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Dynamics of Ionizable Polymers in Ionic Liquid (IL) using Nuclear Magnetic Resonance Spectroscopy

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Abstract

Ionizable polymers usage have increased in many electrochemical applications because of its mechanical durability from their ability to create ionic group aggregates. The hinderance of these ionic clusters affect the higher optimization of the macroscopic ion transport of the system. One way to effectively optimize this transport is to introduce charges to the system. These charge-to-charge interaction are expected to create such an electrostatic dipole promising high performing capacitors. In this study, we choose Ionic Liquids (IL) as promising candidate for charge introduction based on its high ionic conductivity and excellent thermal stability. However, when computing this system, this interaction of the Ionic Liquid to the Ionizable Polymer did not significantly optimize our macroscopic ion transport. In this project, we are studying the dynamics of this Polymer-Ionic Liquid system using NMR techniques to better understand the relation within the dynamics polymer-electrolyte complexes for optimization of systems for clean energy application by characterizing the motion of the IL, understand the effects of ionizable polymers on the diffusion of the IL, and understand the effects of the IL on the motion of the polymer.

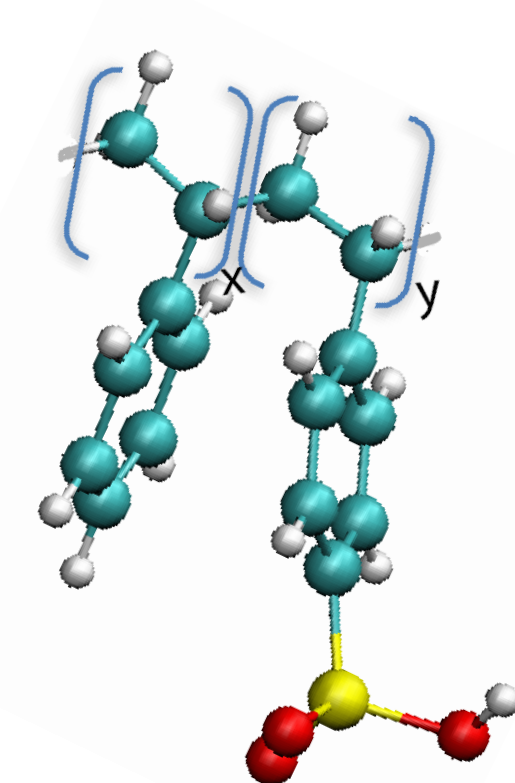
Methodology

Hypothesis: Electrostatic interactions and cluster cohesion determines the structure and dynamics of ionizable polymers

Research Approach : This study will control the cluster formation through interactions with solvents to manipulate the macroscopic transport

