Molecular Simulation of a Hydrated Cation Exchange Membrane System Used in Reverse Electrodialysis

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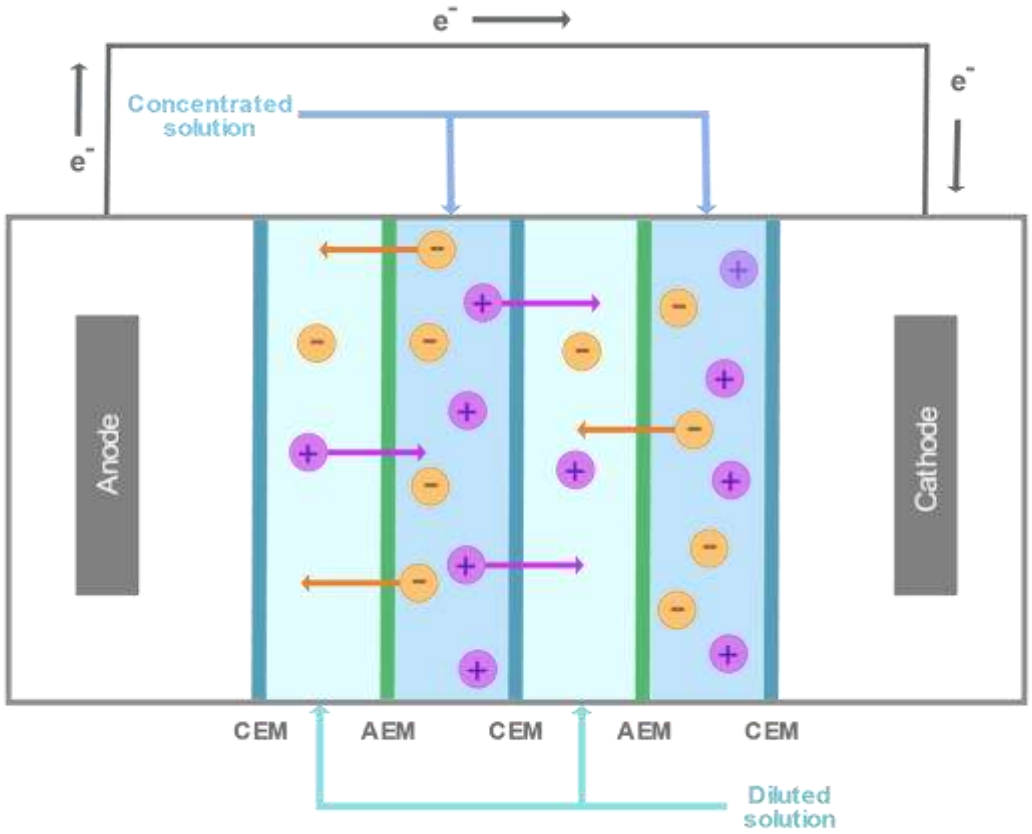
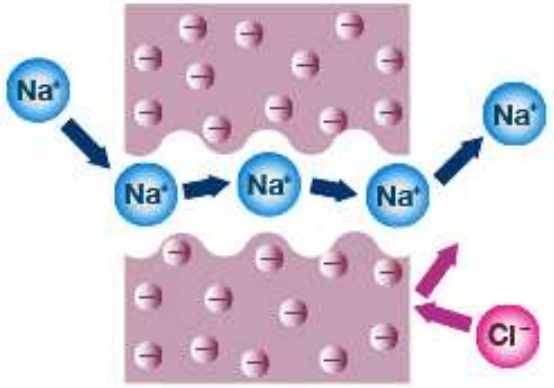
PRINCIPLE OF REVERSE ELECTRODIALYSIS





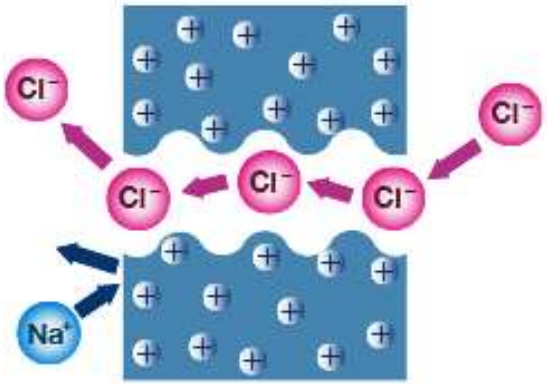


Fig. 1. Schematic representation of the reverse electrodialysis technology.

