Ion Transport in Liquid Electrolytes for Rechargeable Battery Applications

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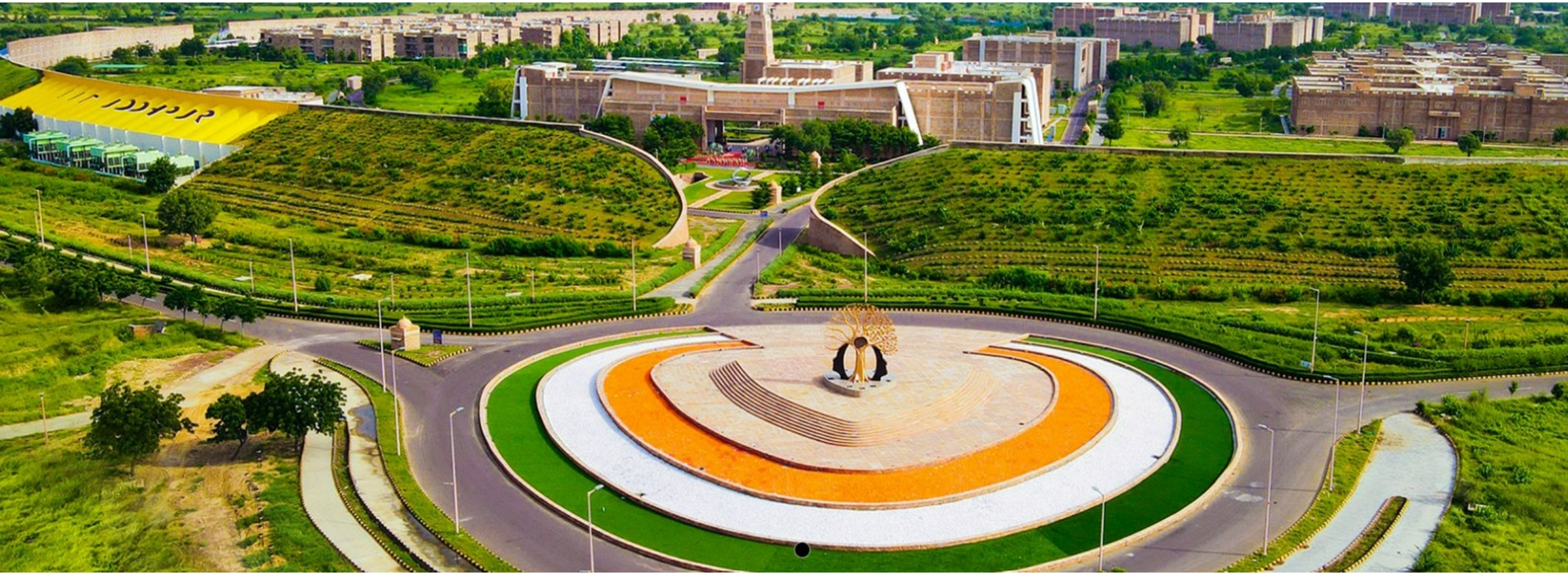
भारतीय प्रौद्योगिकी संस्थान जोधपुर

Indian Institute of Technology Jodhpur

Department of Physics



Stokes-Einstein relation

$$D = \frac{k_B T}{6\pi\eta r} \Longleftrightarrow D \sim 1/\tau_c$$

Coupling between ionic conductivity and viscosity!