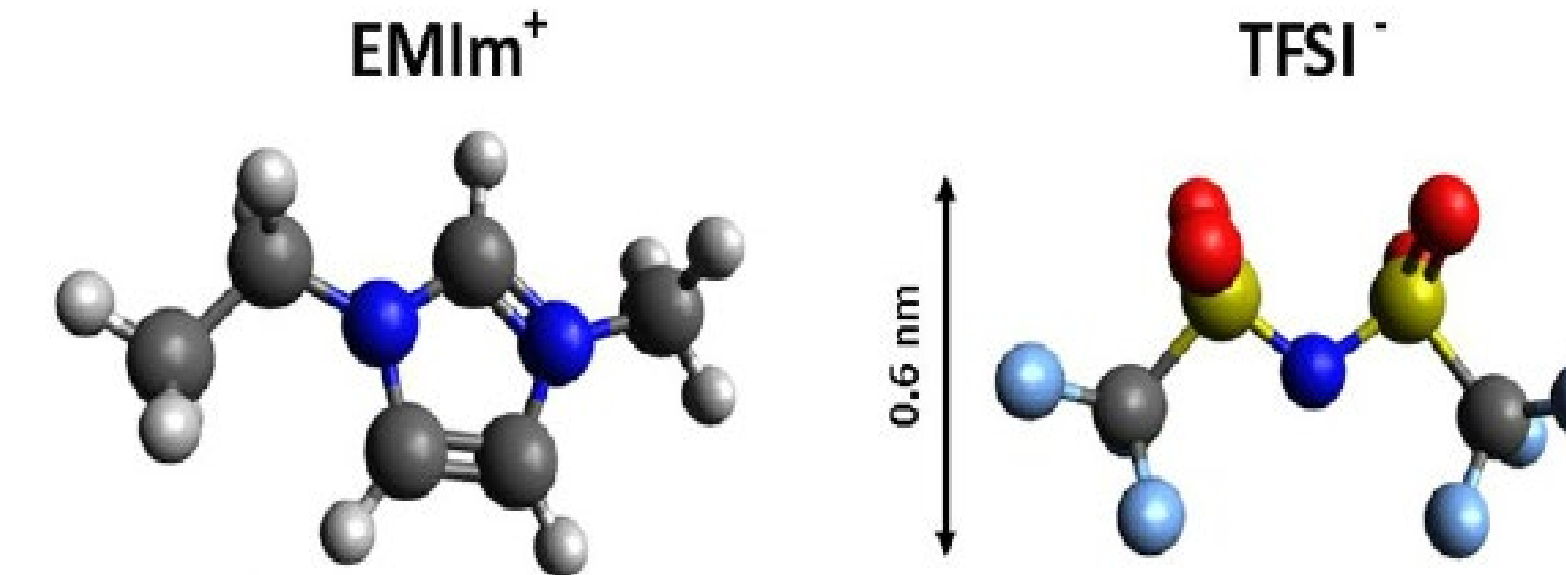
Method: Nuclear Magnetic Resonance Spectroscopy (NMR)

