

Computational studies on Li⁺-Oligoglyme Association in the Presence of Ionic Liquid

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Motivation

- Polymer electrolytes (eg. PEO+lithium salt) are used in ion batteries, fuel cells, electrochemical devices
- Strong Li^+ -polymer interactions and low segmental mobility of polymer decrease ion mobility limit and conductivity of the electrolyte
- Low-weight molecular solvents are commonly used as additives (plasticizers) to improve properties of polymer electrolytes
- Promising alternative to classical molecular solvents are ionic liquids (non-flammable, non-volatile, stable)
- Increased number of experimental works is devoted to ternary PEO/lithium salt/IL electrolytes; computational studies on this subject are less frequent

Investigated systems

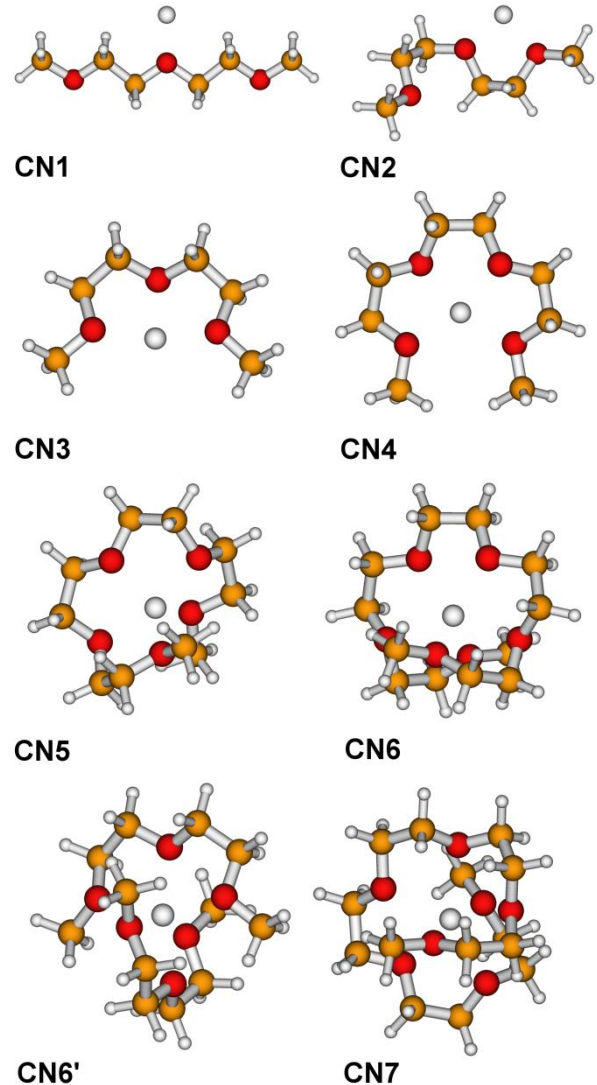
Molecular Dynamics simulations:

- ternary electrolytes: LiAn salt in hexaglyme with increasing content of EMIM-An ionic liquid
- An = BF_4^- , PF_6^- , $\text{B}(\text{CN})_4^-$, FSI^- , TFSI^-
- IL mass percentage: 0, 10, 20 and 50%
- polarizable force-field (based on APPLE&P and our own parameterization) and Tinker v. 5 package
- 15 – 25 ns NPT simulations ($T = 400 \text{ K}$)

