Miscibility and Ion Transport in Blend Polymer Electrolytes

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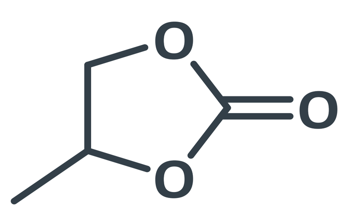
Introduction

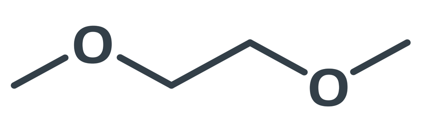
In common lithium-ion battery electrolytes, blends of liquid solvents containing some high polarity component and some high mobility component is common.

Propylene carbonate (PC)

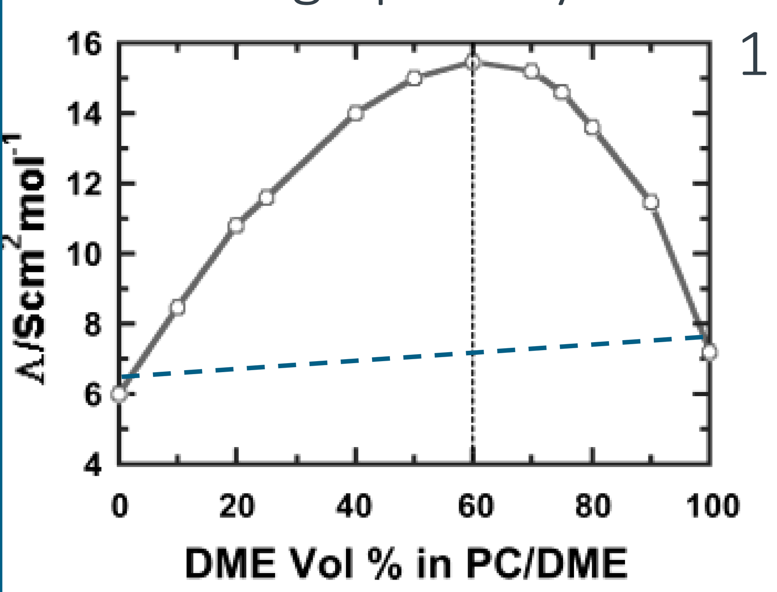


High polarity

Dimethoxyethane (DME)



High mobility

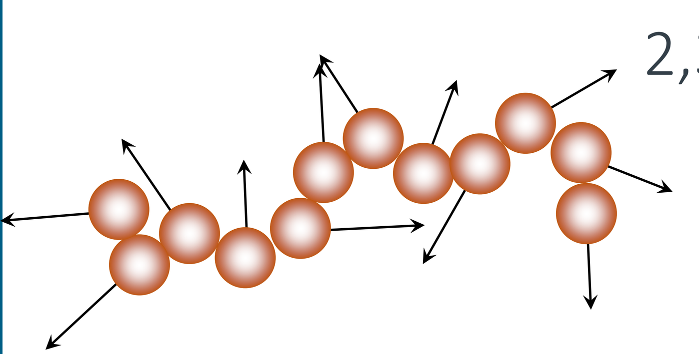


The ionic conductivity of the blend is greater than one would predict by assuming a simple linear mixing relation, given by the dotted blue line.

Can we achieve similar behavior in blends of *polymers* serving as hosts for salt, particularly in the case of polymers with significant polarity and mobility contrast?

Model

We seek to answer two questions: (1) what role does polarity and mobility contrast play in blend polymer electrolytes play and (2) how does the miscibility of a blend electrolyte influence ionic transport?



Stockmayer Polymer Model

- A freely rotating, point dipole embedded in each monomer (μ)
- Lennard-Jones hard-core repulsion (ε)

We will vary the dipole strength of the low polarity host (μ_A), the dipole contrast between low and high polarity hosts ($\Delta\mu=\mu_B-\mu_A$), the Lennard-Jones interaction strength between low and high polarity hosts (ε_{AB}) to control polarity contrast and electrolyte miscibility within a coarse-grained molecular dynamics framework.

