# Influence of Water on the Transport Properties of Ternary Mixtures with Triglyme and $[Li][NTf_2]$

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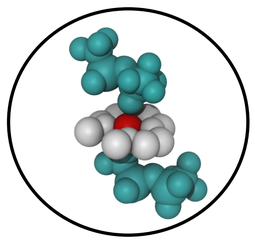
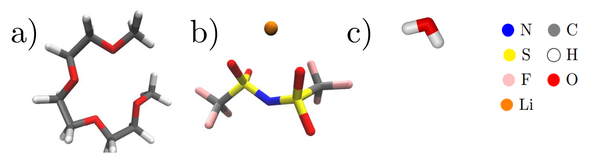
## Introduction

Conventional lithium battery electrolytes often possess undesirable properties like a high combustibility. A possible alternative are equimolar mixtures of lithium salts and glycol ethers known to form pseudo-ionic liquids (ILs) [1]. A previous computational study revealed the formation of 1:1 complexes of $[Li][NTf_2]$ and triglyme leading to the IL-like behaviour of the mixture.



$[Li]^+$: red, $[NTf_2]^-$: cyan, G3: grey, $T = 300\,\mathrm{K}$

This work aims at combining the concepts of pseudo-ILs and water-in-salt (WIS) electrolytes by adding water to the equimolar mixture of $[Li][NTf_2]$ and triglyme. From molecular dynamics (MD) simulations, we obtain insights into the microscopic structure of the ternary mixtures and their mobility. We especially investigate the influence of water cluster formation on the diffusion of the system.