Investigated systems

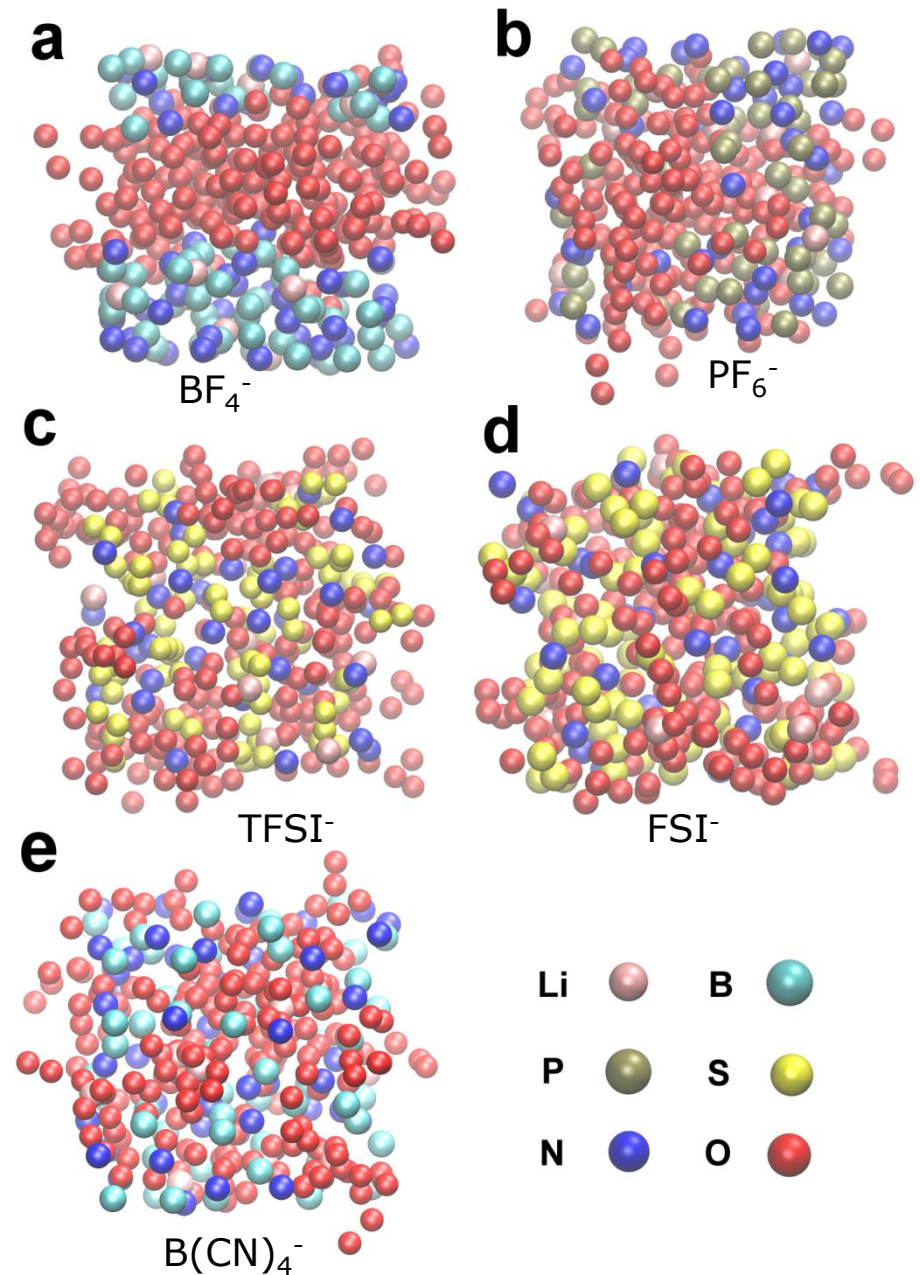
Sequential MD/QC calculations:

- 5 ns NVT MD simulations for Li⁺-oligoglyme complex (frozen at QC geometry) in hexaglyme and ionic liquids
- structures of Li-glyme complex (solute) solvated in increasing amount of hexaglyme or IL extracted using Trajectory Sculptor
- interaction and binding energies calculated using force field or DFT



MD results: structures of electrolytes

- structure of the electrolyte and its homogeneity depends on the salt/IL anion
- phase separation in systems with BF_4^- and PF_6^-
- more homogeneous electrolytes with TFSI^- , FSI^- or $\text{B}(\text{CN})_4^-$