Results

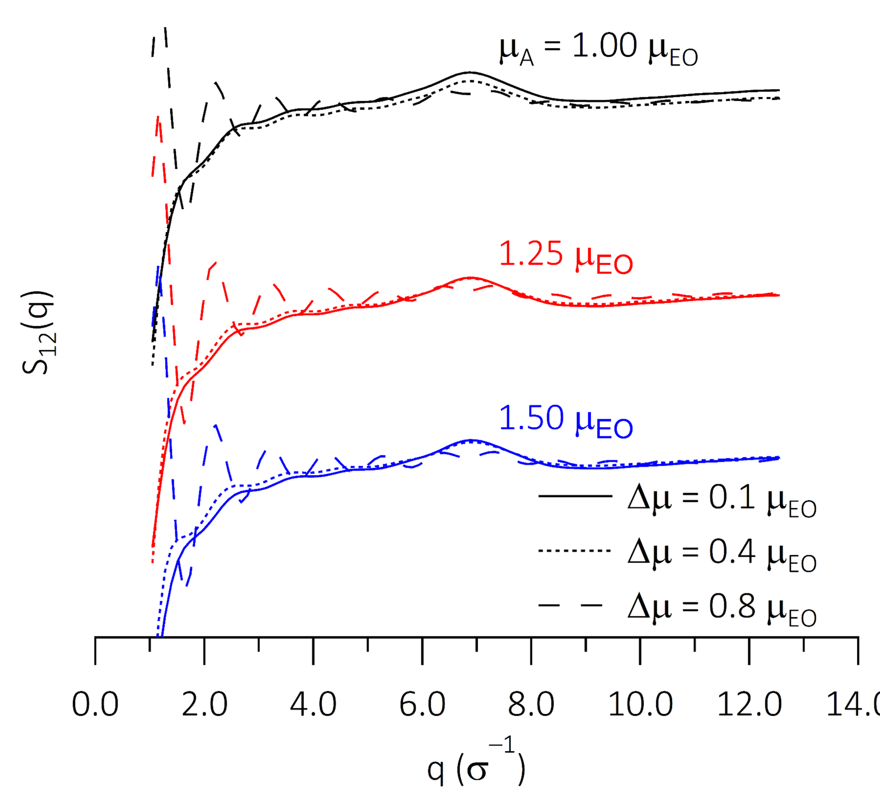
Quantifying miscibility via the structure factor:

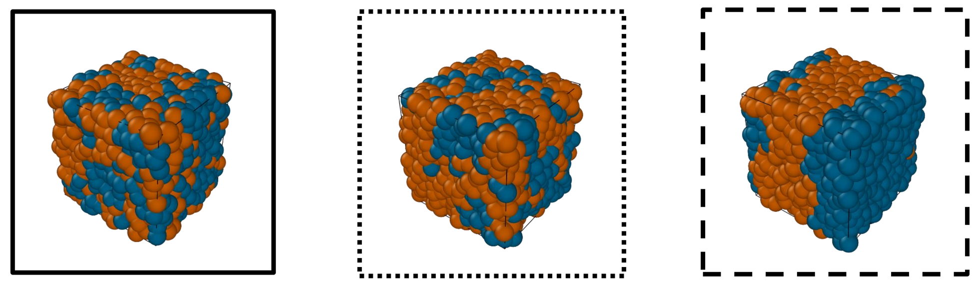
$$S_{AB}(q) = 8\pi\rho x_A x_B \int_0^\infty \frac{\sin(qr)}{qr} g_{AB}(r) r^2 dr \quad 4$$

where $g_{AB}(r)$ is the radial distribution function between monomers of type A and B and x_i is the mole fraction of species i. This measures the spatial correlations between low and high polarity polymers.

Effect of polarity contrast (Δμ) on blend miscibility

We simulated salt-free 50:50 m:m blends to understand the behavior of $S_{12}(q)$ upon phase separation. Regularly spaced peaks form in blends with the largest $\Delta\mu$, which we interpret to correspond to immiscibility.



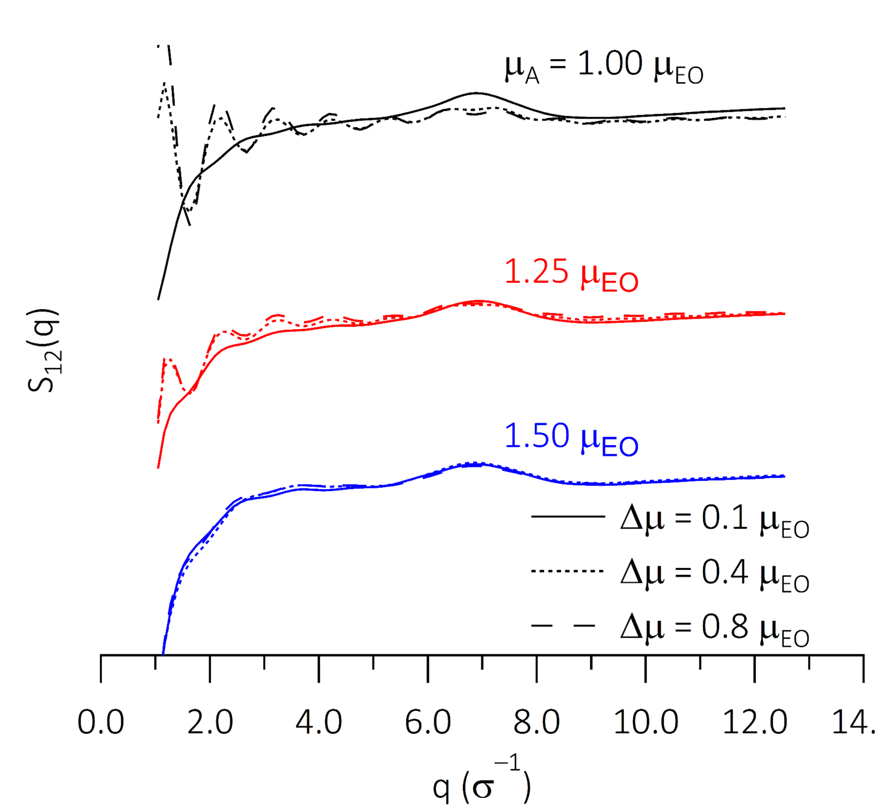


Δμ= 0.1 μ_{EO} | Δμ= 0.4 μ_{EO} | Δμ= 0.8 μ_{EO}

Snapshots corresponding to blends with μ_A = 1.0 μ_{EO}. Note phase separation only in largest Δμ blend.