Ionic conductivity ⇧ Viscosity ⇩

The decoupling scenario

$D \sim \eta^{-1}$ or $D \sim \tau_C^{-1}$

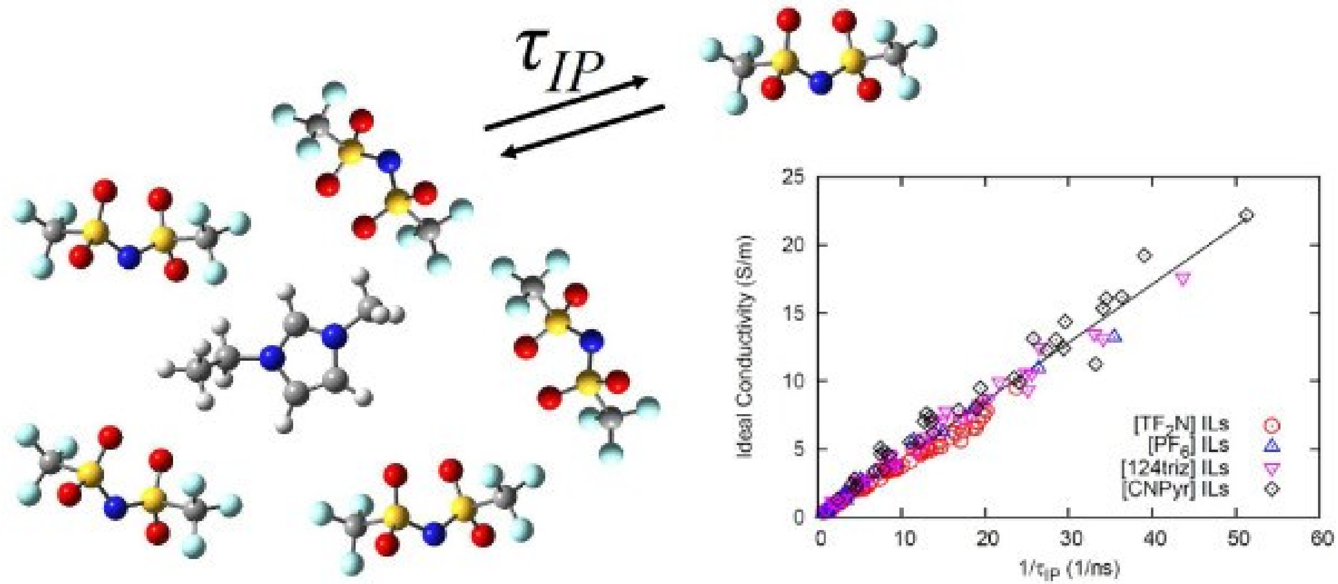
Ionic conductivity ⇧ Viscosity ⇩

What if $D \sim \eta^{-1}$ or $D \sim \tau_C^{-1}$
does not hold?

Ionic conductivity ⇧ Viscosity ⇧

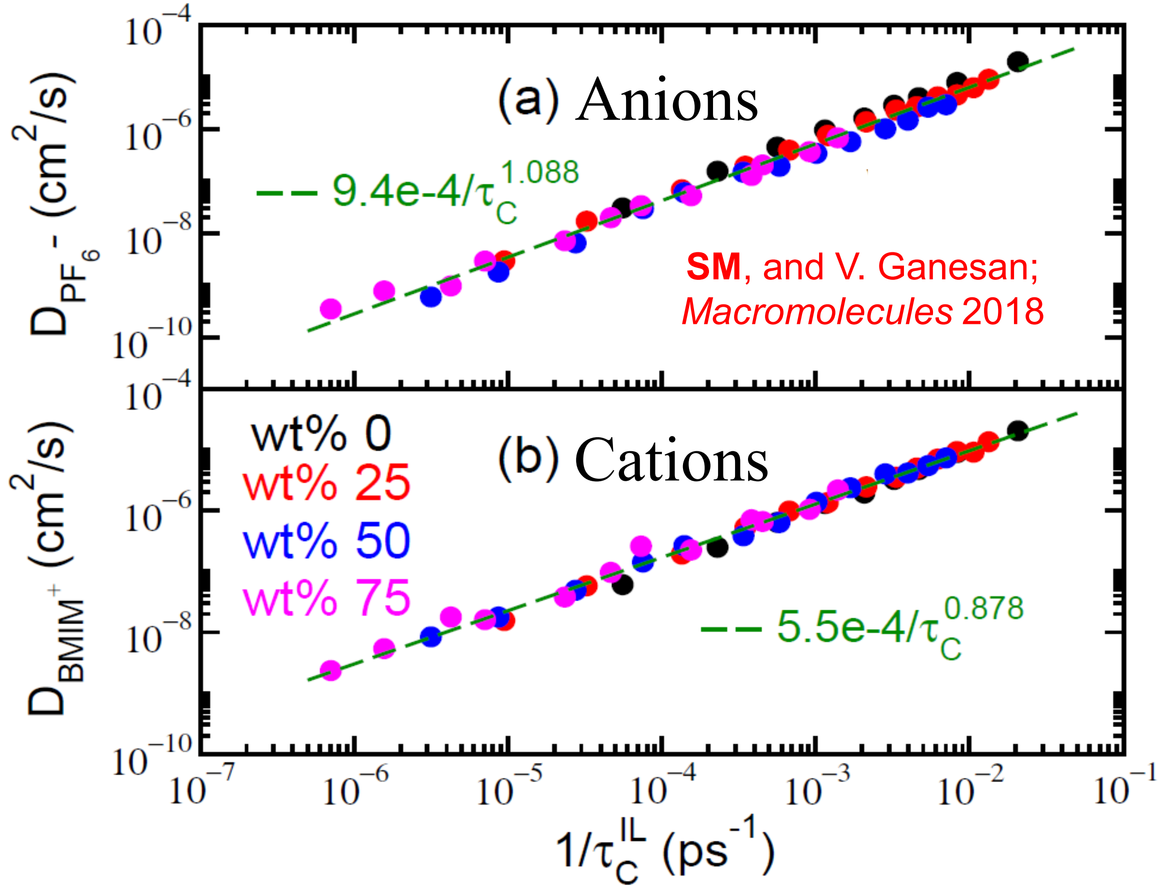
For such systems, if exist, can we
establish the transport mechanisms?