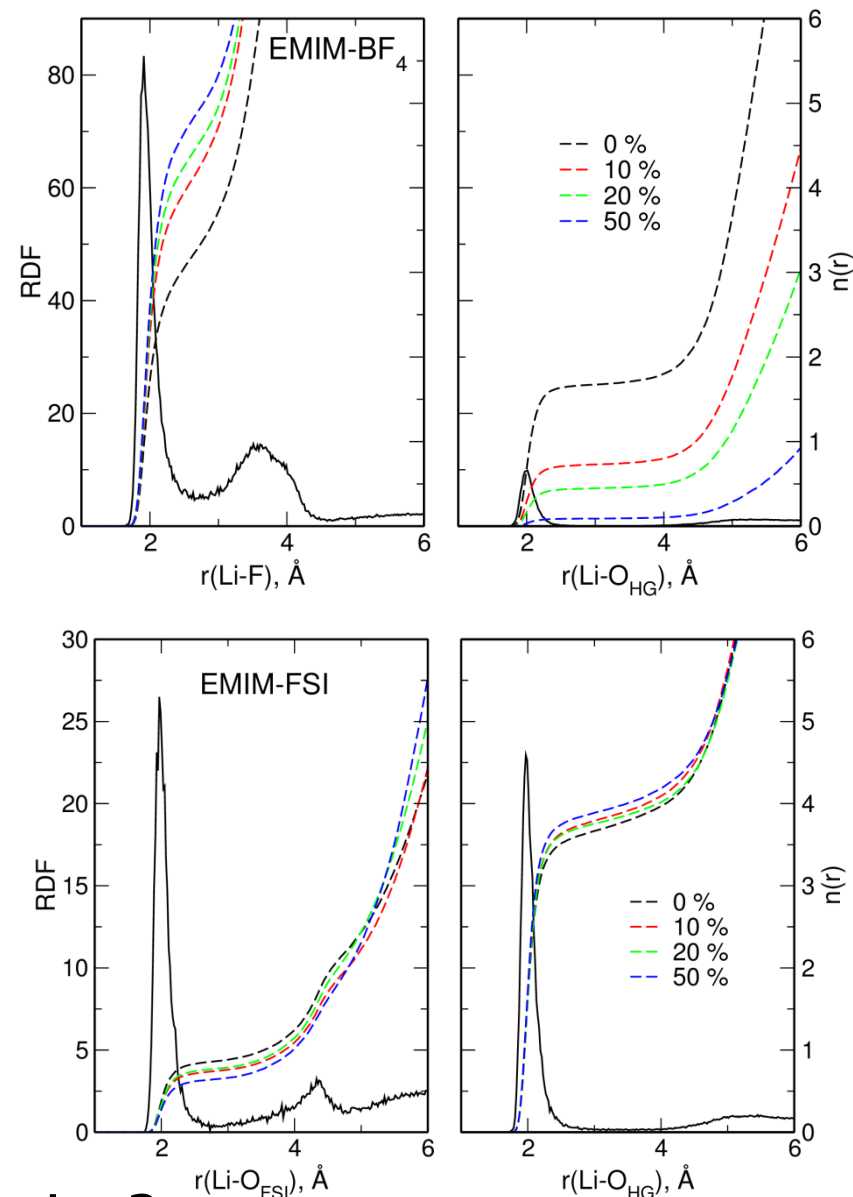


MD results: Li⁺ coordination

Li⁺ coordination to hexaglyme and anions, 400 K, 50% IL:

n_c	BF_4^-	PF_6^-	TFSI ⁻	FSI ⁻	$\text{B}(\text{CN})_4^-$
HG	0.1	2.1	2.2	3.9	4.5
An	4.7	2.2	2.4	0.7	0.1