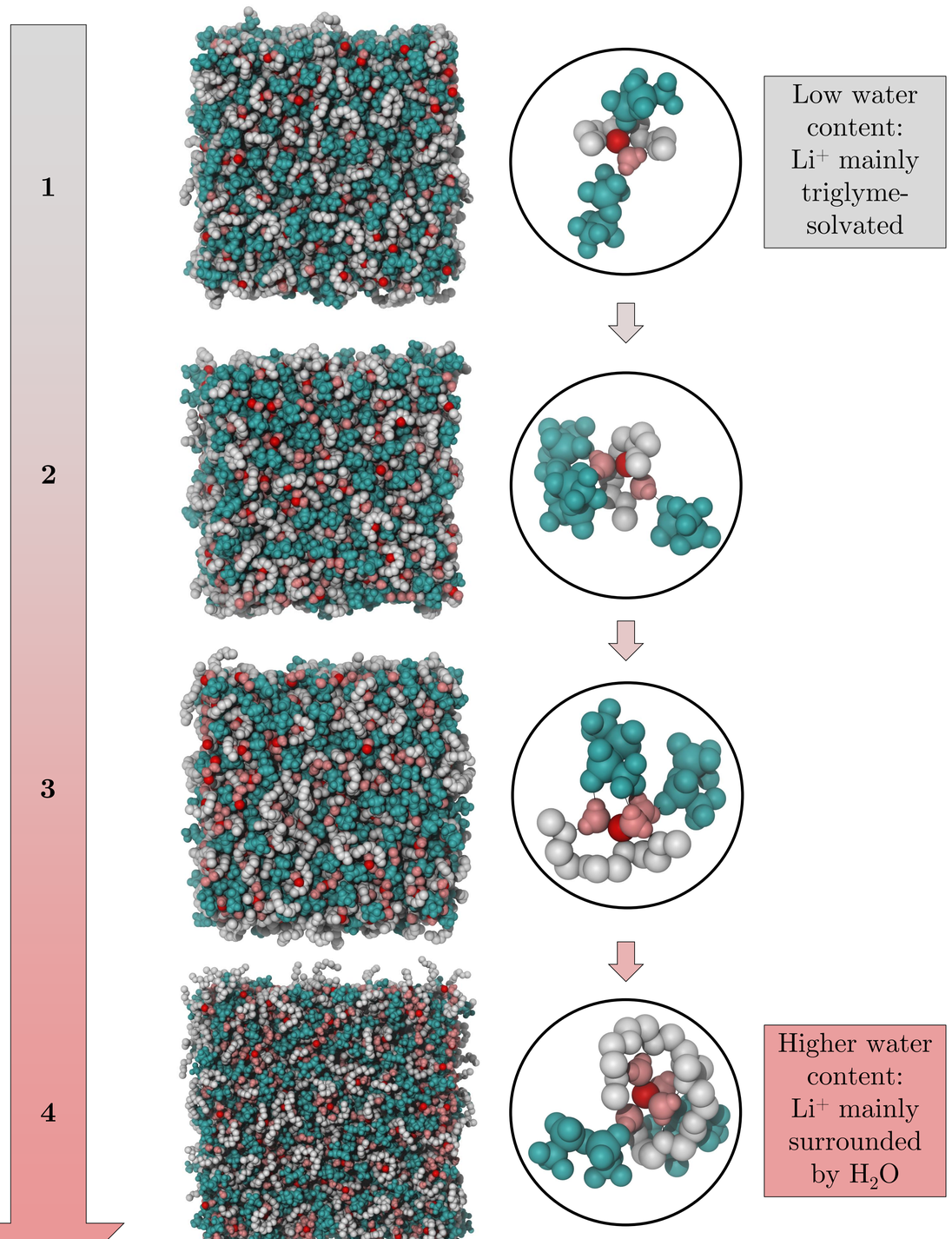



Components of the investigated system:
a) 1,2-Bis(2-methoxy-ethoxy)ethane (triglyme/G3).
b) Lithium bis(trifluoro-methane-sulfonyl)azanide ($[Li][NTf_2]$). c) Water.

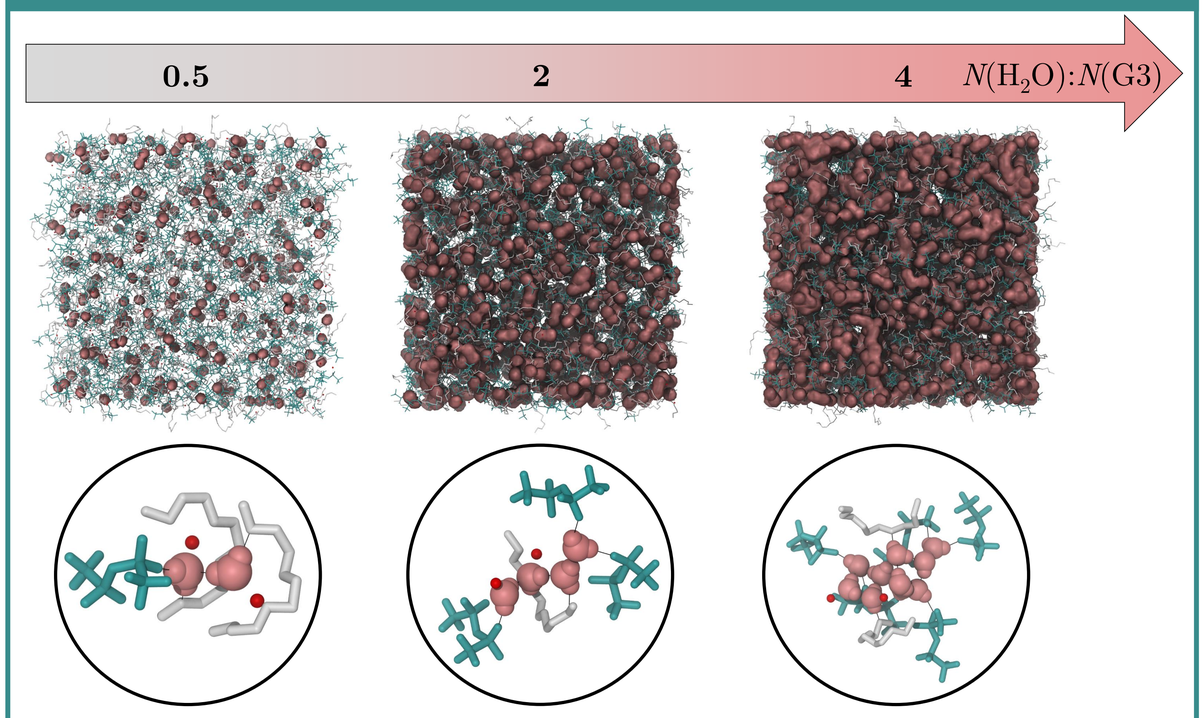
## Molecular Dynamics Simulations

- $NpT$ simulations at $300 - 480\,\mathrm{K}$, $p = 1\,\mathrm{bar}$
- $2\,\mathrm{ns}$ equilibration, $20 - 100\,\mathrm{ns}$ simulation, $\Delta t = 2\,\mathrm{fs}$
- $[Li][NTf_2]$:G3:$H_2O$ = 1:1:0.5, 1:1:1, 1:1:2, 1:1:3, 1:1:4
- 540 ion pairs + 540 triglyme molecules + 270, 540, 1080, 1620 or 2160 $H_2O$ molecules
- GROMACS 2019.6 and MOSCITO 4.180
- Force fields: $[Li]^+$: Joung and Cheatham [2]; $[NTf_2]^-$: NGOLP [3]; G3: Fischer et al. [4]; $H_2O$: TIP4P/2005 [5]