Polymer Model: Sulfonated Polystyrene (PSS) at polyelectrolyte regime



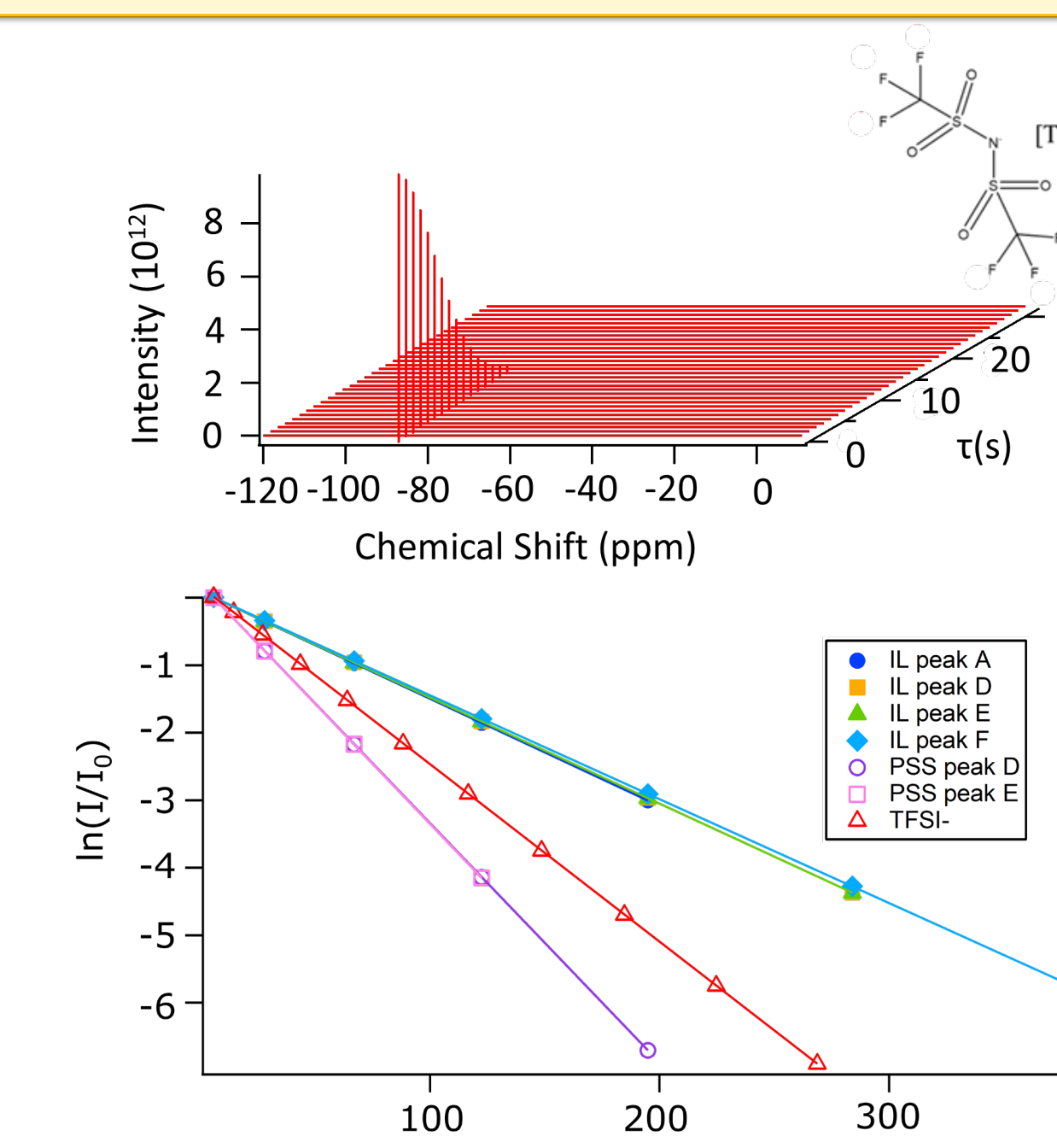
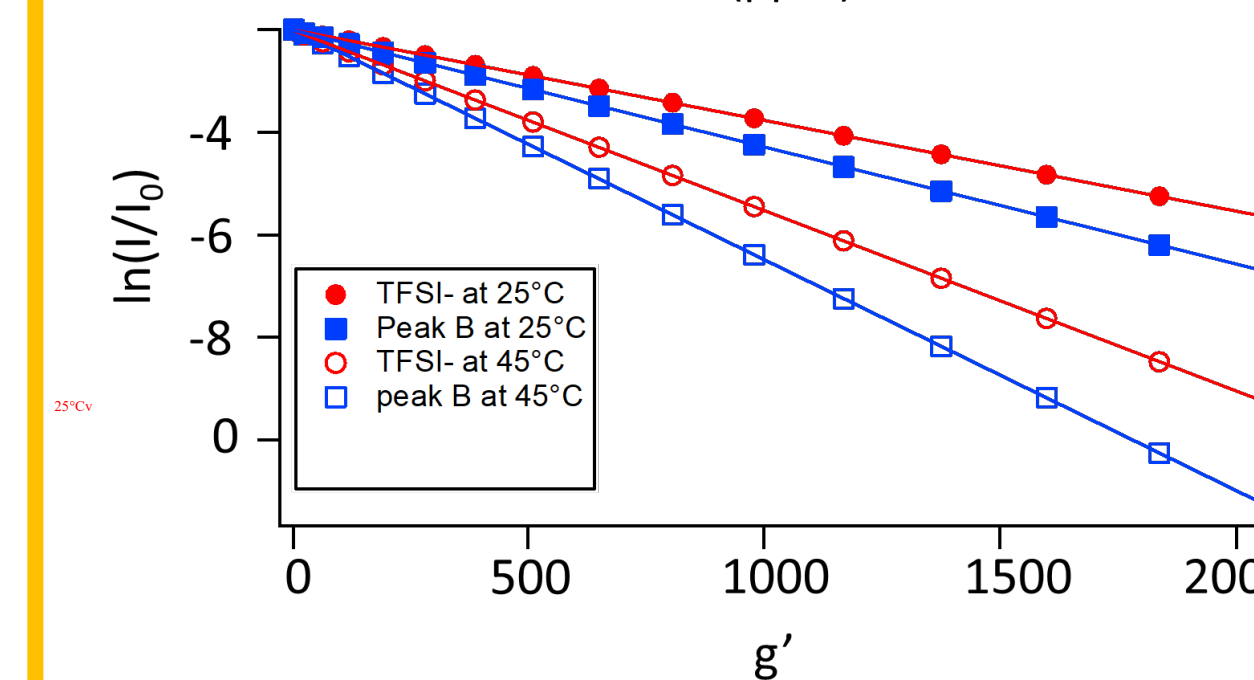