Ion transport mechanisms in neat ILs



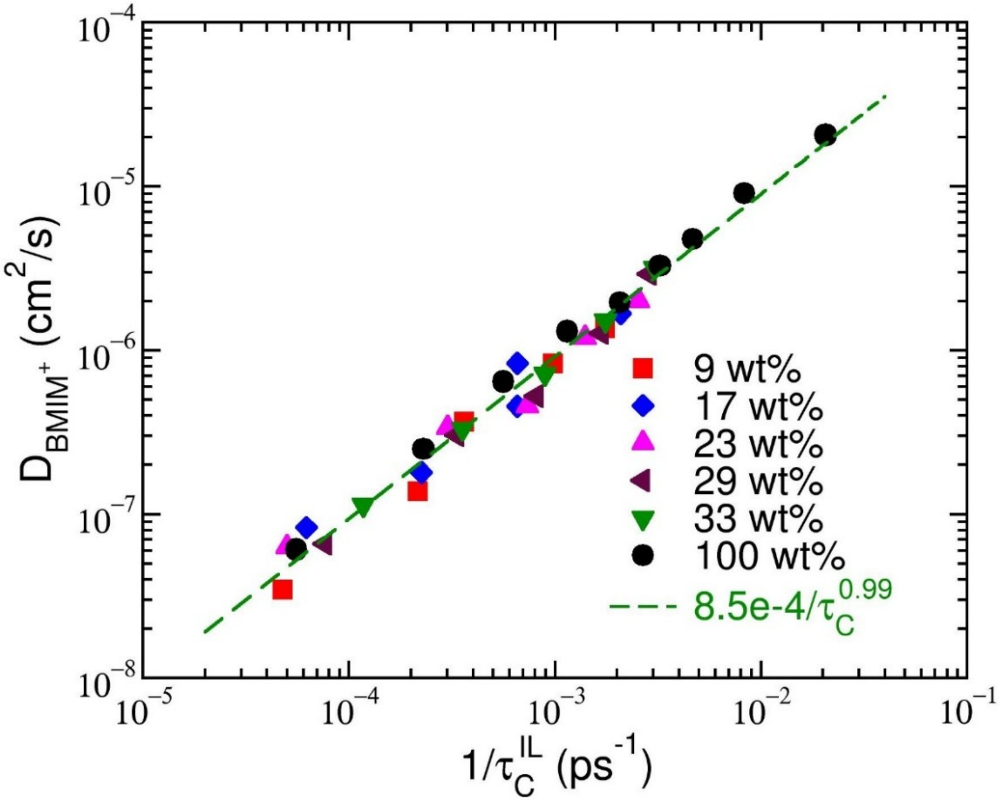
Yong Zhang and Edward J. Maginn
J. Phys. Chem. Lett. 2015, 6, 4, 700–705

Ion transport mechanisms in blend IL-polyIL electrolytes



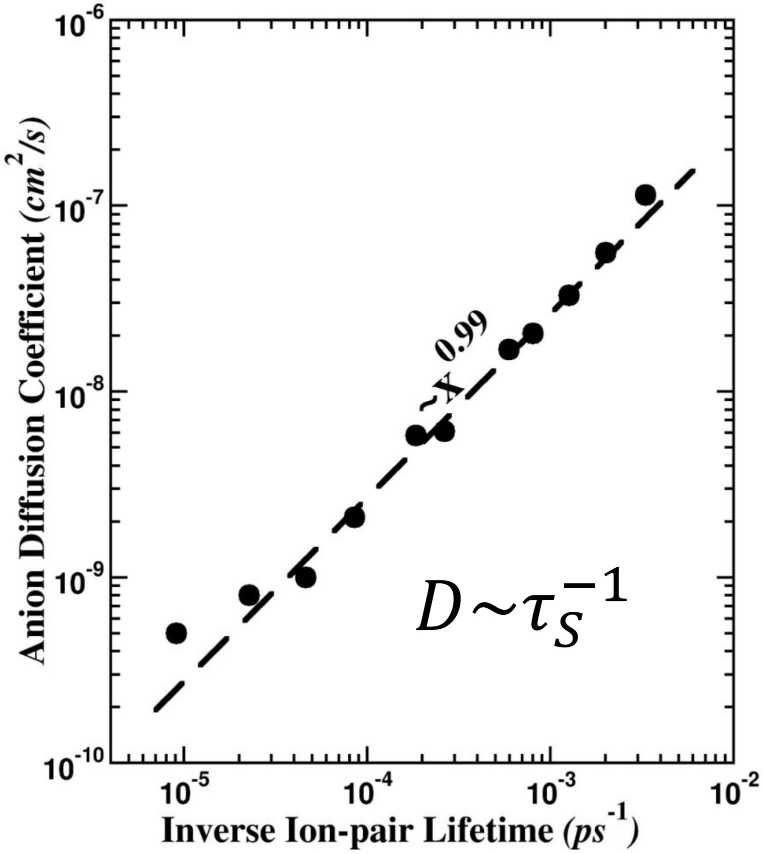
The transport properties are directly correlated to an underlying relaxation phenomena!

Ion transport mechanisms in PEOLiPF$_6$-IL ternary electrolytes



SM and V. Ganesan, *J. Chem. Phys.*, **146** (2017) 074902

Ion transport mechanisms in polyIL



SM, Keith, J., and Ganesan, V., *J. Am. Chem. Soc.* 2017

The transport properties are directly correlated to *certain* relaxation phenomena!