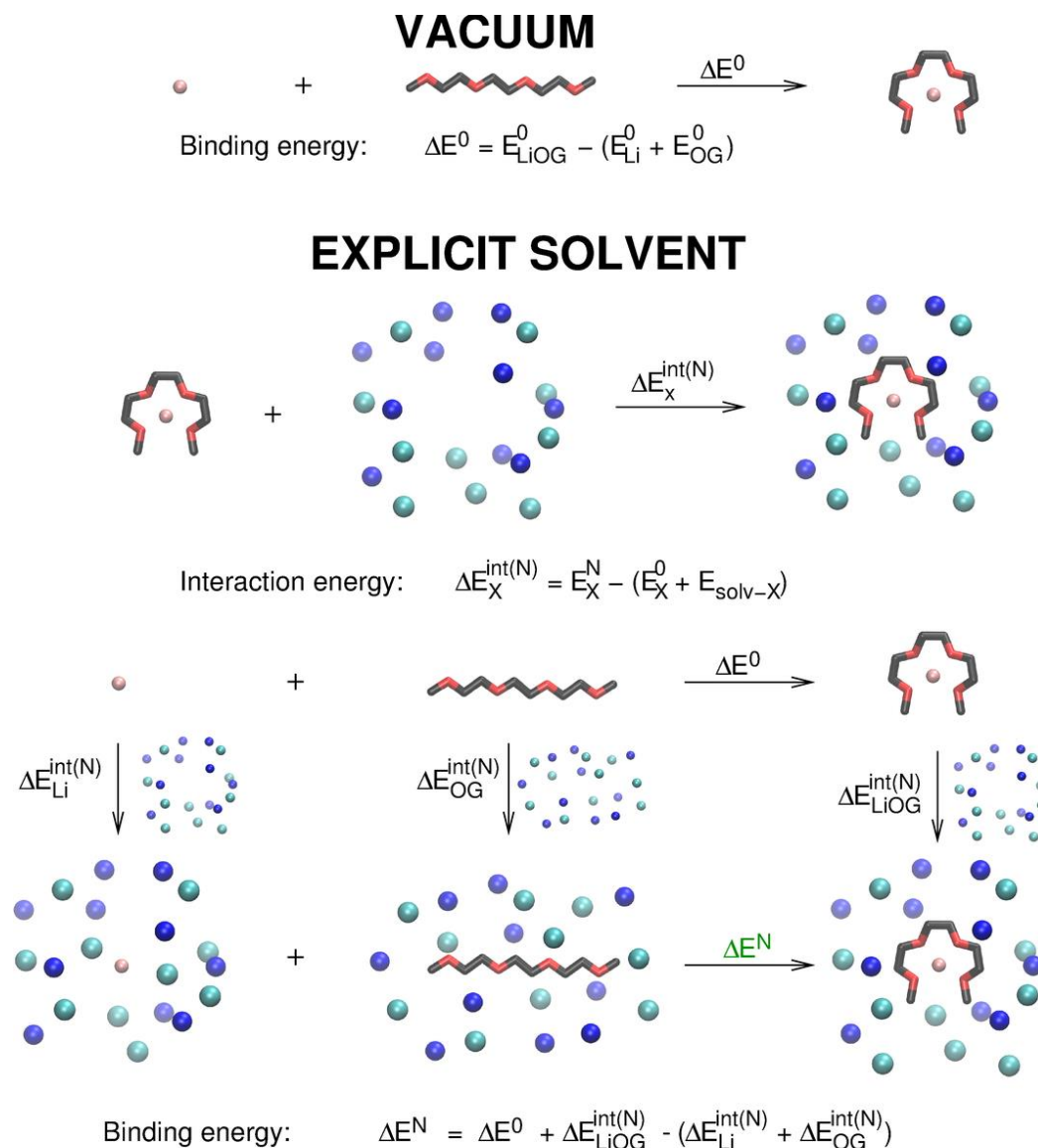
- in systems with EMIM- BF_4 Li⁺ ions reside in IL phase
- in HG/EMIM-FSI or EMIM- $\text{B}(\text{CN})_4$ Li⁺ coordinate to hexaglyme
- intermediate coordination in HG/EMIM- PF_6 or EMIM-FSI