Effect of Multivalent Ions

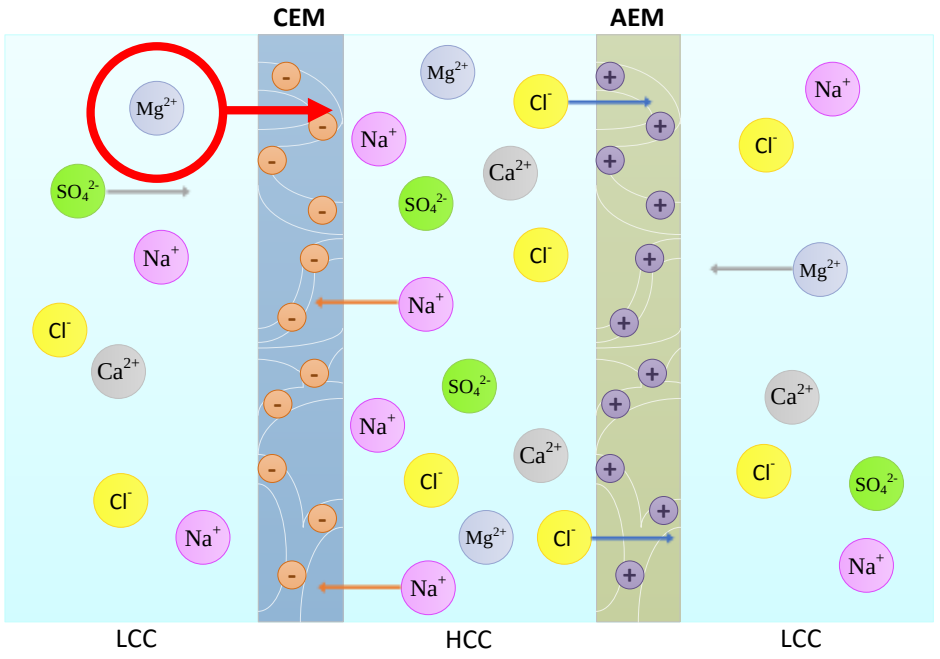


Fig. 2. RED system

- Power density is halved
  - Decrease in the open-circuit potential
  - Uphill transport
  - Increase in ohmic resistance
- Efforts to mitigate side effects consist mainly in the modification of ion exchange membranes.
- CEMs are more susceptible to the effect of multivalent ions.
- Lots of experimentation, lack of theoretical basis.

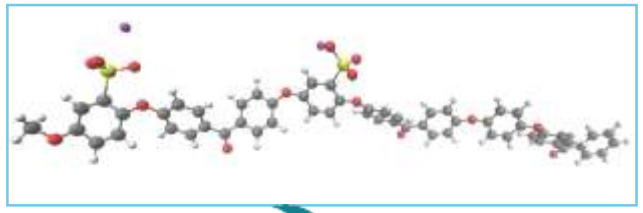
How does the presence of divalent ions impact the efficiency of ion exchange, and how does it affect the diffusion behavior and mobility of ions?

(Besha et al., 2020; Moreno et al., 208; Moya A., 2020; Rijnaarts et al., 2017; Vermaas et al., 2014; Veerman J. 202

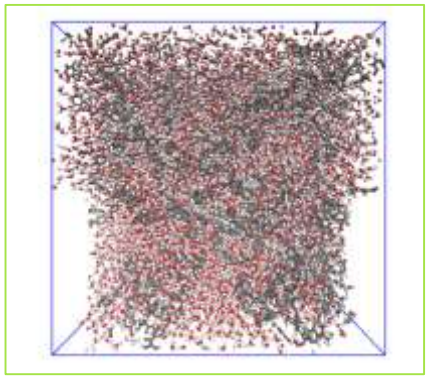
Computational Tools

Molecular simulations provide information on length scales ranging from atomic to nanoscopic, and on time scales from nano to milliseconds.

Density Functional Theory (DFT)