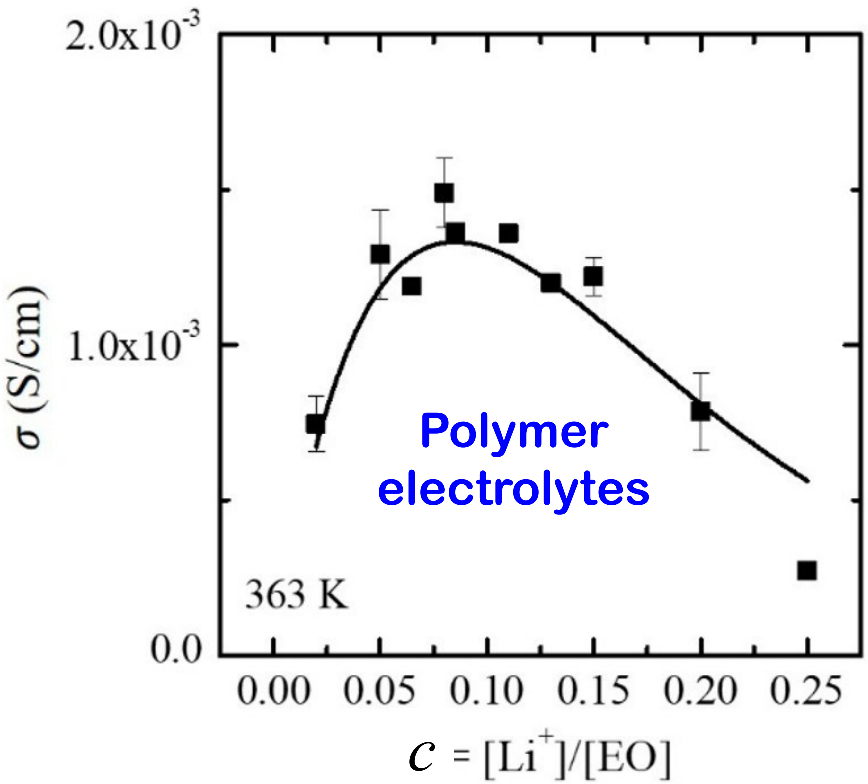
Stokes-Einstein relation

$$D = \frac{k_B T}{6\pi\eta r} \Longleftrightarrow D \sim 1/\tau_c$$

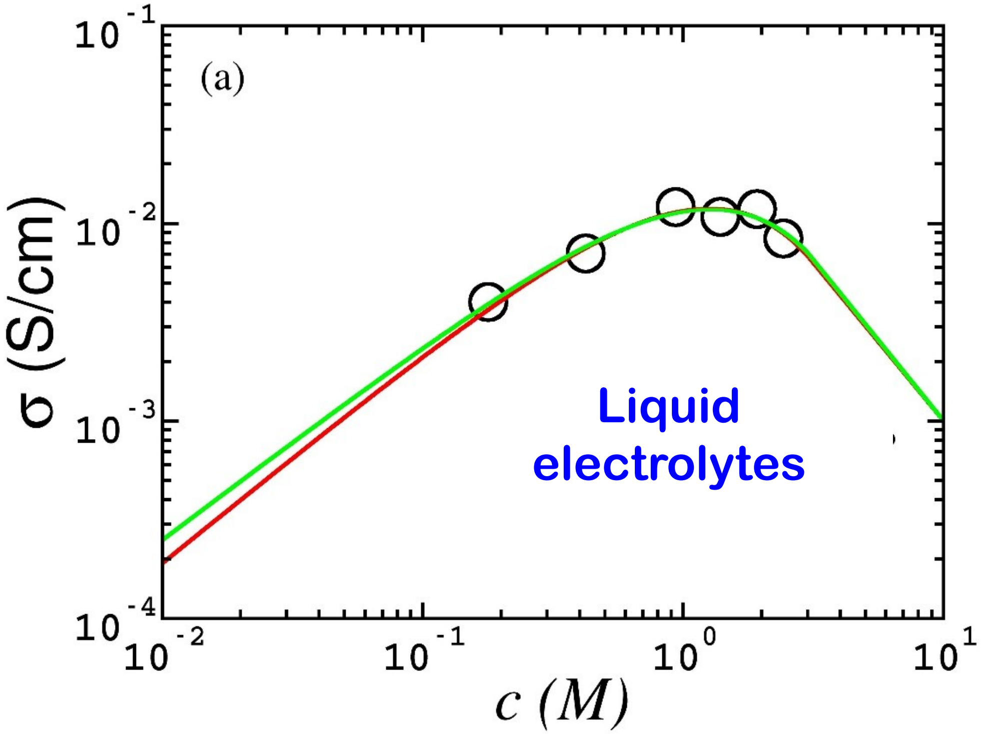
Salt effects on ionic conductivity

$$\sigma(c) \sim c e^{-c/c_0}$$

Nitash P. Balsara
ACS Macro Lett., 2018



Andreas Hauer
Phys. Chem. Chem. Phys., 2023



What are the ionic conductivity mechanisms?

How does the salt concentration influence the power-law relations?

What is the connection between viscosity (η) and ion-pair relaxation times (τ_c)?

Can η and τ_c explain salt effects on ionic conductivity?