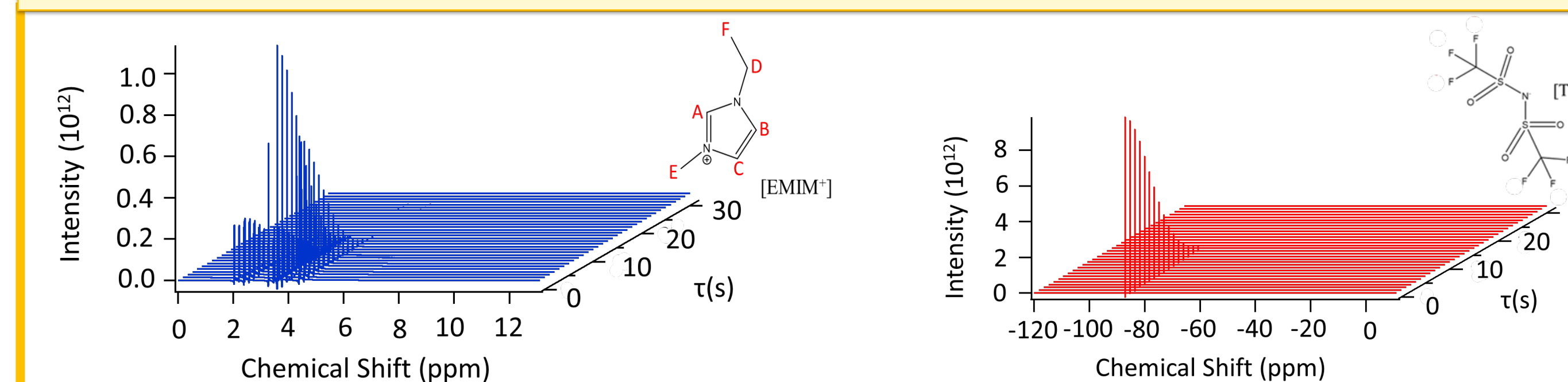
PSS [MW: 10000 g/mol; Sulfonation: 80%]
[(Green: C, Gray: H, Yellow: S, Red: O)]