Molecular Dynamic (MD) simulations



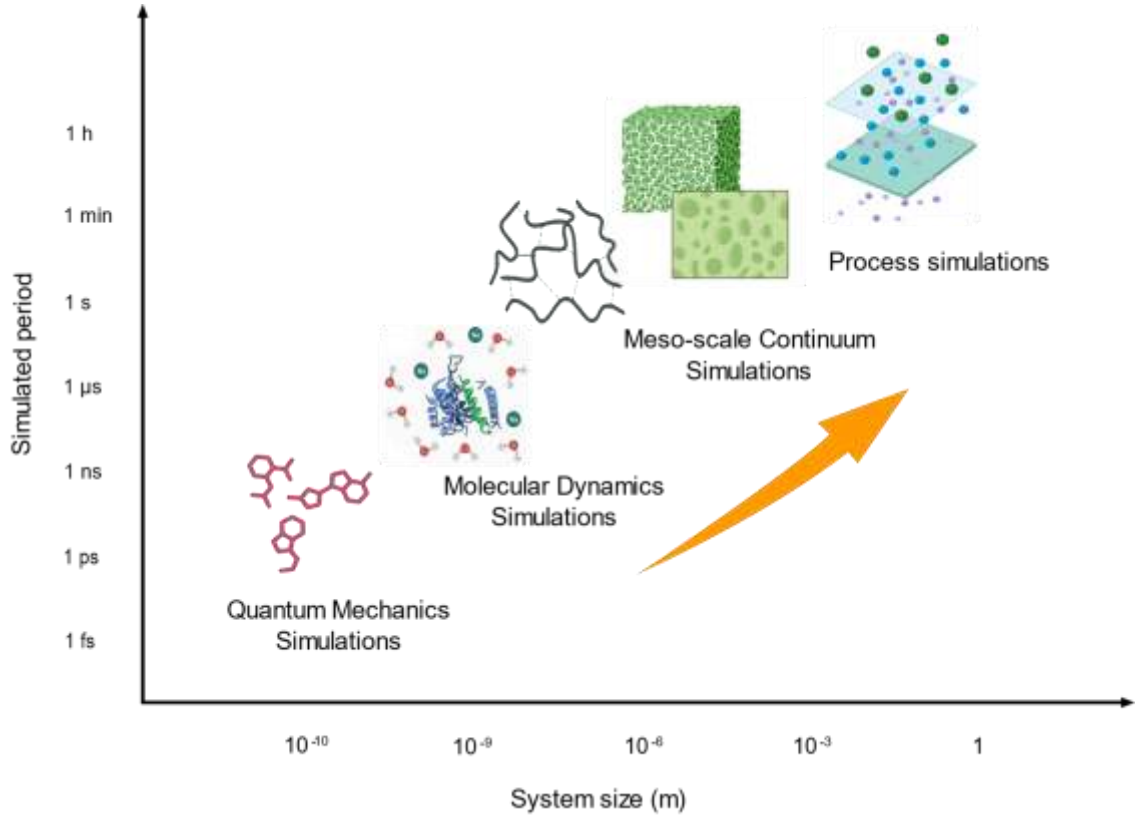


Fig. 3. Time scale vs system size of different simulation methods.

(Fermeglia et al., 2020)

Computational Tools

What is the effect of the degree of hydration, type of ion and composition of the system on the transport properties?

	λ	Water Molecules	Na^+ Ions	Mg^{2+} Ions
S_1	16	6912	432	0
S_2	12.5	5400	368	32
S_3	19.5	8424	368	32
S_4	11	4752	216	108
S_5	16	6912	216	108
S_6	21	9072	216	108
S_7	12.5	5400	62	185
S_8	19.5	5400	62	185
S_9	16	6912	0	216

Table 1. MD simulations. The symbol λ is the hydration level: number of water molecular per functional group.

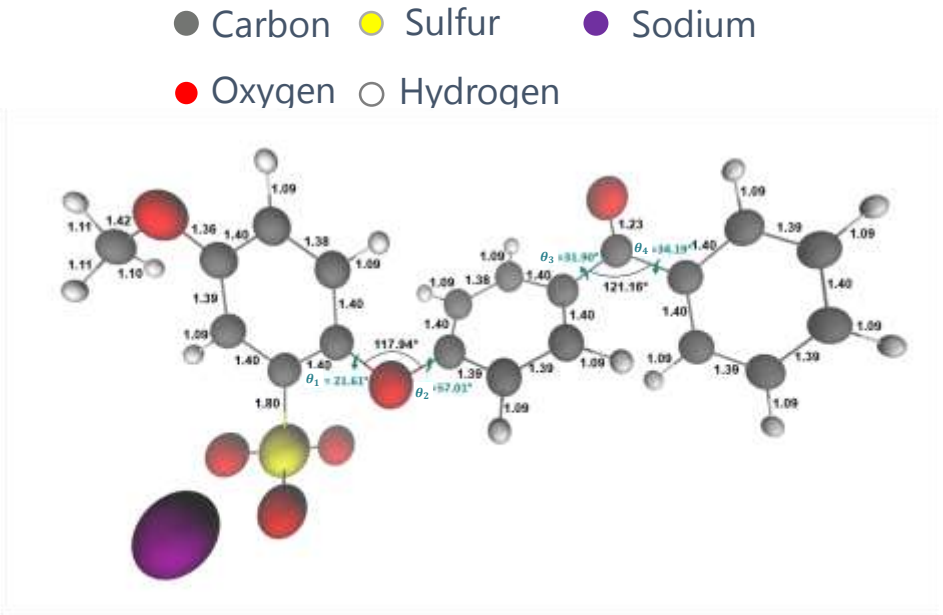


Fig. 4. Snapshot obtained from DFT calculations.