Ionic conductivity

Nernst-Einstein ionic conductivity

$$\sigma_{NE} = \frac{e^2}{V k_B T}(N_+ z_+^2 D_+ + N_- z_-^2 D_-) \Rightarrow$$

Ion-ion correlations are ***not captured***

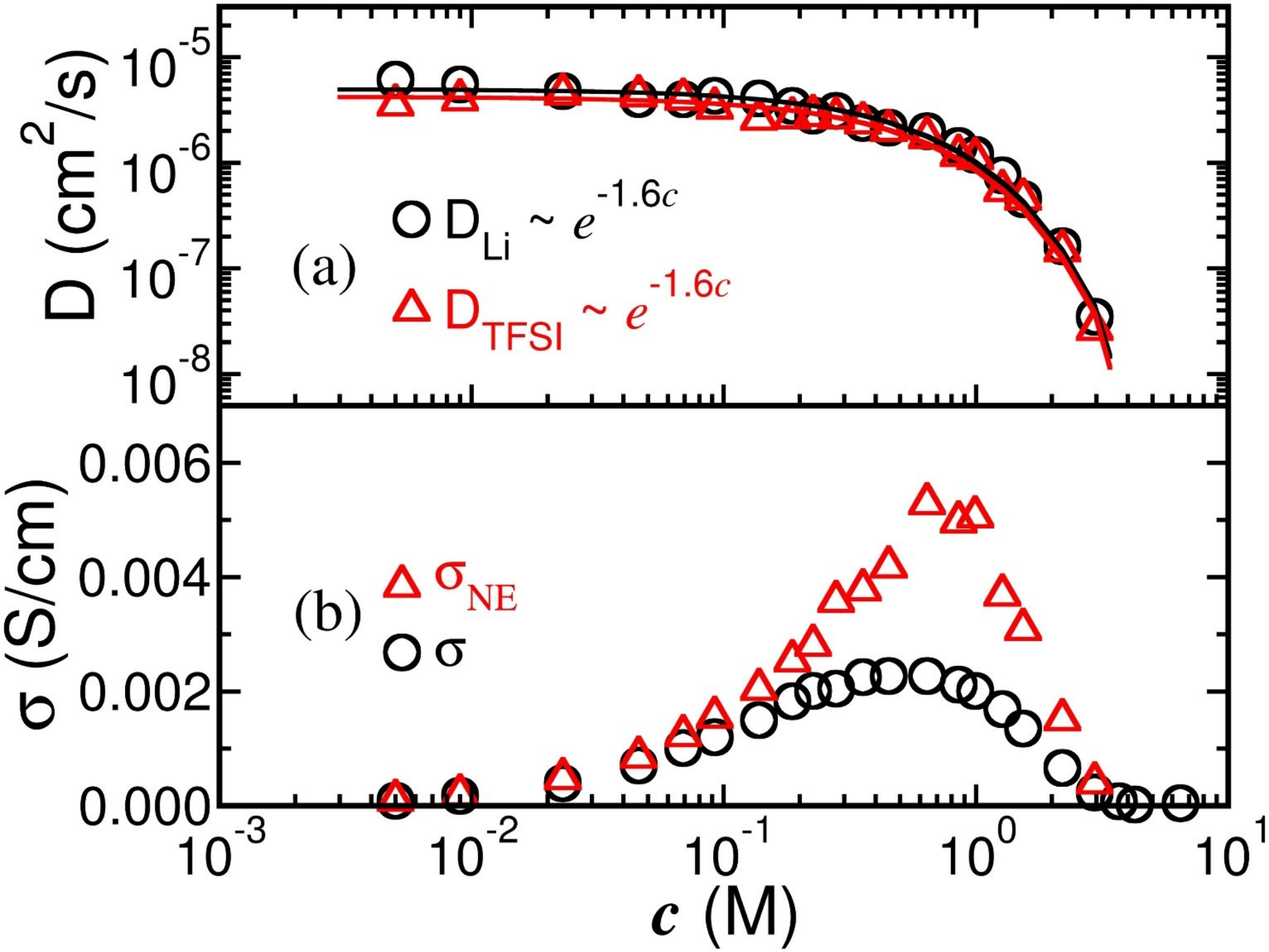
True ionic conductivity

$$\mu = \frac{\langle v_d \rangle}{E}$$

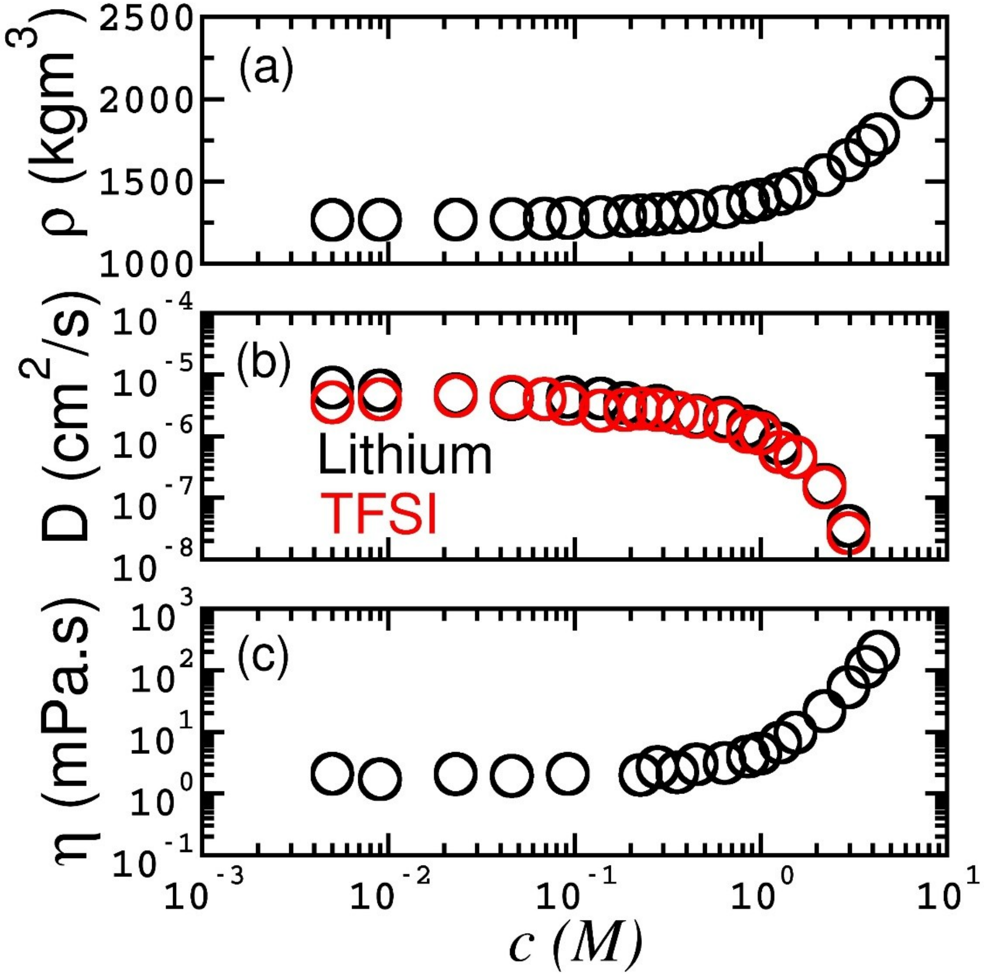
$$\sigma = \sum_i z_i\, c_i \mu_i \Rightarrow$$

