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

Atomistic Insights Into Deep Eutectic Electrolytes: The Influence of Urea On The Electrolyte Salt LiTFSI in View of Electrochemical Applications

SUPPLEMENTARY MATERIAL

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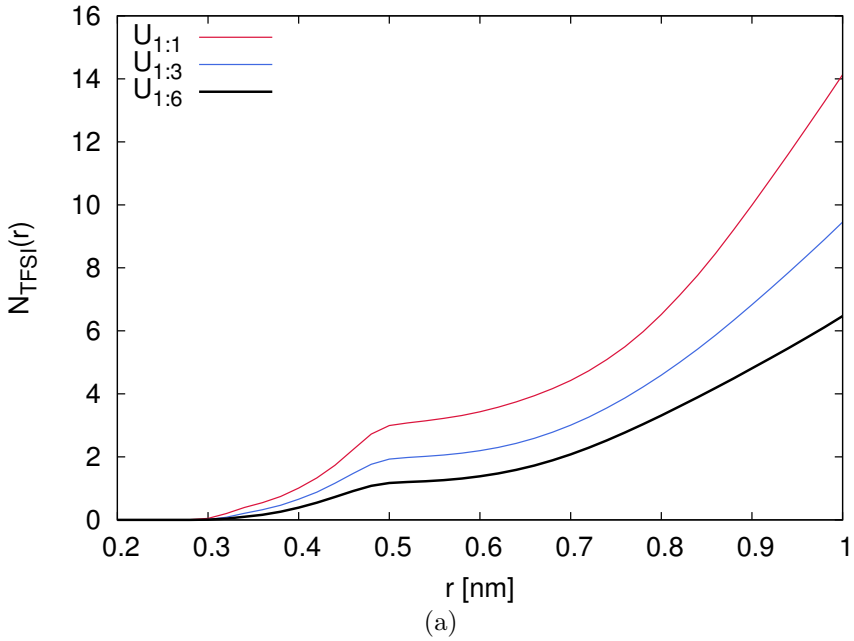
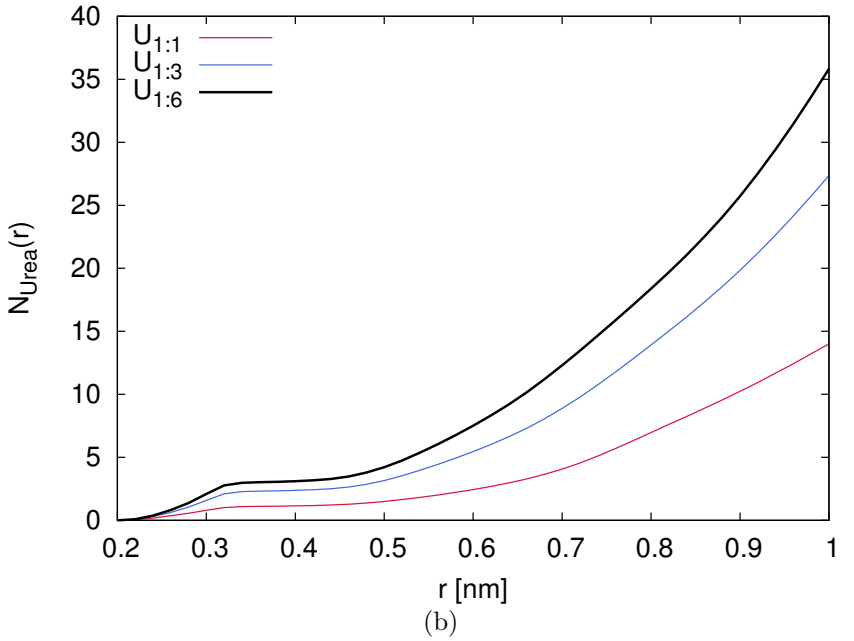
Coordination numbers for urea and TFSI around lithium ions