Self-diffusivity coefficients

Energy interaction

Ionic transport behavior

Self-diffusion Coefficient

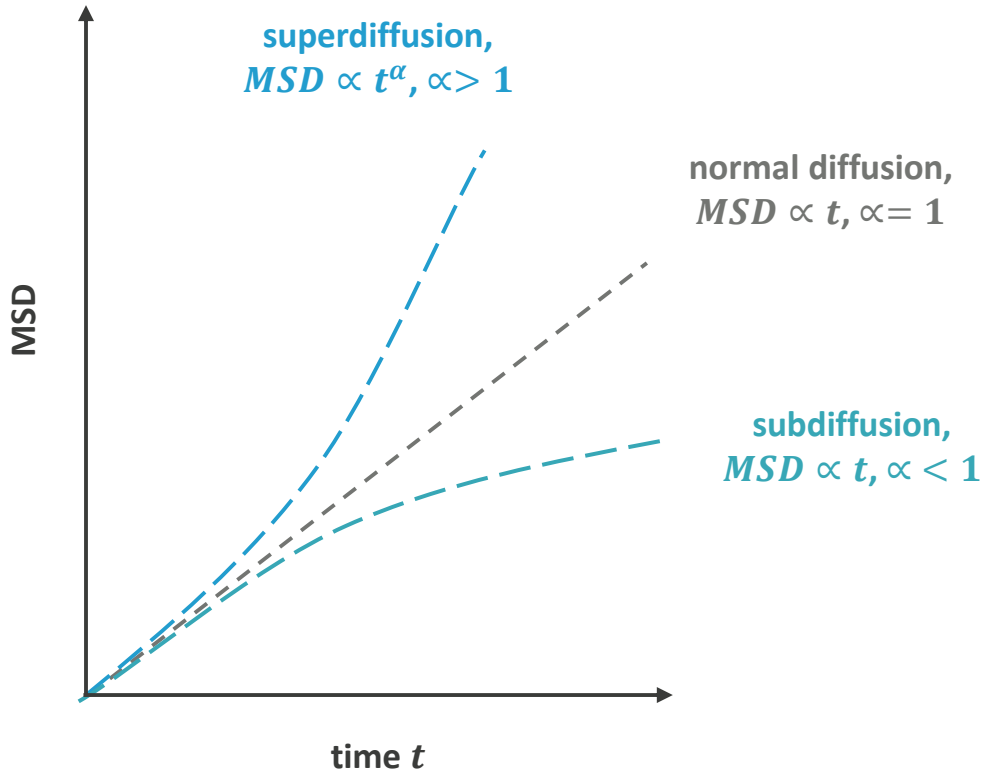


Fig. 5. Mean Squared Displacement (MSD) for different types of diffusion.

From Mean Squared Displacement (MSD):

$$D = \frac{1}{6} \lim_{t \to \infty} \frac{\mathrm{d(MSD)}}{\mathrm{d}t}$$

For sufficiently long times:

- Linear trend for the MSD vs. time plot.
- Slope (α) of the $\log_{10}$(MSD) vs. $\log_{10}$(time) plot should approach unity.

Values between 0.8 and 1 are satisfactory for considering the diffusion as normal.

(Frenkel, D., and Smit, B., 2023)