## Structural Motifs of Different Mixtures



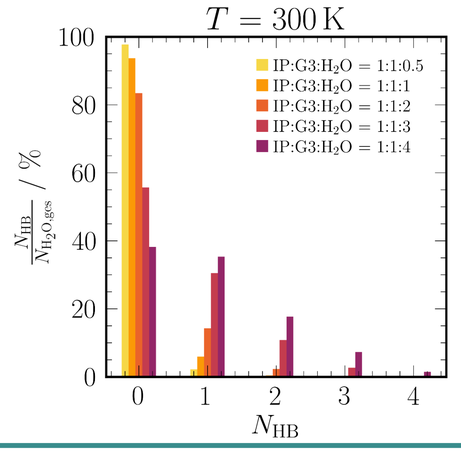

## Water Cluster Formation



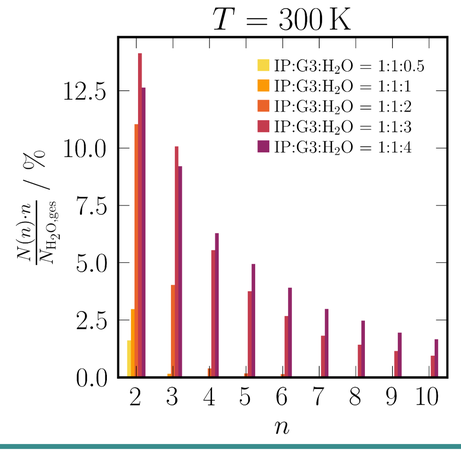

➢ Water cluster sizes increase rapidly at higher water ratios

## Structural Motifs of Different Mixtures

Hydrogen bonds per $H_2O$ molecule:

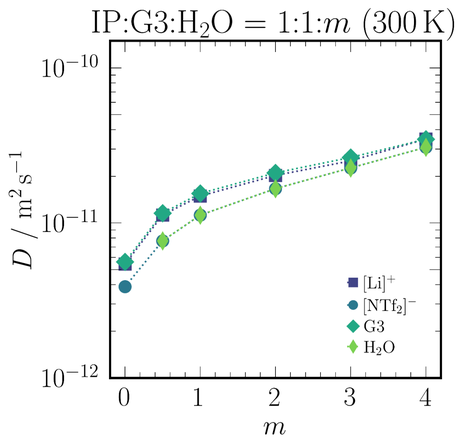


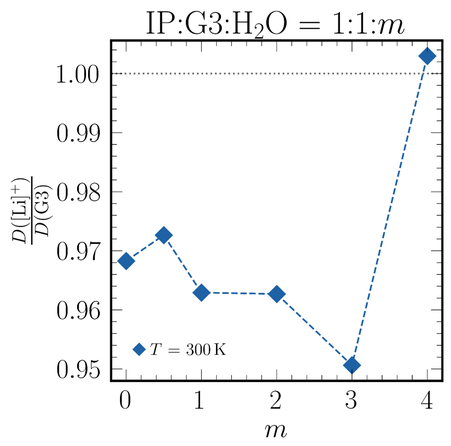

Cluster size distribution:




## Influence on Self-Diffusion

➢ Calculated from mean squared displacement via Einstein equation




## Conclusion

The MD simulations give important insights into the microscopic origin of macroscopic properties. This work demonstrates that in mixtures containing only water, triglyme and $[Li][NTf_2]$, the water molecules favourably insert themselves between triglyme and the lithium cations. Also, at low water content, the water molecules are shielded from each other by hydrogen bonds to the counterions. The isolated water molecules potentially have WIS-like properties which needs further investigations. However at high water ratios, water eventually forms clusters where water should behave similar to bulk-phase water. For all ternary mixtures we could show that adding water results in increased self-diffusion of all species and improves the transport properties of the pseudo-IL.

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Acknowlegements

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