Effect of addition of salt on blend miscibility

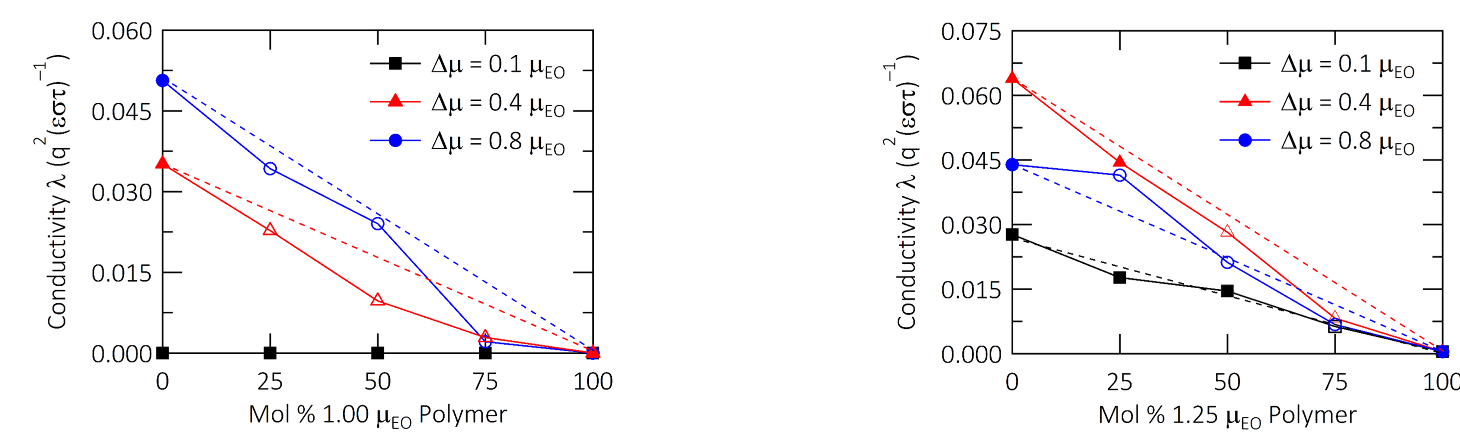
We first simulated 50:50 m_A:m_B blends with [salt] = 16 [cations]/[monomer] to understand the effect of salt on miscibility.

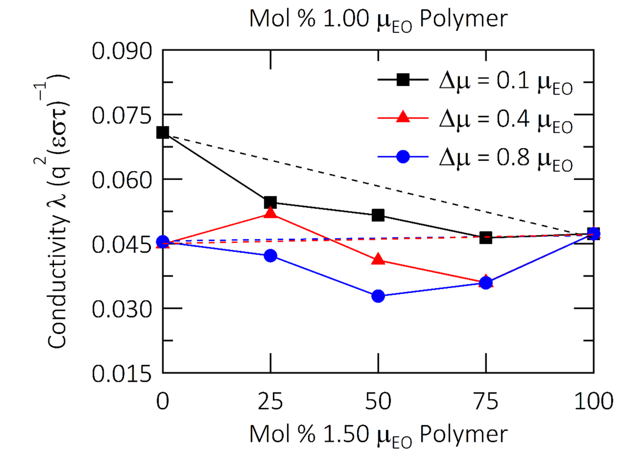


- Addition of salt decompatibilizes (peaks appear) blends with Δμ = 0.4 μ_{EO}, but the effect is lessened with increasing μ_A
- Contrariwise, salt *compatibilizes* (decreases peak height) blends with Δμ = 0.8, but the effect *increases* with increasing μ_A

Results Cont'd

Ionic conductivity measurements





- Hollow: immiscible
- Filled: miscible
- Conductivities seem to follow linear mixing or *negatively* deviate, regardless of miscibility

Conclusions

- Salt-free blends become more immiscible with increasing Δμ
- Blend electrolytes can become more or less miscible as a function of both μ_A and Δμ
- Ionic conductivities *negatively* deviate or follow a linear mixing relation, seemingly independent blend electrolyte miscibility

Future Work

- Simulate electrolytes with variable ε_{AB} to obtain electrolytes that are miscible/immiscible independent of μ_A and Δμ
- Examine the full effect of miscibility and polarity contrast on ionic conductivity in all electrolytes

Acknowledgments

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