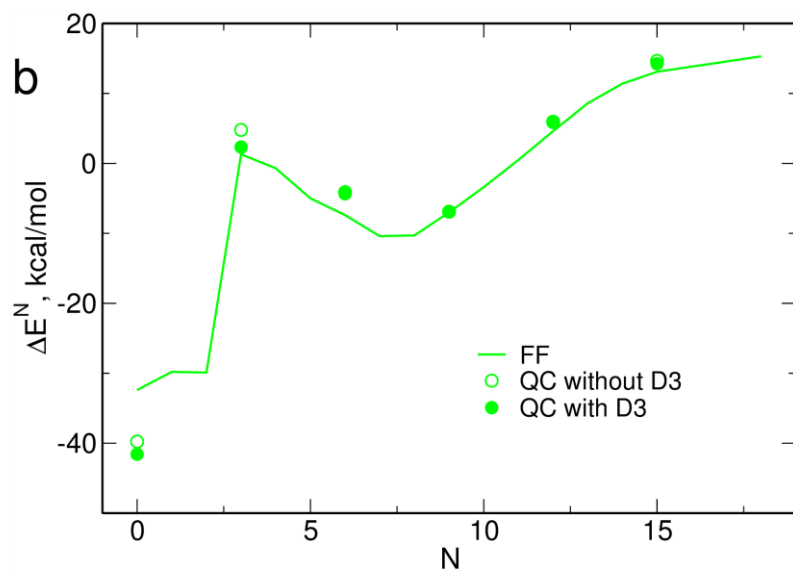
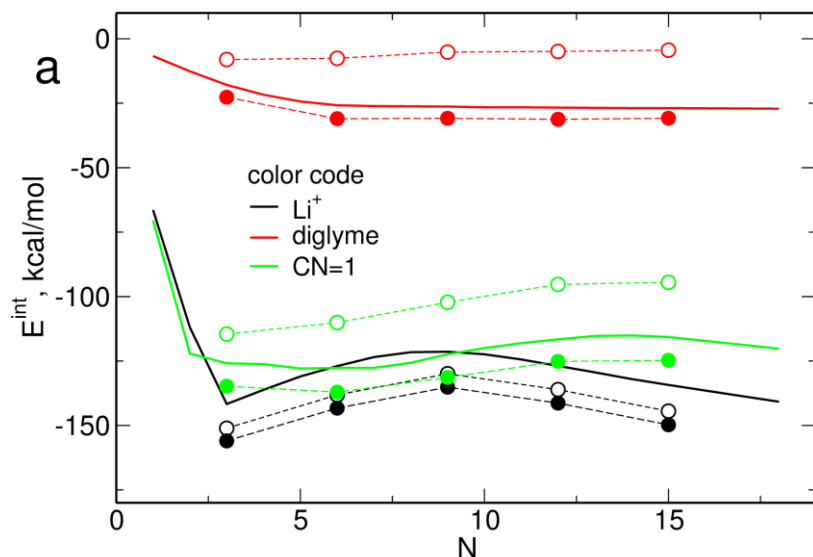
Can we rationalize it from binding energies?

Energy calculations

- Li⁺- glyme binding energies and interaction energies in vacuum and in explicit solvent
- energies calculated from force field or at the CAM-B3LYP/6-31+G* level
- thermodynamic cycle used to obtain values in the solvent



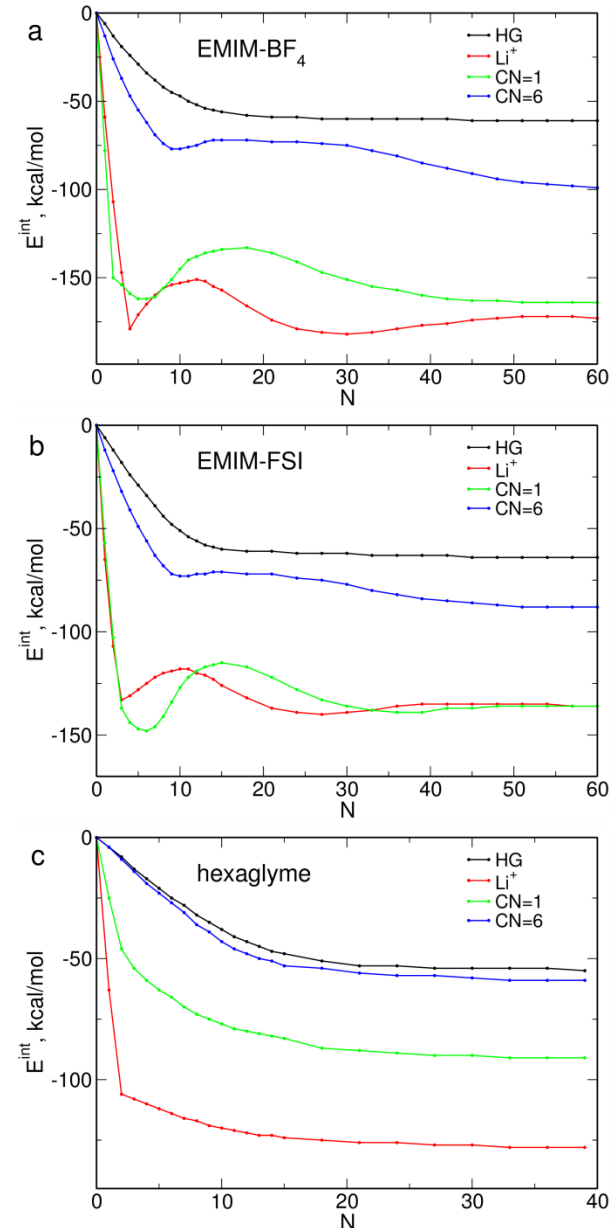
Energy calculations: QC versus FF



- energies calculated from force field or at the CAM-B3LYP/6-31+G* level
- TeraChem v. 1.5K used to obtain QC values
- FF-based values reproduce fairly well trends obtained from prohibitively expensive QC calculations

