MOLECULAR DYNAMICS SIMULATIONS OF NOVEL SODIUM BORATE ELECTROLYTES

Performing molecular dynamics simulations to analyze and optimize conductivity for various sodium borate electrolyte salts

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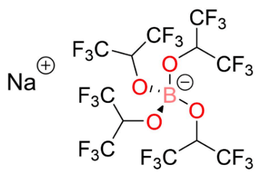
Abstract

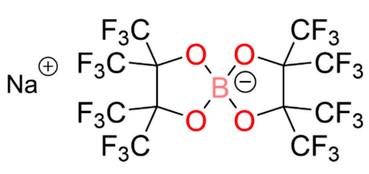
- Sodium-ion batteries are a promising alternative to lithium-ion batteries. However, commonly used sodium-ion battery electrolytes have drawbacks.
- Newly synthesized borate anions have performed well in electrochemical studies, and offer a number of attractive features as electrolyte salts [1].
- This project involved performing molecular dynamics simulations of three sodium borate electrolyte salts in order to analyze and explain their performance, and compare with experimental findings.

"Salt 1a"



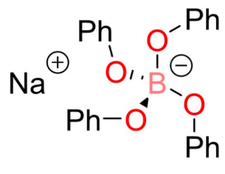
$Na[B(hfip)_4]\cdot DME$

"Salt 1b"



$Na[B(pp)_2]\cdot 3\,DME$

"Salt 1f"



$Na[B(OPh)_4]$

Methods

- NPT and NVT molecular dynamics simulations were run using LAMMPS for three different electrolyte salts of varying concentrations, resulting in the generation of trajectory files.
- Python scripts were written to analyze these trajectory files and calculate useful quantities, e.g. diffusion coefficients, viscosities, RDFs, residence time functions.

$$D_i = \lim_{t\to\infty} \frac{1}{6t} \left\langle \frac{1}{N_i} \sum_i (\mathbf{x}_i(t) - \mathbf{x}_i(0))^2 \right\rangle$$

Einstein relation for determining diffusion coefficients

$$\eta = \frac{V}{k_B T} \int_0^\infty \langle P_{\alpha\beta}(t) \cdot P_{\alpha\beta}(0) \rangle \, dt$$

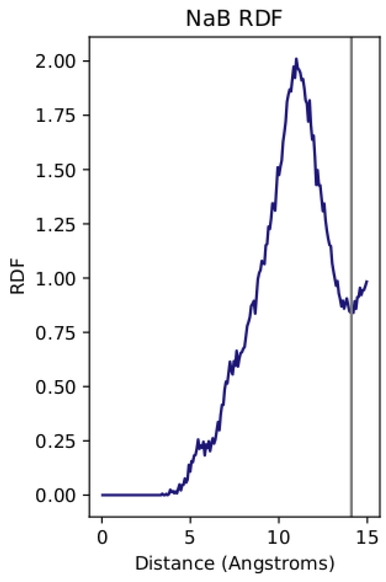
Green-Kubo relation for determining viscosity

Significant findings: If ion pairing doesn't determine diffusion coefficient, then what does?

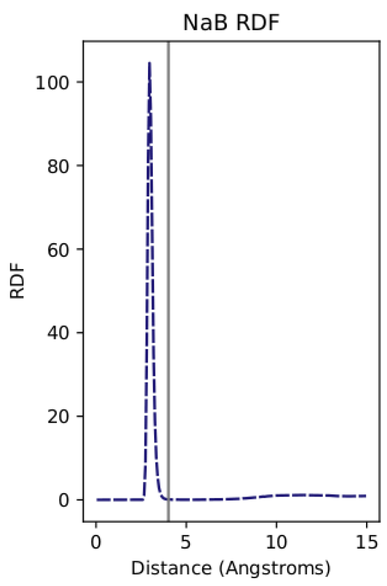
	D_{Na}(sim)	D_{Na}(exp)	D_B(sim)	D_B(exp)
Salt 1a (0.5M)	2.95	3.78	2.87	3.17
Salt 1b (0.1M)	4.51	4.57	4.51	3.76
Salt 1b (0.5M)	1.57	4.29	1.57	2.49
Salt 1f (0.5M)	0.50		0.56	1.59

Table showing diffusion coefficients for Na and B atoms, comparing values from simulations and experimental results

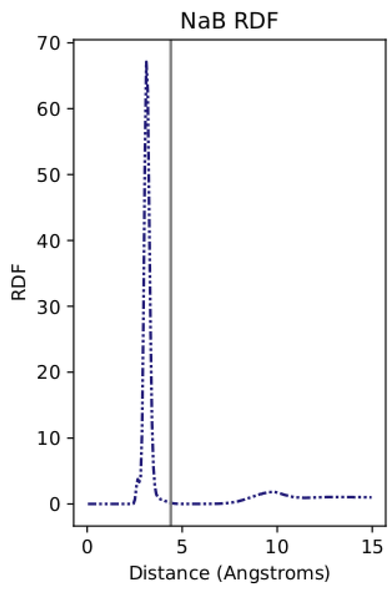
- From the table above, simulated trends generally agree with experimental data and follow expected physics.
- However, from the shapes and peak heights of the graphs below, salts 1b and 1f exhibit similar ion pairing to each other, but different to 1a.
- It is often assumed that ion pairing determines diffusion coefficient, but results from this project suggest otherwise: Salts 1a and 1b have similar diffusion coefficients, but very different ion pairing, while Salt 1b and 1f have similar ion pairing and different diffusion coefficients.