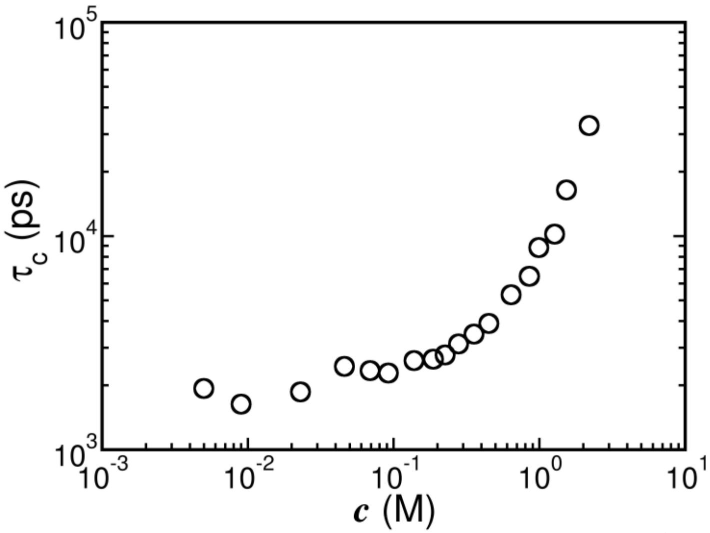
Ion-ion correlations are ***captured***

Diffusivities and ionic conductivity in EC-LiTFSI electrolytes



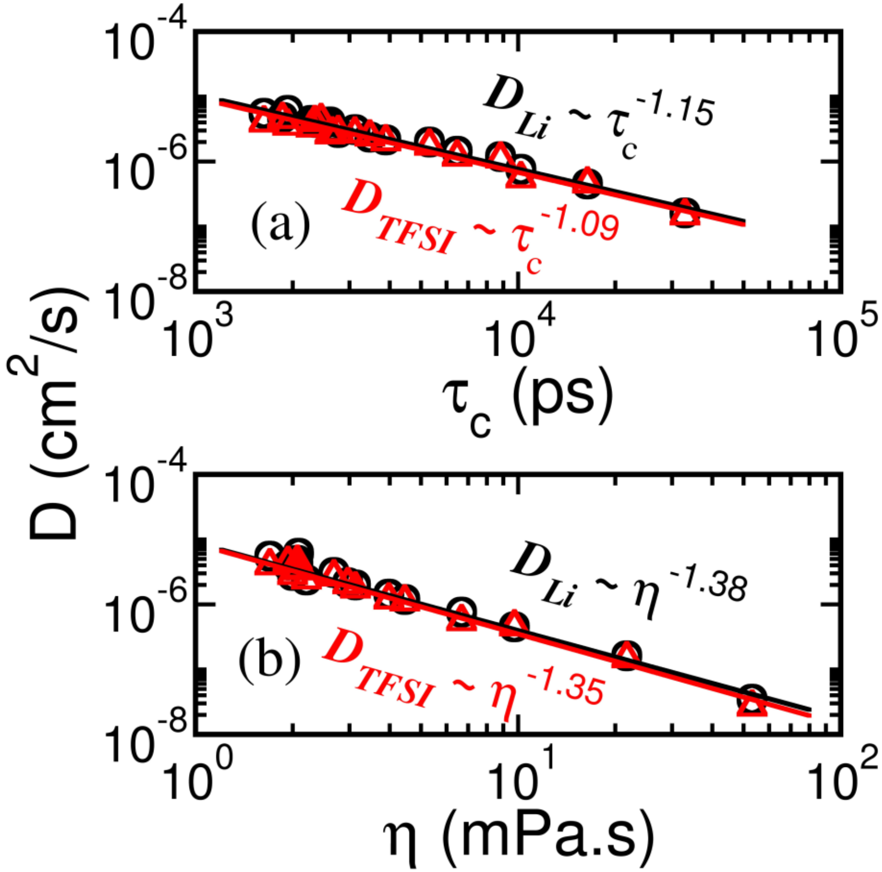
