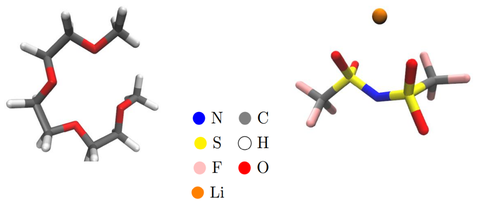
Cluster Formation in Mixtures of $[Li][NTf_2]$, Triglyme and Water

J. K. Philipp[1], *D. Paschek*[1] *and R. Ludwig*[1,2]

Introduction

- Conventional lithium battery electrolytes often possess undesirable properties like a high combustibility
- Possible alternatives: certain mixtures of Li salts and glycol ethers known to form pseudo-ionic liquids (Ils) [1]
- This work:
  - ➢ Insights into microscopic structure of pseudo-IL and mobility from molecular dynamics (MD) simulations

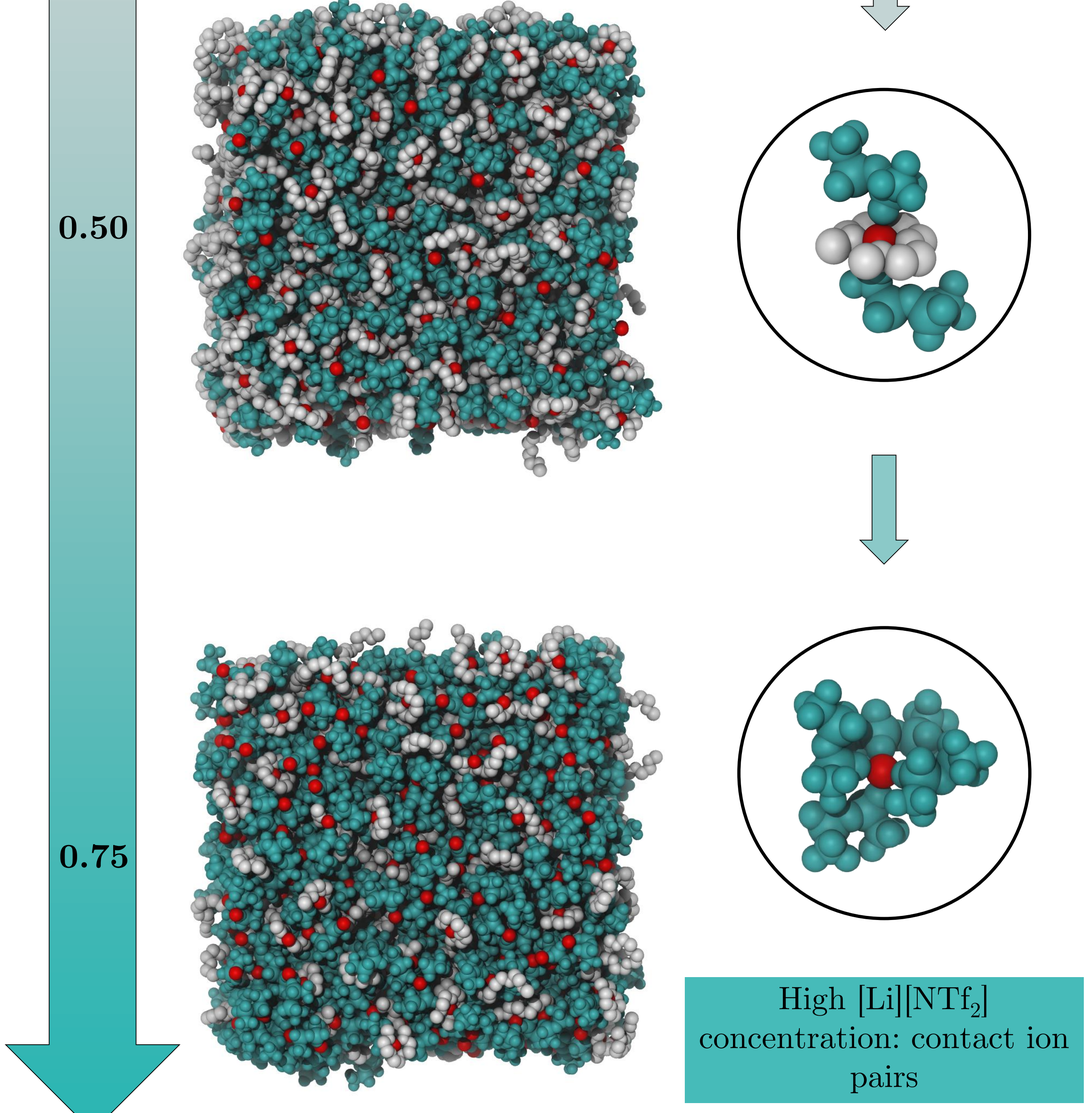


➢ Components of the investigated system: Left: 1,2-Bis(2-methoxy-ethoxy)ethane (triglyme/G3). Right: Lithium bis(trifluoro-methane-sulfonyl)azanide ($[Li][NTf_2]$).