Radial distribution graph for Na and B atoms in Salt 1a, 0.5M



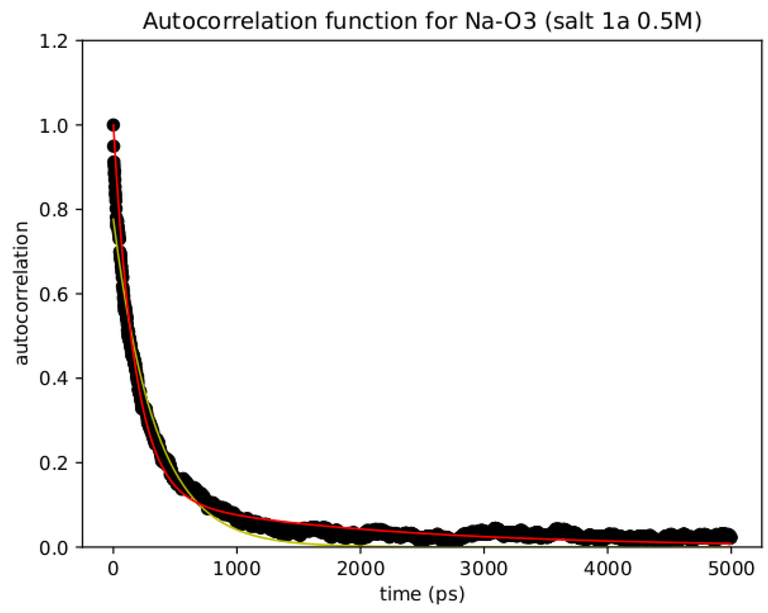
Radial distribution graph for Na and B atoms in Salt 1b, 0.5M



Radial distribution graph for Na and B atoms in Salt 1f, 0.5M

Diffusion mechanisms for sodium borate salts:

Graph showing residence time autocorrelation function for sodium ions and carbonyl oxygens (located on EC and DEC solvent molecules) in salt 1b 0.5M



Red biexponential fit:

$$a\exp\left(\frac{-t}{\tau_{ij}^{res}}\right)^{\beta} + (1-a)\exp\left(\frac{-t}{\tau_{ij}^{short}}\right)$$

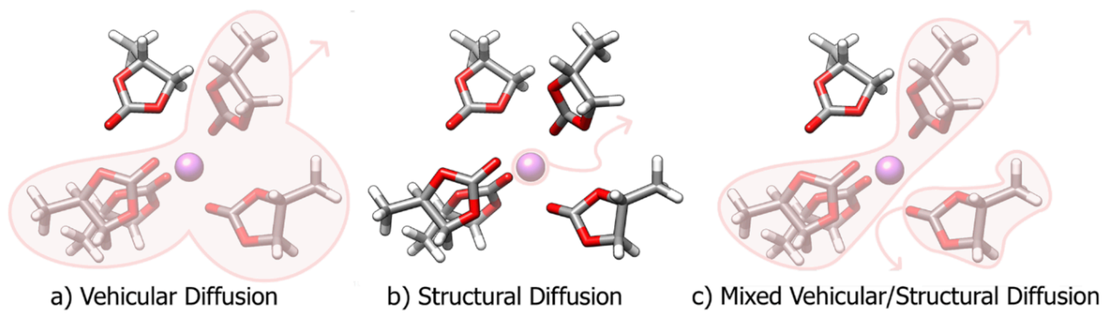
- An established protocol was applied to the borate salt simulations to answer the following question: "What is the main mode of diffusion between sodium ions and EC and DEC solvent molecules in the salts?" [2]
- Protocol involves calculating the characteristic diffusional length between two species and comparing the value to the radius of the solvation shell
- Results show that the main mode of diffusion between sodium ions and solvent molecules in salts 1a, 1b, and 1f was vehicular diffusion.

$$L_{ij}^{c} = \sqrt{6 D_i \tau_{ij}^{res}}$$

Characteristic diffusional length scale, calculated from diffusion coefficient and residence time

$L_{ij}^{c} > L^{S}$ vehicular motion

$L_{ij}^{c} < L^{S}$ structural diffusion



Different diffusion mechanisms between two species in a system

Next steps

- Increase the complexity of computational simulations to more accurately reflect the real system, e.g. by including DME cosolvent molecules in the simulations of salt 1a
- Calculate more physical quantities, such as conductivity and transference number, in order to get a more complete picture of electrolyte performance.

References

[1] Ould D.M.C. et al. "Sodium Borates: Expanding the Electrolyte Selection for Sodium-Ion Batteries", *Angewandte Chemie International Edition,* Volume 61, Issue 32, August 8 2022

[2] Self J. et al. "Transport in Superconcentrated $LiPF_6$ and $LiBF_4$/Propylene Carbonate Electrolytes", *ACS Energy,* 2019, 4, 2843–2849

Intern bio

Luke is studying BSc Mathematics and Physics at University College London.

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