Energies: dependence on the number of solvent ions/molecules

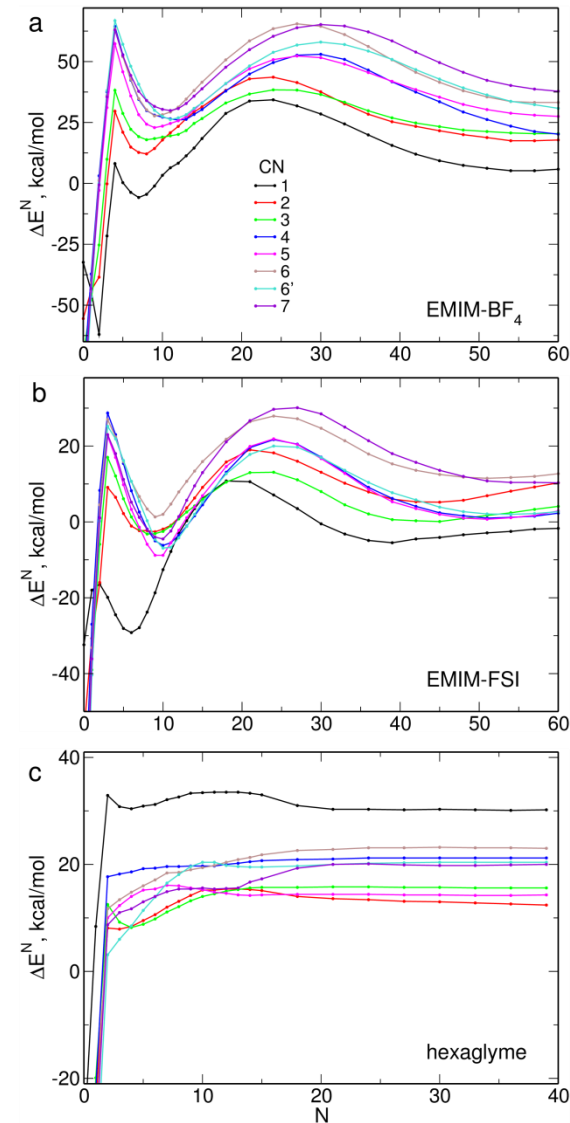
- calculated values depend on the amount of solvent surrounding the solute
- in hexaglyme energies decrease monotonically
- oscillations appear in ILs, because of structured solvation shell