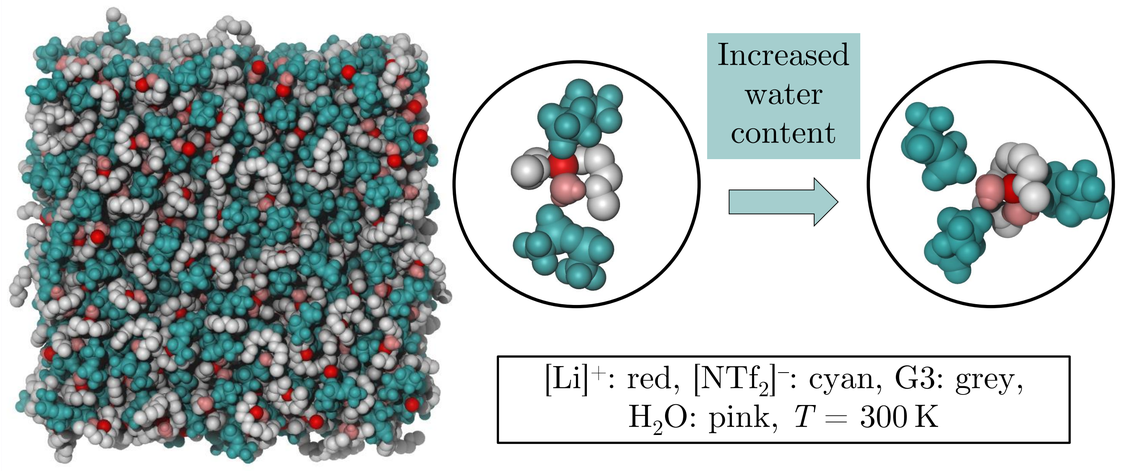
Molecular Dynamics Simulations

- NpT simulations at 300 – 480 K, $p = 1$ bar
- 2 ns equilibration, 20 – 100 ns simulation, $\Delta t = 2$ fs
- $x_{IP} \cdot 1080$ ion pairs and $(1 - x_{IP}) \cdot$ triglyme molecules
- $x_{IP} = 0.037$ (1 IP : 26 G3) – 0.75 (3 IP : 1 G3)
- for $x_{IP} = 0.5$ also water molecules added (IP:G3:H_2O = 0.5:1:1, 1:1:1, 2:1:1)
- GROMACS 2019.6
- MOSCITO 4.180
- Force fields:
  - $[Li]^+$: Joung and Cheatham [2]
  - $[NTf_2]^-$: NGOLP [3]
  - G3: Fischer et al. [4]
  - H_2O: TIP4P/2005 [5]