Results: Self-diffusion Coefficients

MSD for Sodium Ion

MSD for Magnesium Ion

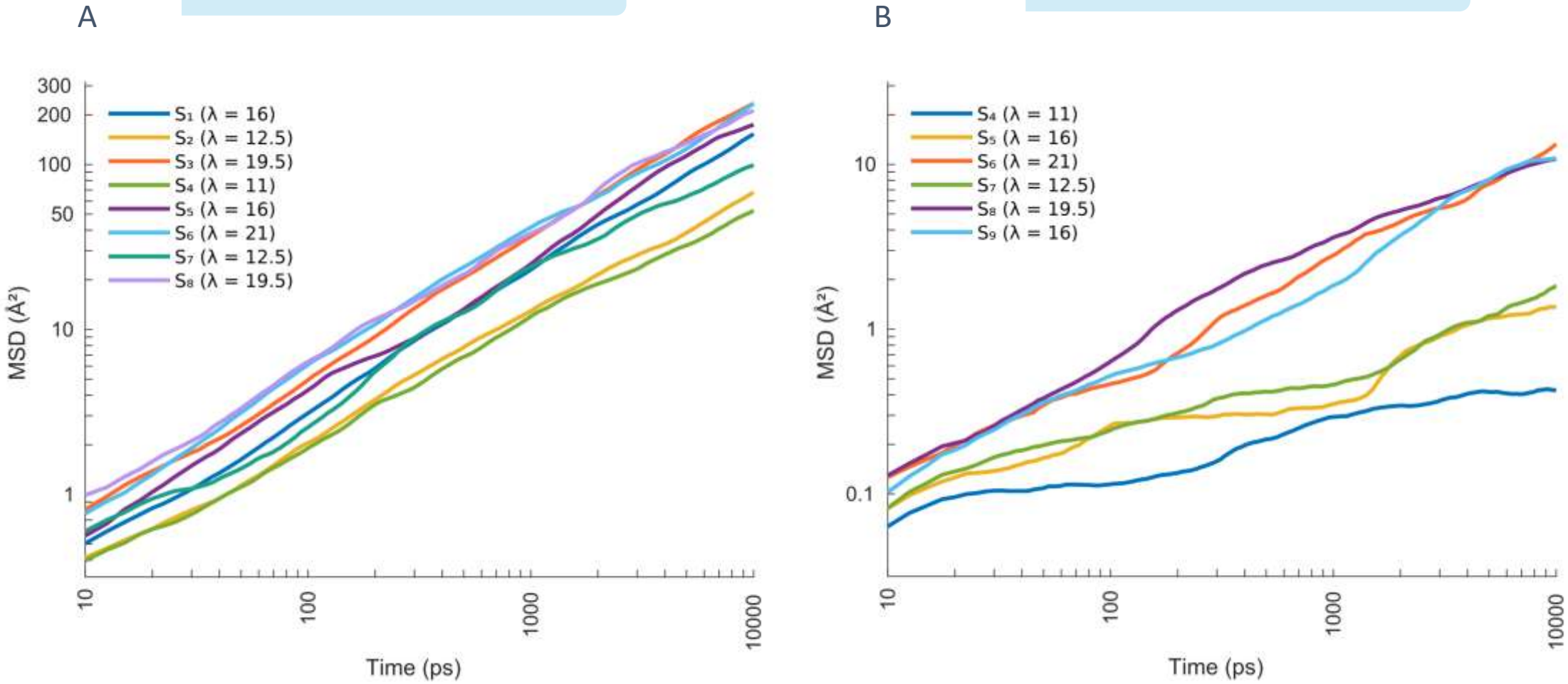
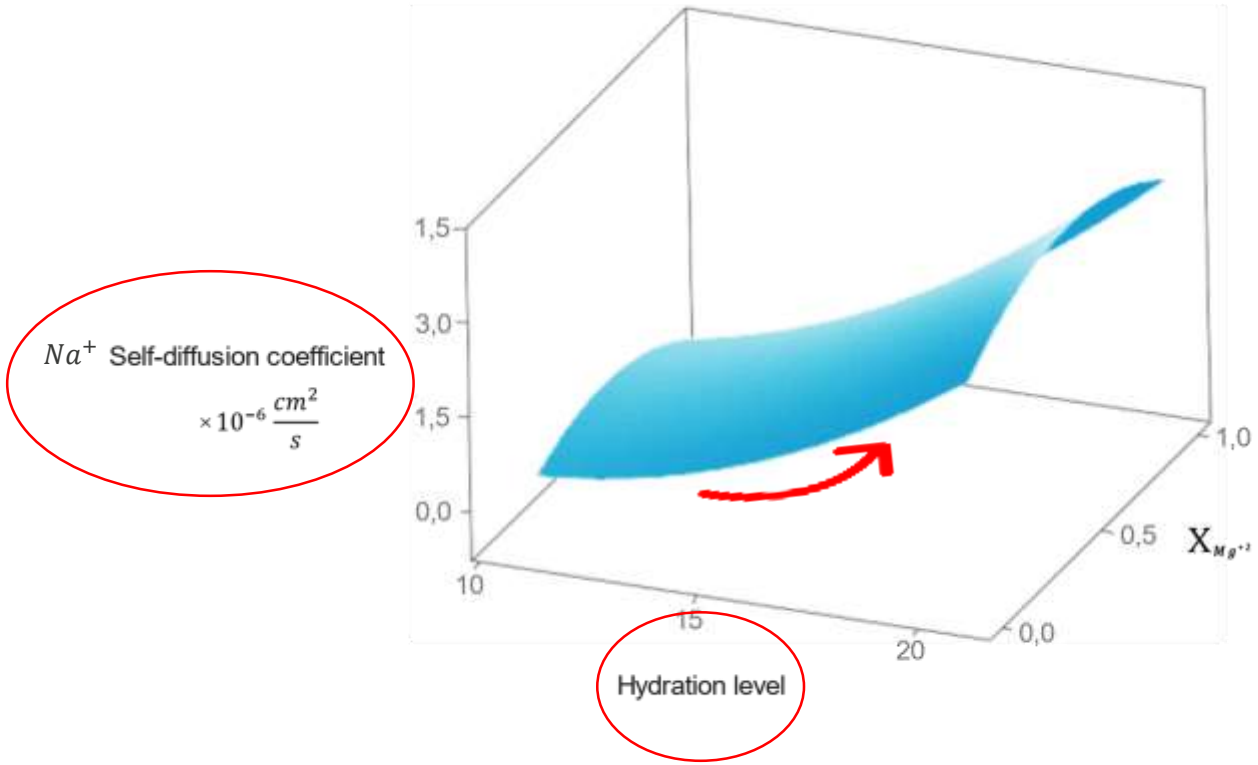


Fig. 6. The Mean Squared Displacement is displayed on the left side (A) for sodium ions and on the right side (B) for magnesium ions.

Results: Self-diffusion Coefficients



- Increase in the coordination number of ions or fixed charged groups is not observed as the degree of hydration increases.
- In cases of lower hydration levels, there is a more pronounced tendency towards subdiffusion.