interaction energies

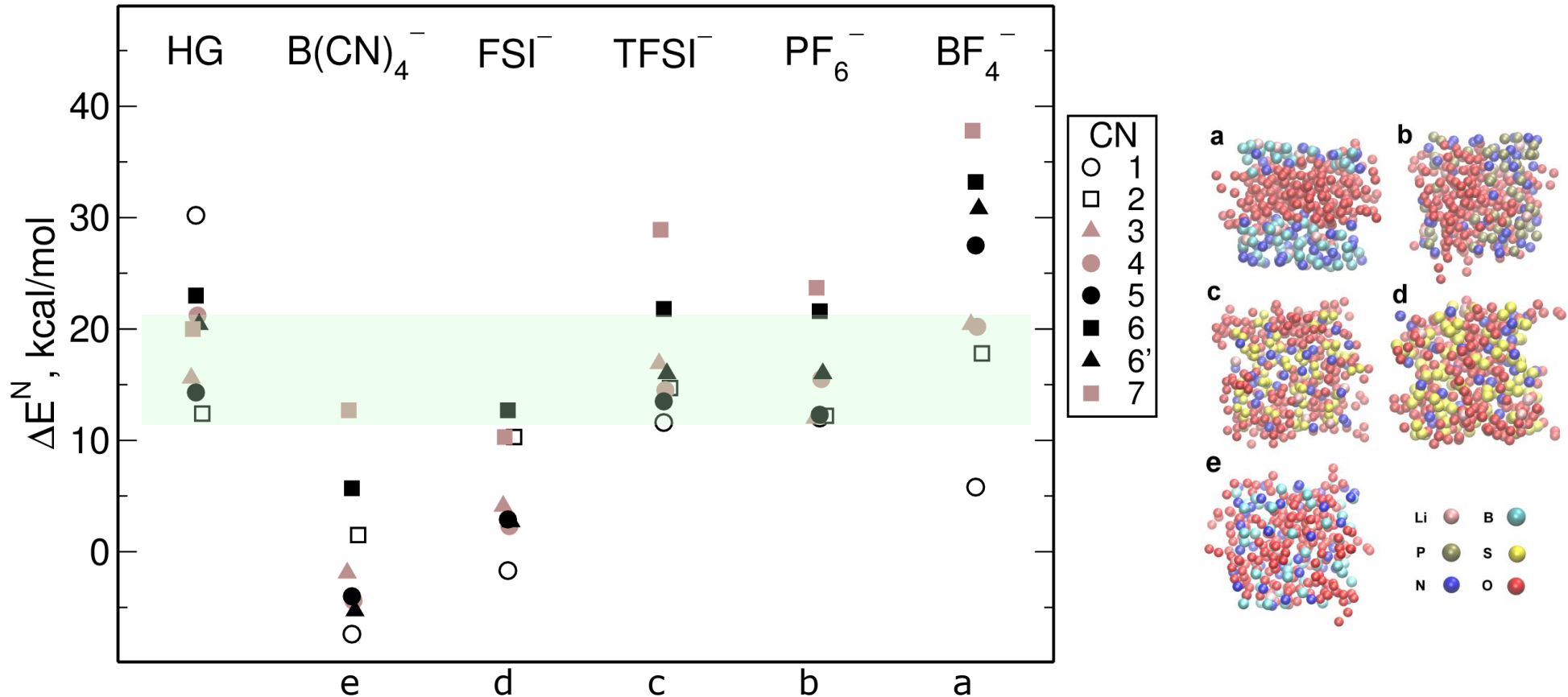
Energies: dependence on the number of solvent ions/molecules

- calculated values depend on the amount of solvent surrounding the solute
- in hexaglyme energies change rather monotonically
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binding energies

Binding energies in explicit solvent



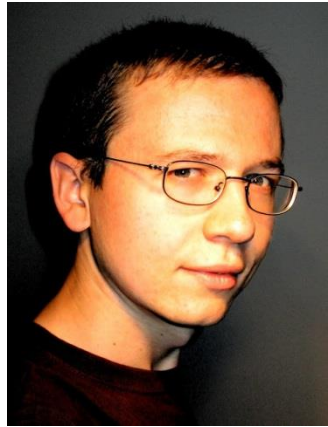
- relative binding energies of Li^+ -glyme in different ionic liquids correlate with structure of electrolytes and preferred coordination of Li cations

Summary

- structures of LiAn/hexaglyme/EMIM-An electrolyte and Li⁺ coordination depend on the anion An⁻
- long-range electrostatic interactions and structure of solvation shell cause necessity to include fairly large amount of solvent in explicit solvent calculations
- binding energies of Li⁺-glyme in different liquids help to understand observed structures of electrolytes
- implicit solvent models will not predict differences between investigated ionic liquids; explicit approach is necessary

A. Eilmes, P. Kubisiak, *Li⁺-Oligoglyme Association in the Presence of Ionic Liquid Studied by Molecular Dynamics and Explicit or Implicit Solvent Model*, J. Phys. Chem. B **2015**, **119**, 11708.

Acknowledgments



Co-worker:

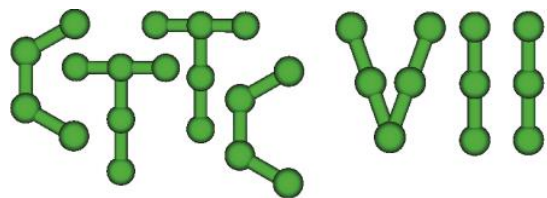
Dr Piotr Kubisiak (UJ)

PL-Grid infrastructure was used in calculations



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