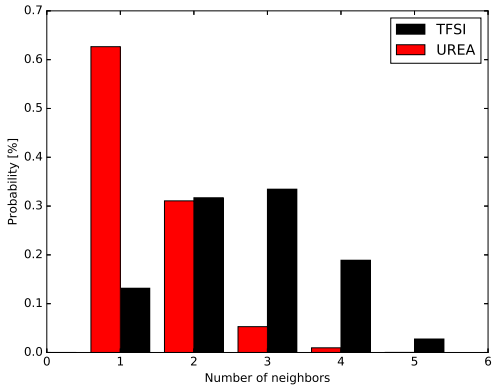
(a)



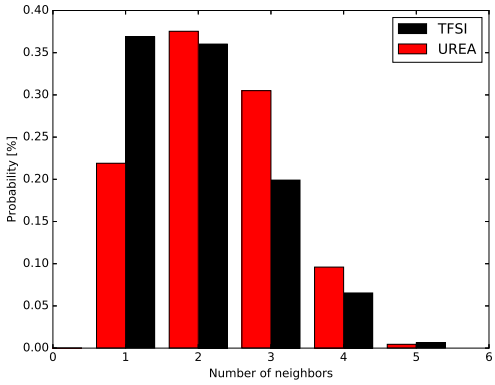
(b)

Figure 1: Coordination number of TFSI (a) and urea (b) molecules around lithium ions.

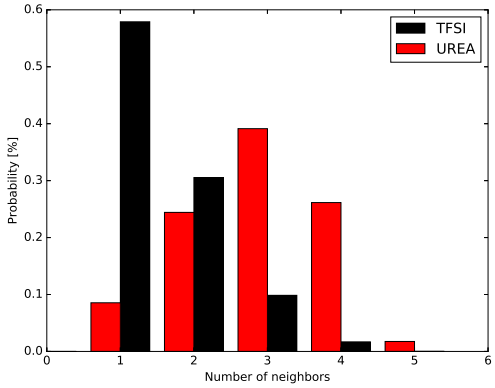
Occurrence probabilities for neighboring TFSI and urea molecules around lithium ions



(a) $U_{1:1}$



(b) $U_{1:3}$



(c) $U_{1:6}$

Figure 2: Probability for a coordination of lithium ions by a specific number of TFSI and urea molecules in the first coordination shell.

Residence times of TFSI ions around lithium

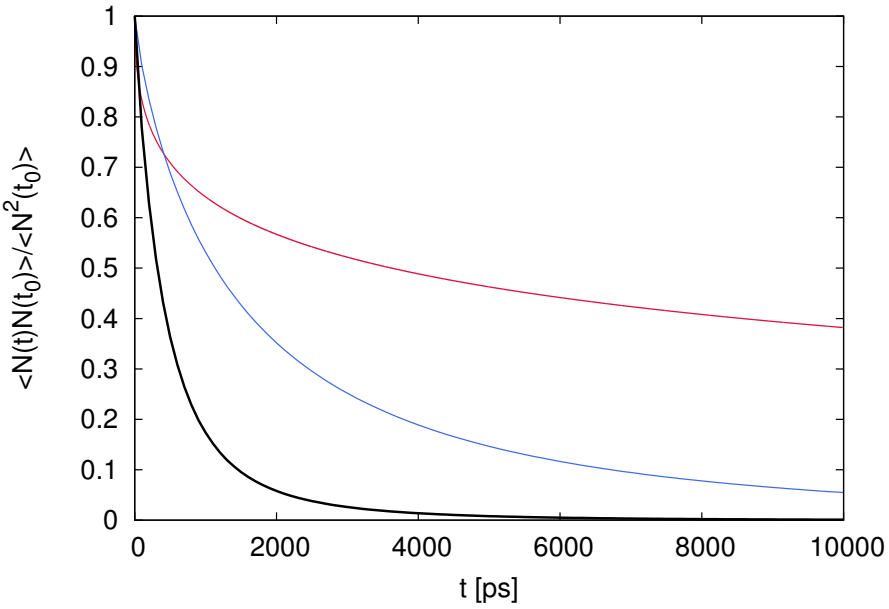


Figure 3: Autocorrelation function to determine the residence time τ of TFSI in the first coordination shell of lithium ions with a distance criterion of $r = 0.27$ nm. The colors denote different urea concentrations according to $U_{1:1}$ (red line), $U_{1:3}$ (blue line) and $U_{1:6}$ (black line).