Solvent: Ionic Liquid (IL) (1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide)



Ionic Liquid: [EMIM]⁺[TFSI]⁻ [MW: 391.31 g/mol; $\epsilon = 14.79$ (25°C)]
[(blue: N, Black: C, Gray: H, Light Blue: F, Yellow: S, Red: O)]

Results: PFG Self-Diffusion



Ion	D (m ² /s) at 298K (Actual Data)	D (m ² /s) at 318K (Actual Data)	D (m ² /s) at 353K (Literature)
[EMIM] ⁺	0.23 x 10 ⁻¹⁰	0.45 x 10 ⁻¹⁰	2.80 x 10 ⁻¹⁰
[TFSI] ⁻	0.18 x 10 ⁻¹⁰	0.32 x 10 ⁻¹⁰	1.65 x 10 ⁻¹⁰

1% PSS: IL: EtOD	D (m ² /s) at 298K (Actual Data)
[EMIM] ⁺	0.95 x 10 ⁻¹⁰
[TFSI] ⁻	0.17 x 10 ⁻¹⁰
PSS (f=0.8)	0.21 x 10 ⁻¹⁰

Background

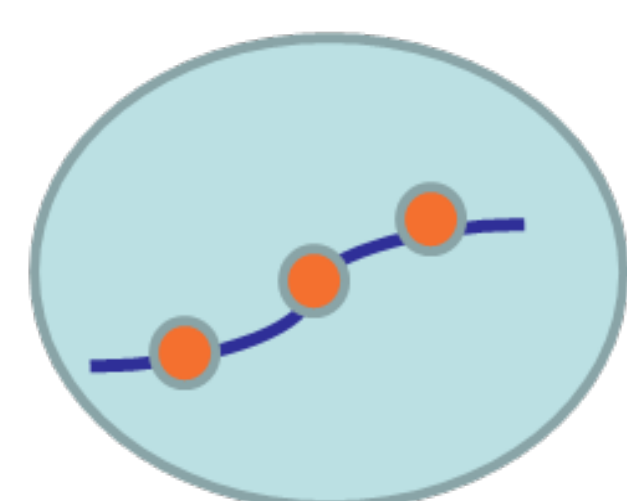
Ionic Liquids (IL) exhibit broad liquid state temperature window, high chemical/thermal stability, non-flammability, high ionic conductivity, etc. make them promising candidates as high performing electrolytes

The structure of ionizable polymers depends on the aggregation of these ionic groups which later affects the macroscopic ion transport for application

Challenge: Optimizing ion transport and stabilities of polymer electrolytes

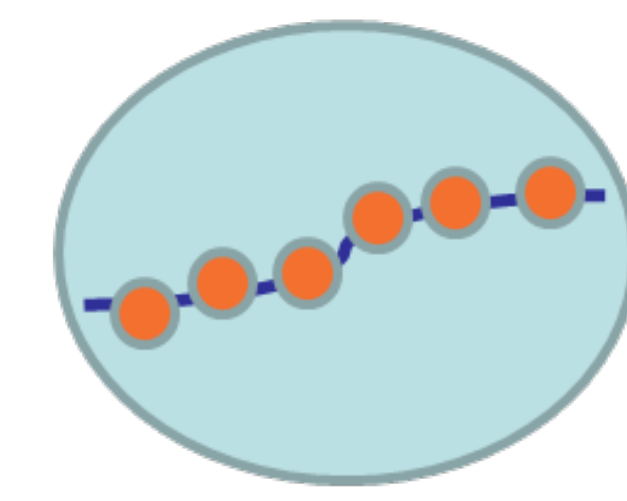
Ionizable polymers usage have increased for many electrochemical applications.

Ionomers:



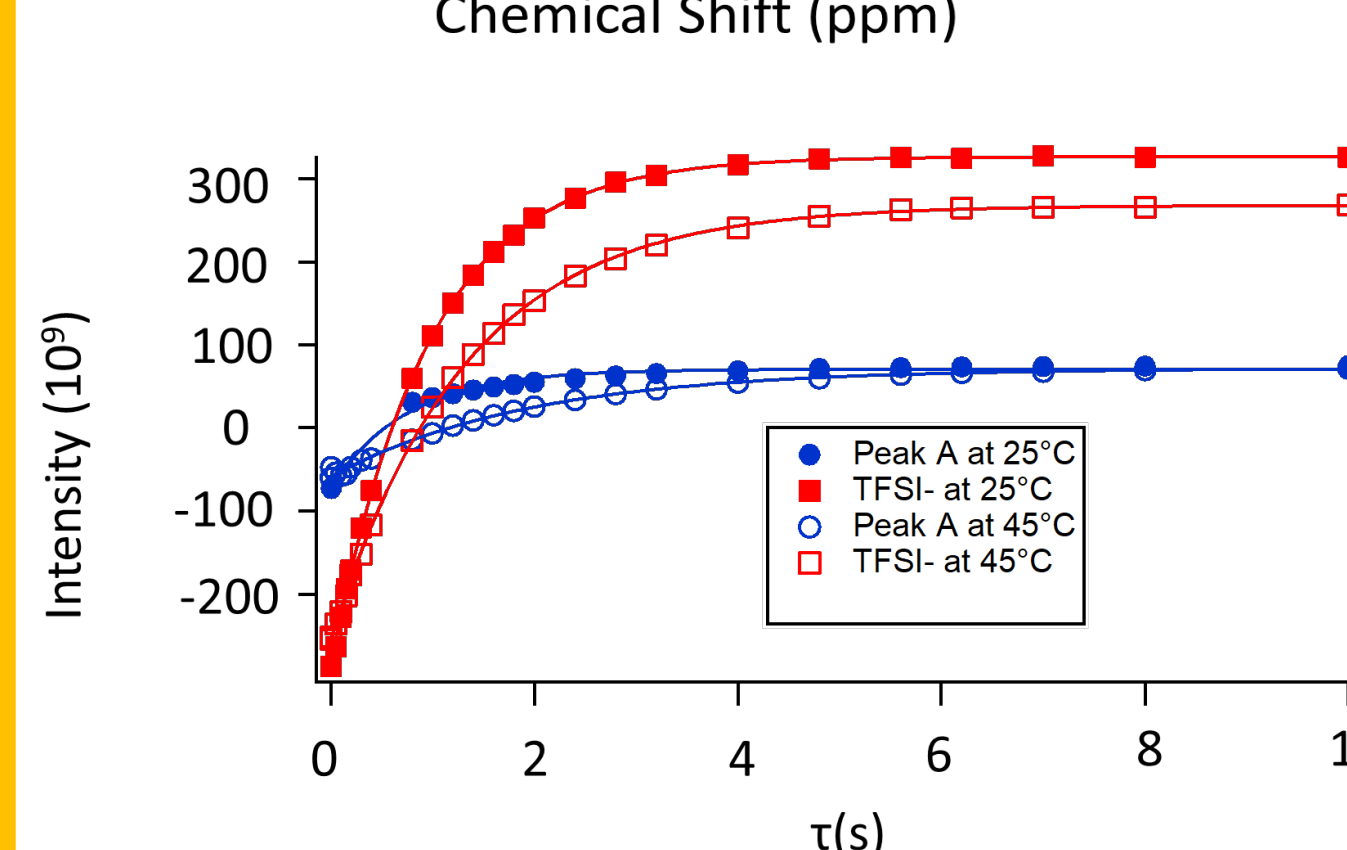
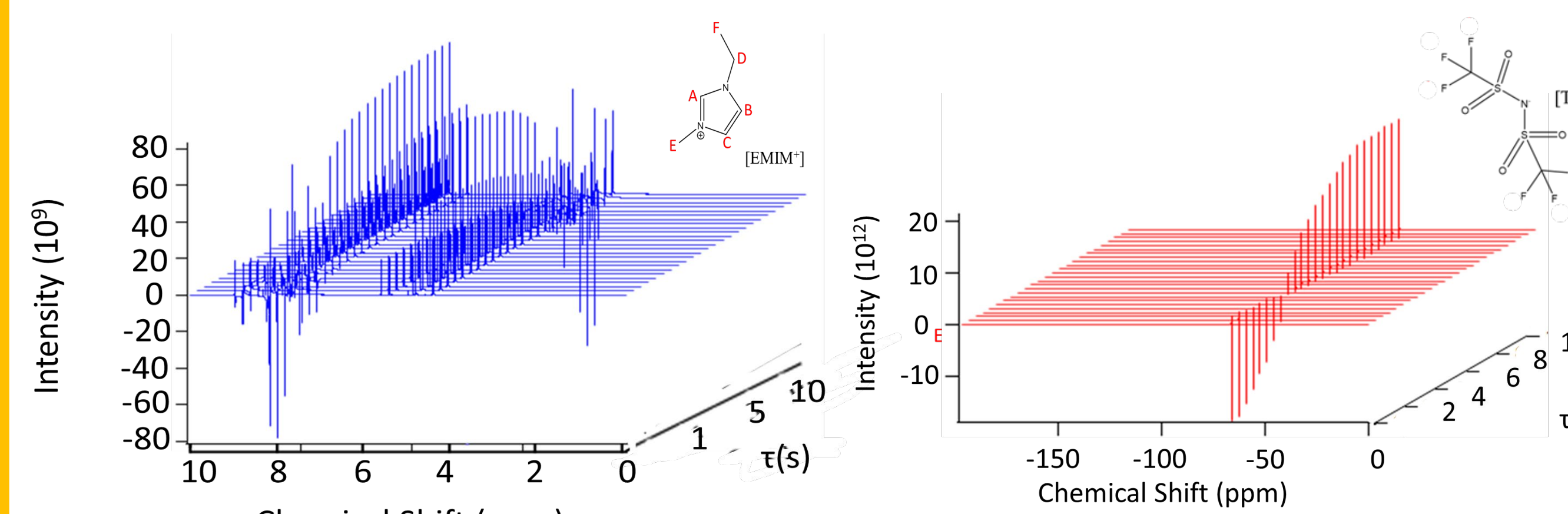
- Creates small ionic clusters
- Properties depend on both the polymer chain and ionic groups