Results: Transport of ions in a CEM

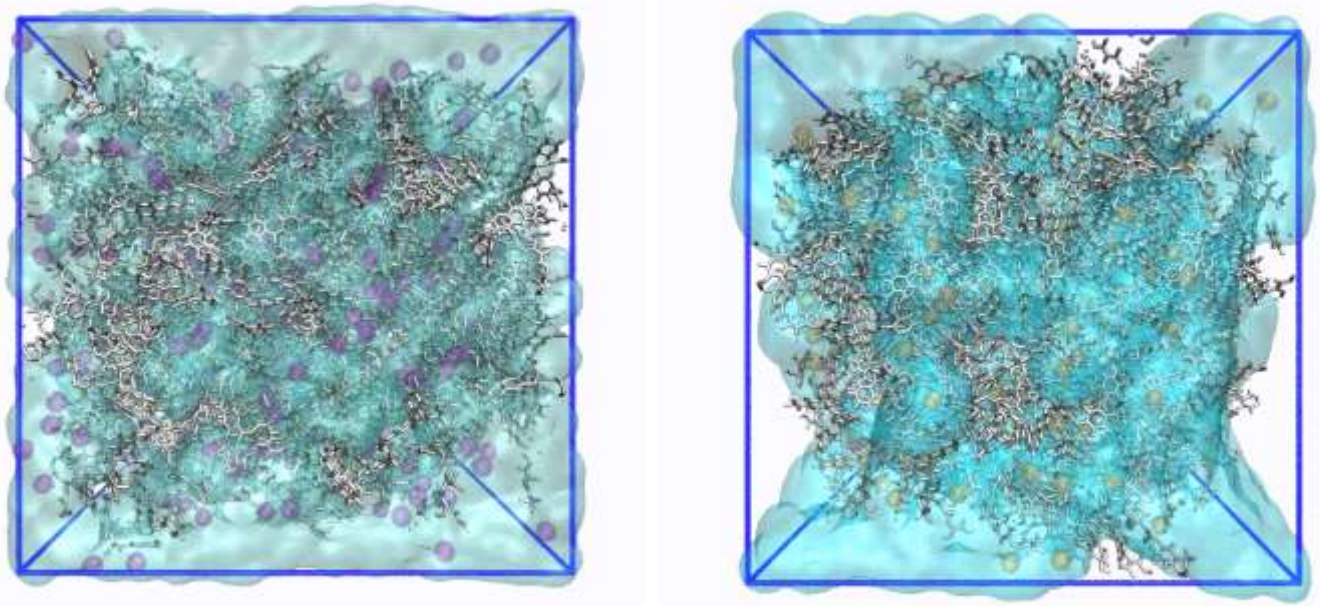


Fig. 8. MD simulations: (A) Hydrated sPEEK polymer and Na^+ ions. (B) Hydrated sPEEK polymer and Mg^{2+} ions.

- In most simulations, Mg^{2+} follows a sub-diffusive behavior, characterized by α values below 0.5.

$$r^2(t) = MSD \sim 6D_a\, t^{\alpha}$$

- The self-diffusion coefficient for magnesium is ten times lower than the self-diffusion coefficient for sodium.