Salt concentration effects





It appears that ρ, η, and τ_c can explain salt effects on diffusion

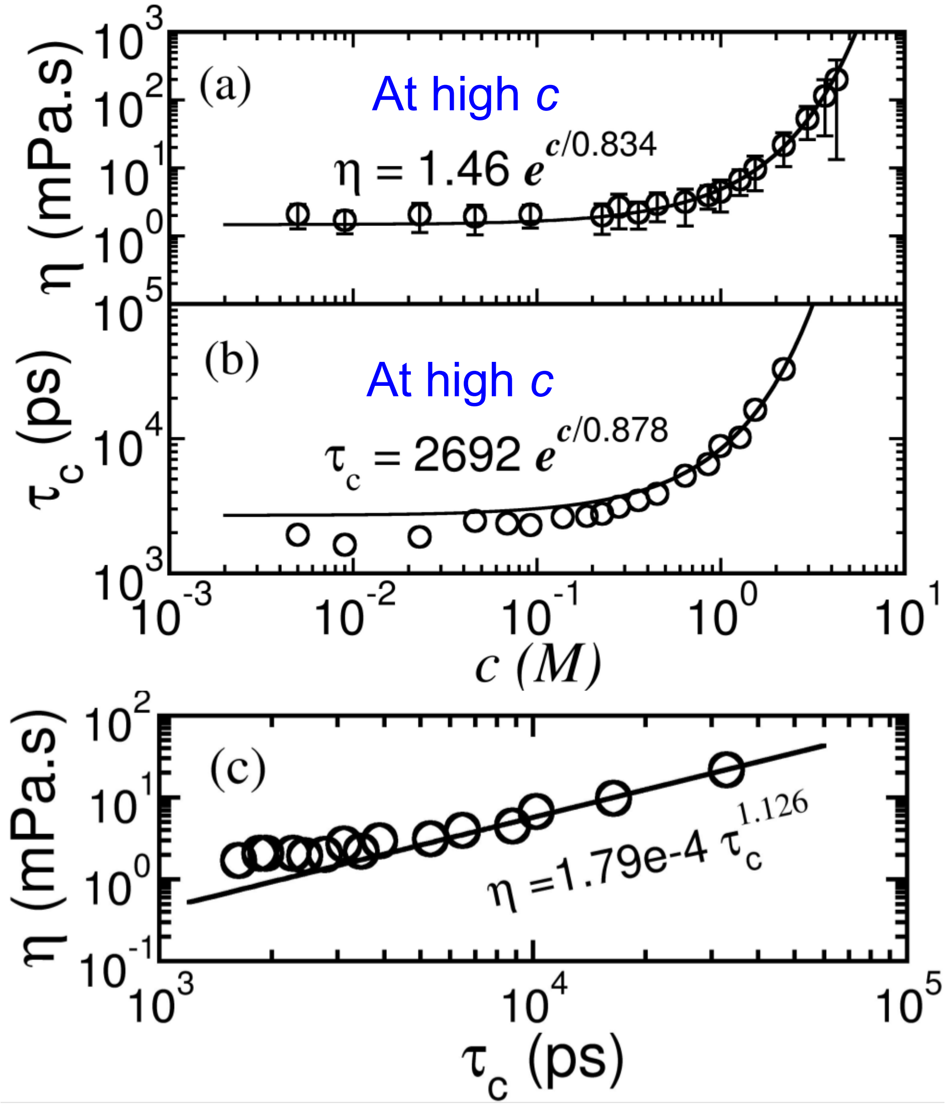
Can η, and τ_c explain salt effects on diffusion?