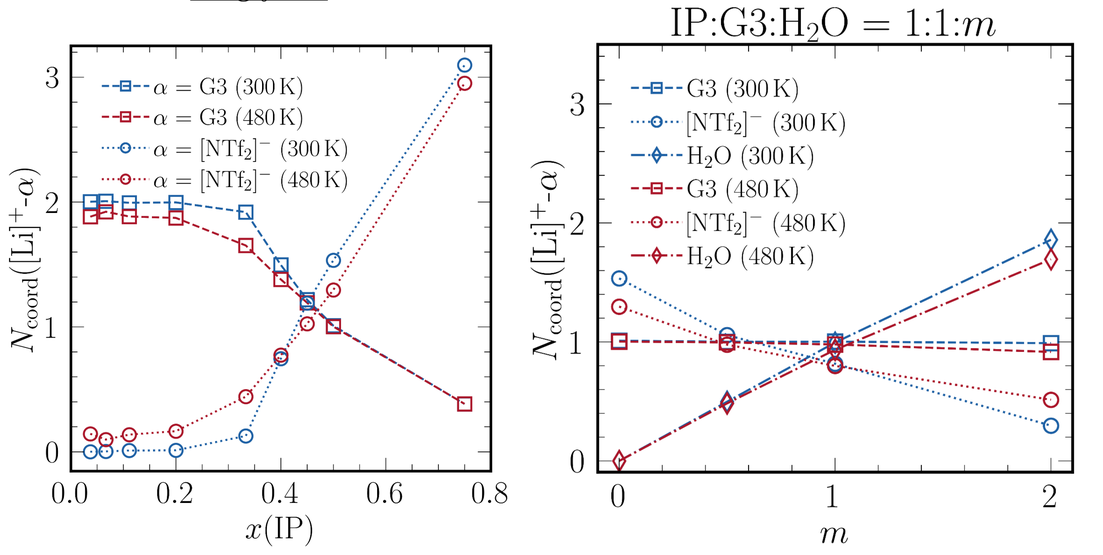
Structure of Mixtures without Water



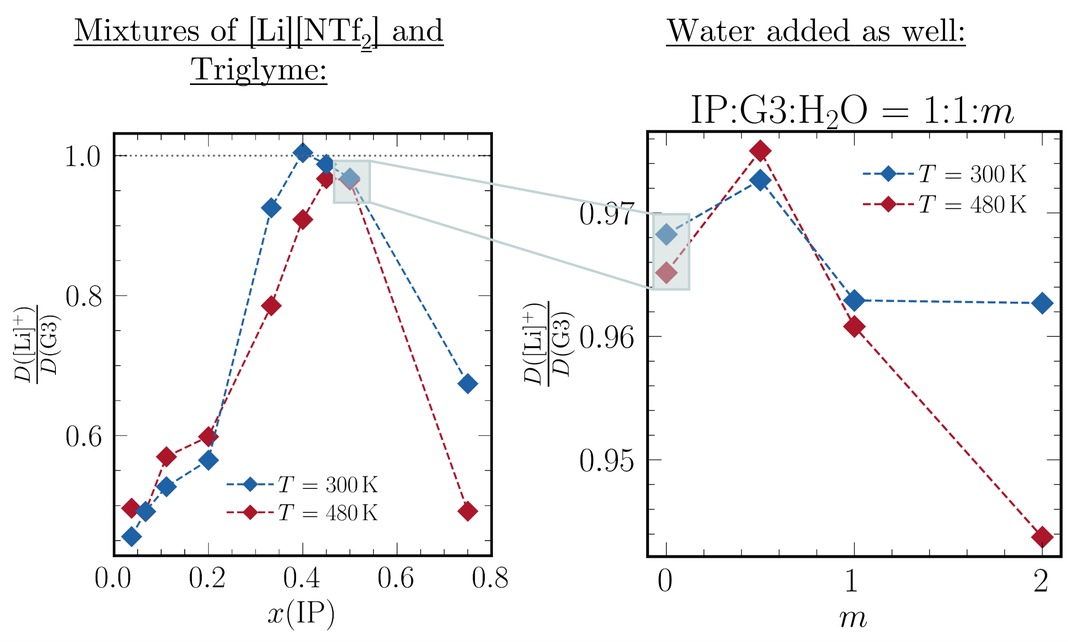
Structure of Mixtures with Water



Coordination Number



Self-Diffusion



Conclusion

- Added triglyme leads to one-fold or two-fold lithium coordination state
  - ➢ Charge separation and correlated movement of cations and triglyme molecules → Pseudo-IL obtained
- Water intercalates between triglyme and lithium and is additionally shielded by hydrogen bonds to counterions
- Simulations give insights into microscopic origin of macroscopic properties

References

[1] M. Watanabe, K. Dokko, K. Ueno, M. L. Thomas, *Bull. Chem. Soc. Jpn.* **2018**, 91, 1660-1682.
[2] I. S. Joung, T. E. Cheatham, *J. Phys. Chem. B* **2008**, 112, 9020–9041.
[3] J. Neumann, B. Golub, L.-M. Odebrecht, R. Ludwig, D. Paschek, *J. Chem. Phys.* **2018**, 148, 193828.
[4] J. Fischer, D. Paschek, A. Geiger, G. Sadowski, *J. Phys. Chem. B* **2008**, 112, 8849–8850.
[5] J. F. L. Abascal, C. J. Vega, *Chem. Phys.* **2005**, 123, 234505

Acknowlegements

DFG Deutsche Forschungsgemeinschaft

Email: jule.philipp@uni-rostock.de

[1] Physical and Theoretical Chemistry | University of Rostock | Albert-Einstein-Straße 27 | 18059 Rostock | Germany
[2] Leibniz-Institute for Catalysis at the University of Rostock | Albert-Einstein-Straße 29a | 18059 Rostock | Germany

www.ludwig.chemie.uni-rostock.de