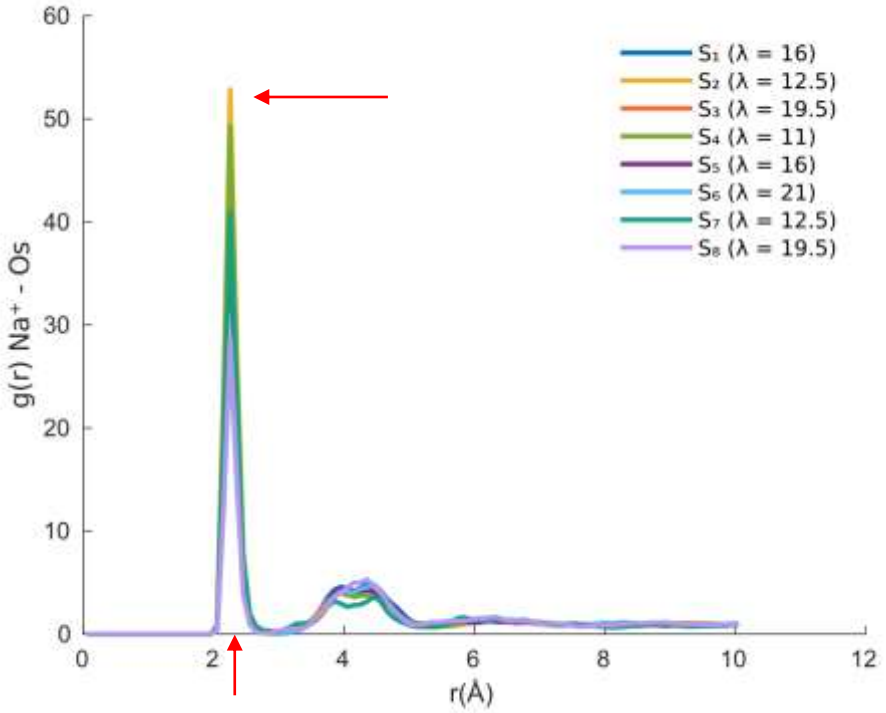
Membrane

$$\frac{D_{Mg^{2+}}}{D_{Na^+}} = 0.122$$

Solution

$$\frac{D_{Mg^{2+}}}{D_{Na^+}} = 0.502$$

Sodium – sulfonate group



Magnesium – sulfonate group

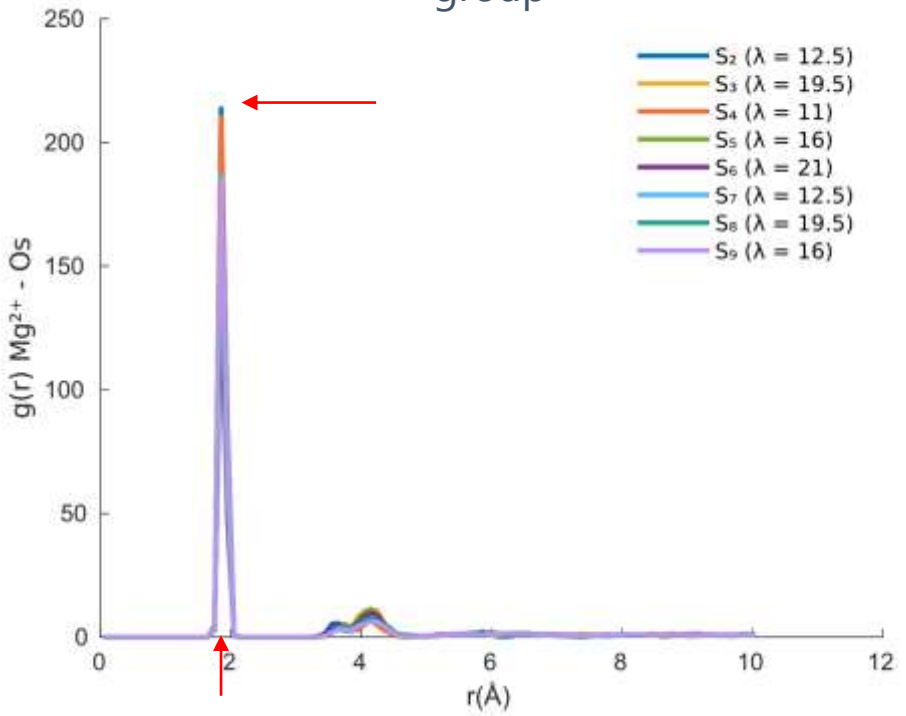
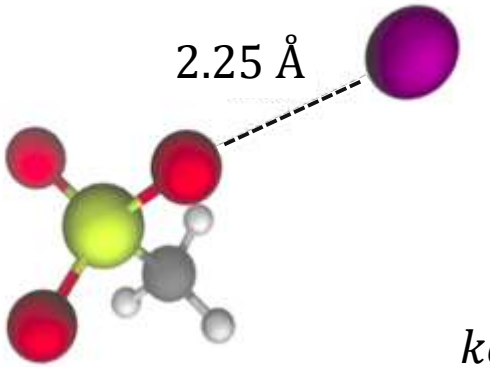
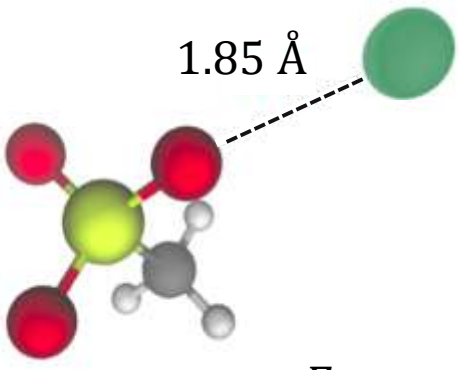


Fig. 9. Radial Distribution Function (RDF): A) Na^+ - Os . (B) Mg^{2+} - Os.