Radial distribution functions

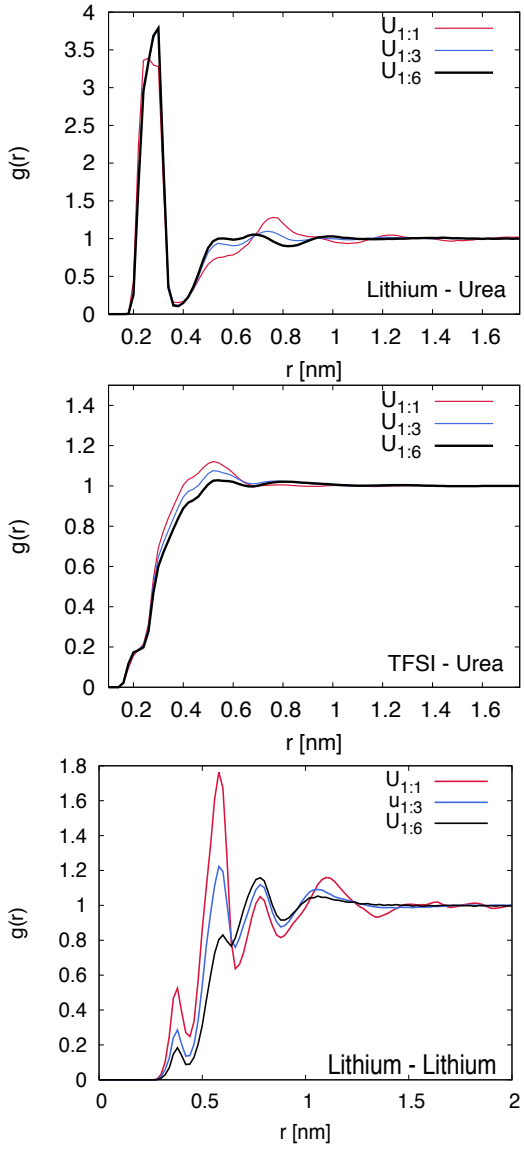


Figure 4: Center-of-mass radial distribution functions $g(r)$ for urea around lithium (top), urea around TFSI (middle) and lithium around lithium (bottom) for different urea concentrations as denoted in the legend.

Local/bulk partition coefficient

The coordination numbers of species β and γ around lithium ions were used to calculate the local/bulk partition coefficient

$$K_p(r) = (\langle N_\beta(r)\rangle / \langle N_\gamma(r)\rangle)/(N_\beta^0/N_\gamma^0) \tag{1}$$

which expresses the affinity to lithium ions. The brackets $\langle..\rangle$ denote the mean coordination number at distance r and the superscript $'0'$ indicates the total number of molecules in the simulation box[1,2].

