with slope $m = 4.5 \pm 0.4$ and an abscissa value of $\sigma^0_{\mathrm{id}}(\mathrm{NVE}) = 0.7 \pm 1.4$.

References

[1] William L Jorgensen, David S Maxwell, and Julian Tirado-Rives. Development and testing of the opls all-atom force field on conformational energetics and properties of organic liquids. *J. Am. Chem. Soc.*, 118(45):11225–11236, 1996.

[2] David Chandler. *Introduction to Modern Statistical Mechanics.* Oxford University Press, 1987.