Polyelectrolytes:



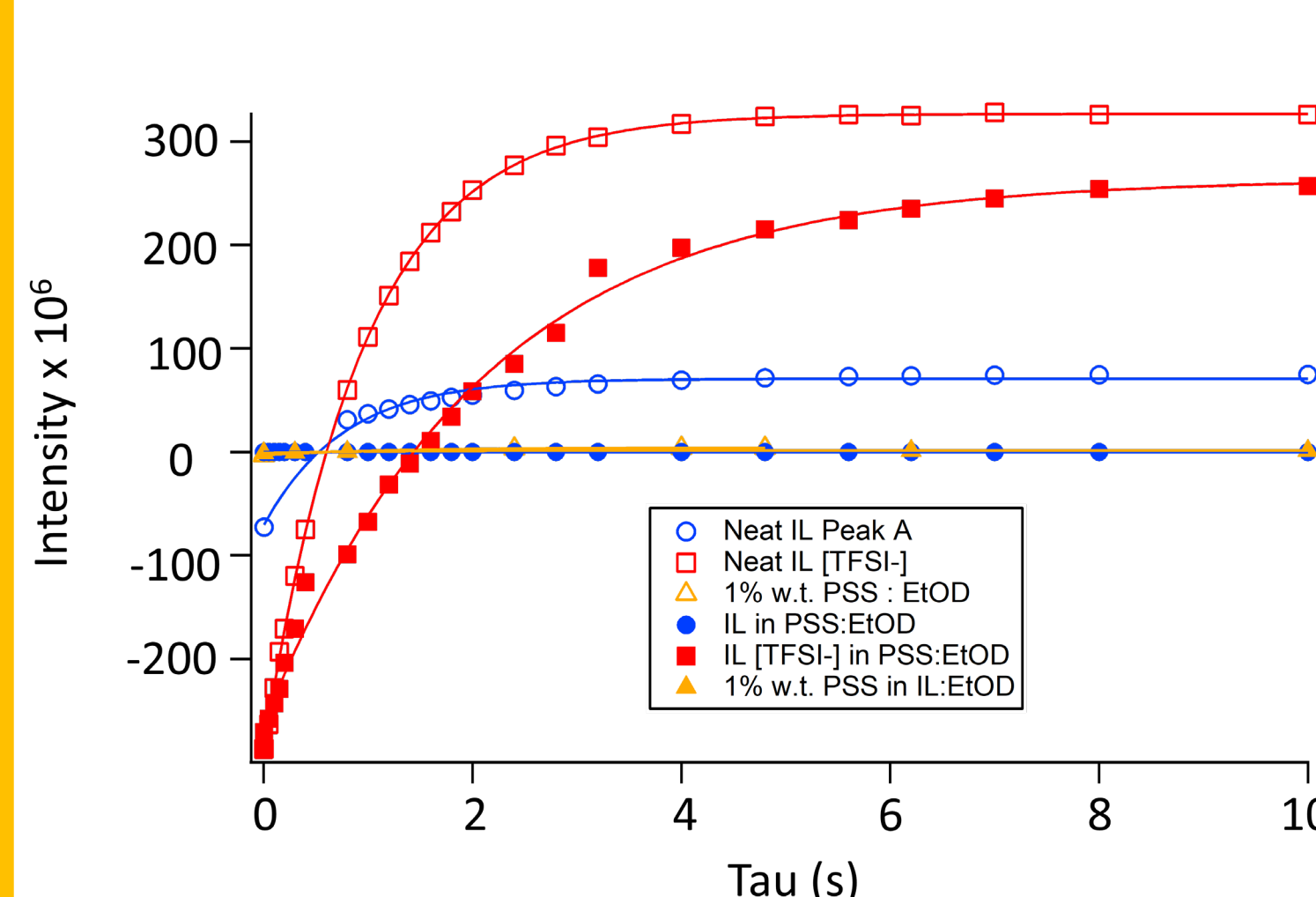
- Creates dense ionic network
- Properties depend on ionic groups