$$E_{elec} = 21718\ \frac{kcal}{mol}$$



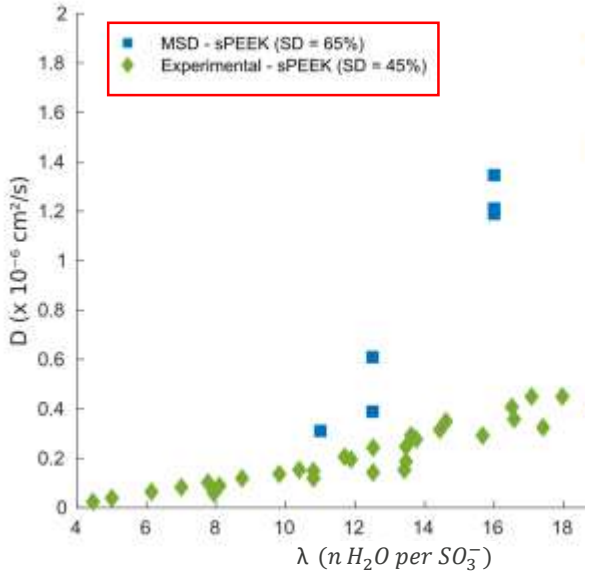
$$E_{elec} = 32577 \frac{kcal}{mol}$$

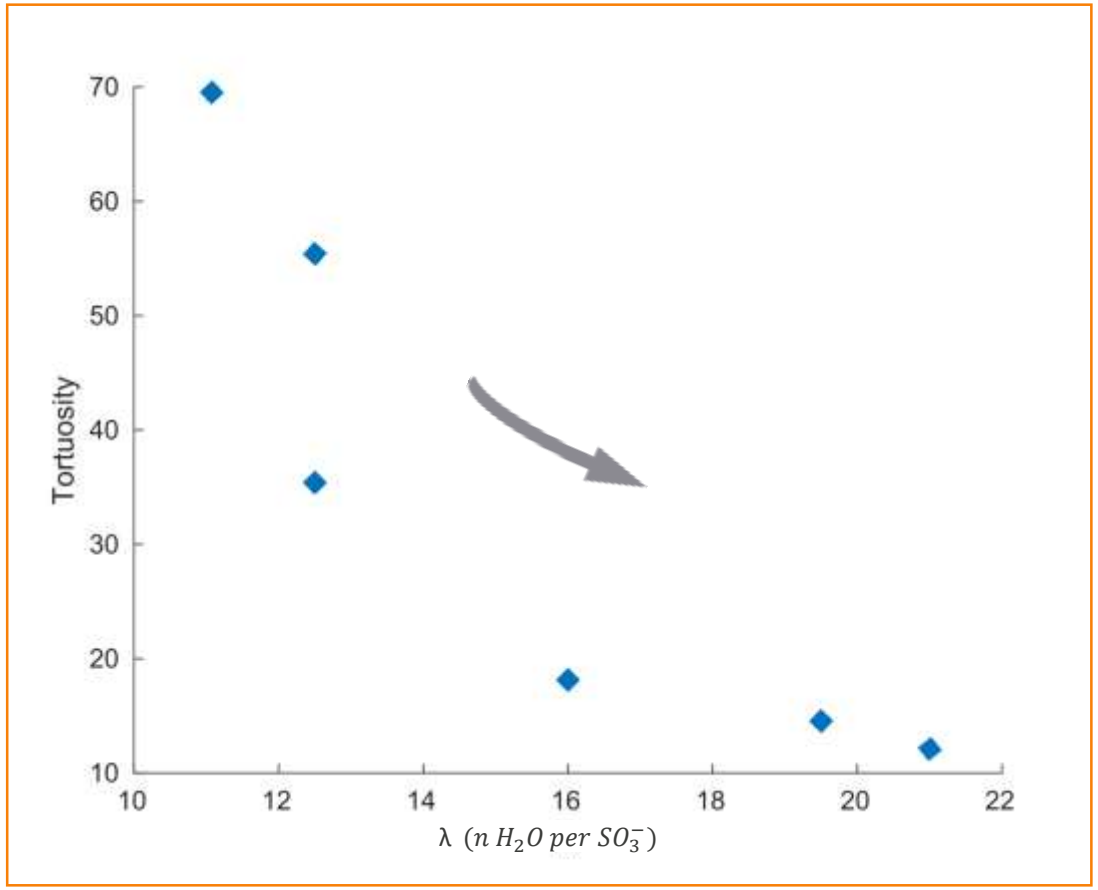
- A stronger interaction is established between magnesium and the functional group.

Results: Anomalous Diffusion Coefficient

A

Water





Magnesium Mg^{2+}

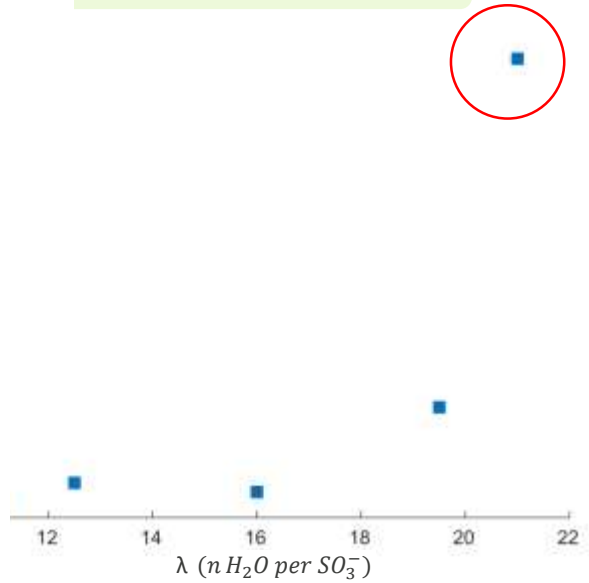


Fig. 10. (A) Water anomalous diffu h diffusion coefficients obtained from NMR measurements (Woudstra, J icient. (C) Mg^{2+} anomalous diffusion coefficient.

Conclusions

- Magnesium ion has a lower mobility than sodium ion. A lower mobility leads to higher solution resistance, impacting the overall electrical conductivity of the system.
- The synthesis of ion exchange membranes with a more interconnected water network favors ion transport. Macroscopic properties such pore sizes (Pore-Limiting Diameter) and tortuosity can be tuned for the design of selective ion exchange membranes.
- Computational modeling and simulation techniques play a crucial role in understanding the transport dynamics of multivalent ions in RED systems.

Future Work

- Study the effect of coions: Manning's theory applied to systems with multiple ions to study the effect of ion condensation on the polymer.
- Simulation of ion transport in the presence of an electric field.
- Perform non-equilibrium molecular dynamics simulations.

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Thank you

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