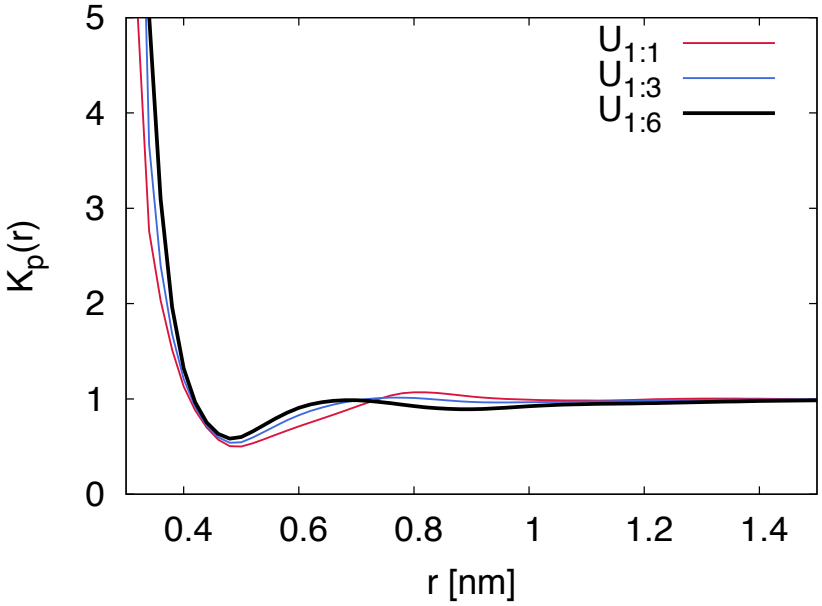


Figure 5: Local/bulk partition coefficient $K_p(r)$ for urea (β) and TFSI ions (γ) around lithium ions.

Diffusion coefficients

Table 1: Diffusion coefficients D_i in $1 \times 10^{-5}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$ for all three species depending on the urea concentration. The late onset of diffusive motion inhibits the calculation of D_i for the $\mathrm{U}_{1:1}$ mixture.

Species	D_i ($\mathrm{U}_{1:3}$)	D_i ($\mathrm{U}_{1:6}$)
urea	0.026	0.152
TFSI	0.007	0.067
lithium	0.010	0.072

Potential energies

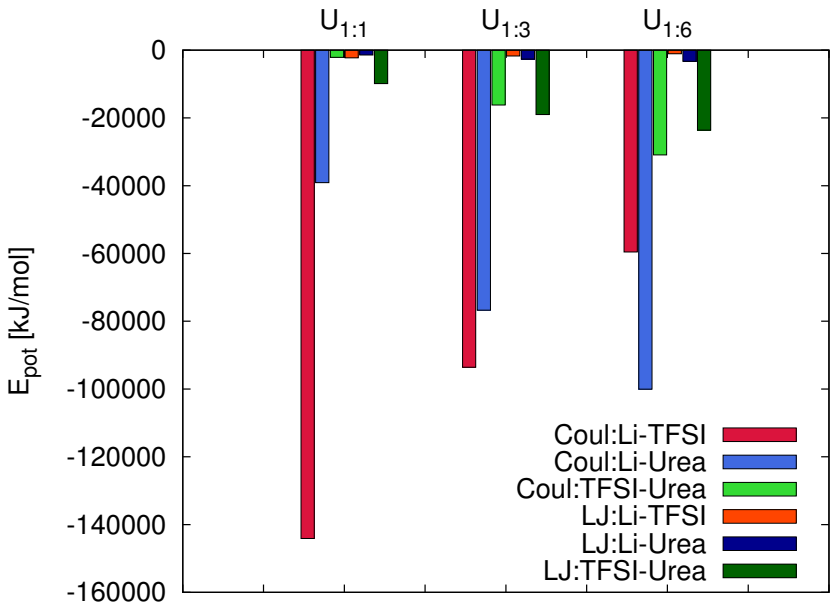


Figure 6: Coulomb (Coul) and Lennard-Jones (LJ) potential energies between the different compounds for the different mixtures.

References

(1) Courtenay, E.; Capp, M.; Anderson, C.; Record, M. Vapor pressure osmometry studies of osmolyte-protein interactions: implications for the action of osmoprotectants in vivo and for the interpretation of osmotic stress experiments in vitro. *Biochemistry* **2000**, *39*, 4455–4471.

(2) Micciulla, S.; Michalowsky, J.; Schroer, M. A.; Holm, C.; von Klitzing, R.; Smiatek, J. Concentration dependent effects of urea binding to poly(N-isopropylacrylamide) brushes: a combined experimental and numerical study. *Phys. Chem. Chem. Phys.* **2016**, *18*, 5324–5335.