Results: Spin-Lattice Relaxation



Peak assignment	T ₁ /s at 298 K (Actual Data)	T ₁ /s at 306 K (Literature)	T ₁ /s at 318 K (Actual Data)
A	0.76	1.80	1.92
B	1.18	1.90	2.08
C	2.55	1.90	2.08
D	1.11	0.70	1.02
E	0.70	0.90	0.98
F	2.00	1.10	1.54
TFSI-	0.95	1.10	0.29

Spin-Lattice Relaxation of pure IL



Peak Assignment	T ₁ /s at 298 K (Actual Data)
IL peak A	1.18
IL peak D	1.10
IL peak E	1.09
IL peak F	1.43
PSS peak B,C	0.97
TFSI-	2.78

Spin-Lattice Relaxation of 1%PSS:EtOD:IL

Conclusions

Higher temperature causes a higher T₁ Relaxation, a longer time to relax to equilibrium, and a higher diffusion rate.

The IL [EMIM⁺][TFSI⁻] relaxes at slower rate than the sulfonated polymer.

The anion relaxes and diffuses differently than the cation and each separate species within the cation relax differently.

The presence of PSS polymer slows the diffusion of the cation IL but has no effect on the anion.

The polar co-solvent, d₆-Ethanol, aid the interaction between the polymer, Sulfonated Polystyrene (f=0.8), and the IL.

The similar dynamics of the most 'acidic' hydrogen from the IL compound, Hydrogen A, and from the PSS polymer, aromatic hydrogens, hint a possible optimal point of interaction.

Goal

Understand the relation between the dynamics of polymer-electrolyte complexes for optimization of systems for clear energy application

Future Aspiration

Understand the effect of higher concentration of IL on PSS by increasing IL concentration

Understanding the dynamics of d₆-Ethanol and its effect on the interaction between PSS : IL

References

¹D'Agostino, Carmine, et al. "Diffusion, Ion Pairing and Aggregation in 1-Ethyl-3-Methylimidazolium-Based Ionic Liquids Studied by 1H and 19F PFG NMR: Effect of Temperature, Anion and Glucose Dissolution." ChemPhysChem 19.9 (2018): 1081-1088.

²Suarez, Sophia N., et al. "Do TFSI anions slither? Pressure exposes the role of TFSI conformational exchange in self-diffusion." The Journal of Physical Chemistry B 119.46 (2015): 14756-14765.

Acknowledgments

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