Power-law exponents

Neither $D \sim \eta^{-1}$ nor $D \sim \tau_C^{-1}$

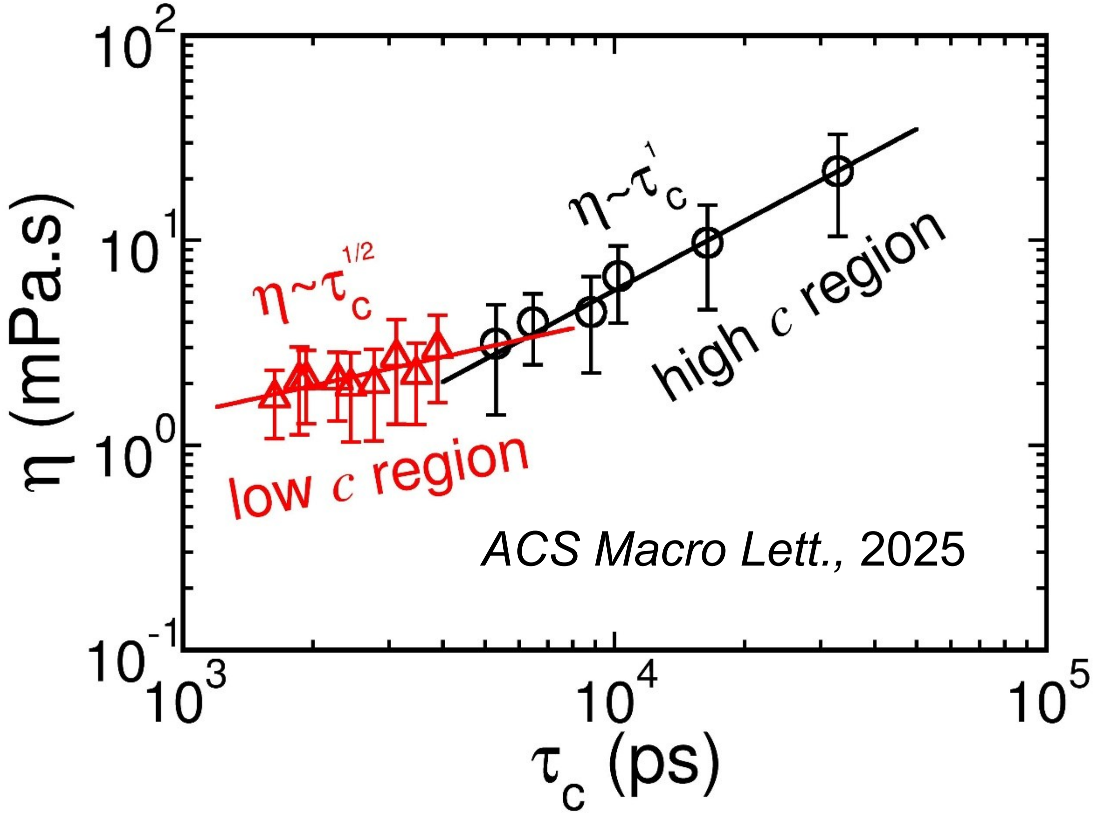
Viscosity and ion-pair relaxation times



It appears that both η and τ_c can explain salt effects on ionic conductivity at high *c* [yes]

~~It appears that η can explain salt effects on ionic conductivity across the range of *c*.~~

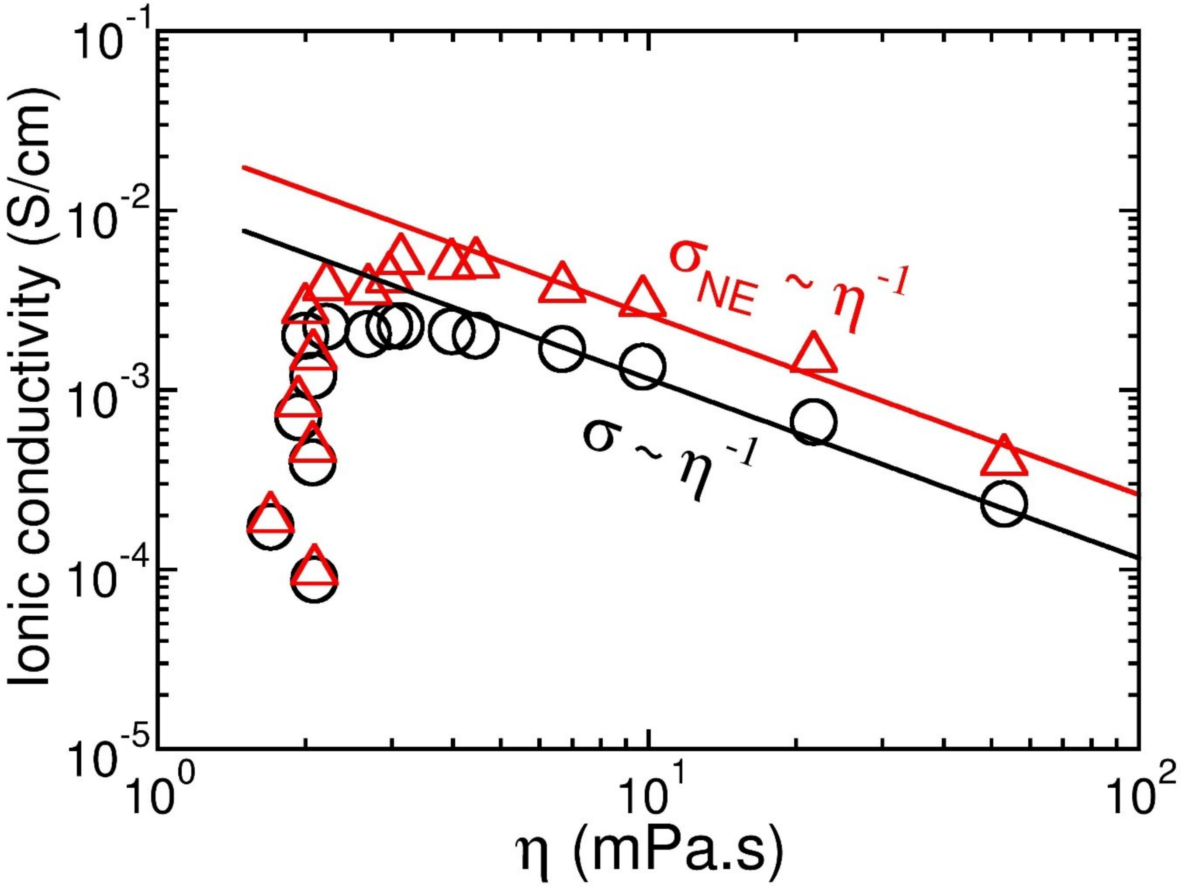
Viscosity vs. ion-pair relaxation times



Stokes-Einstein relation

$$D = \frac{k_B T}{6\pi\eta r} \iff D \sim 1/\tau_c$$

Does viscosity explain salt effects on ionic conductivity?



Low *c*: No
Intermediate *c*: No
High *c*: Yes

Does viscosity explain salt effects on ionic conductivity?

At low *c*: σ is independent of η and τ_c

Ions move with the solvation shell -> *vehicular* transport mechanism

$$\Rightarrow \sigma \sim c^{\alpha} \text{ --------- (A)}$$

α takes into account the marginally present ion-ion correlations at low *c*!

Does viscosity explain salt effects on ionic conductivity?

At high *c*

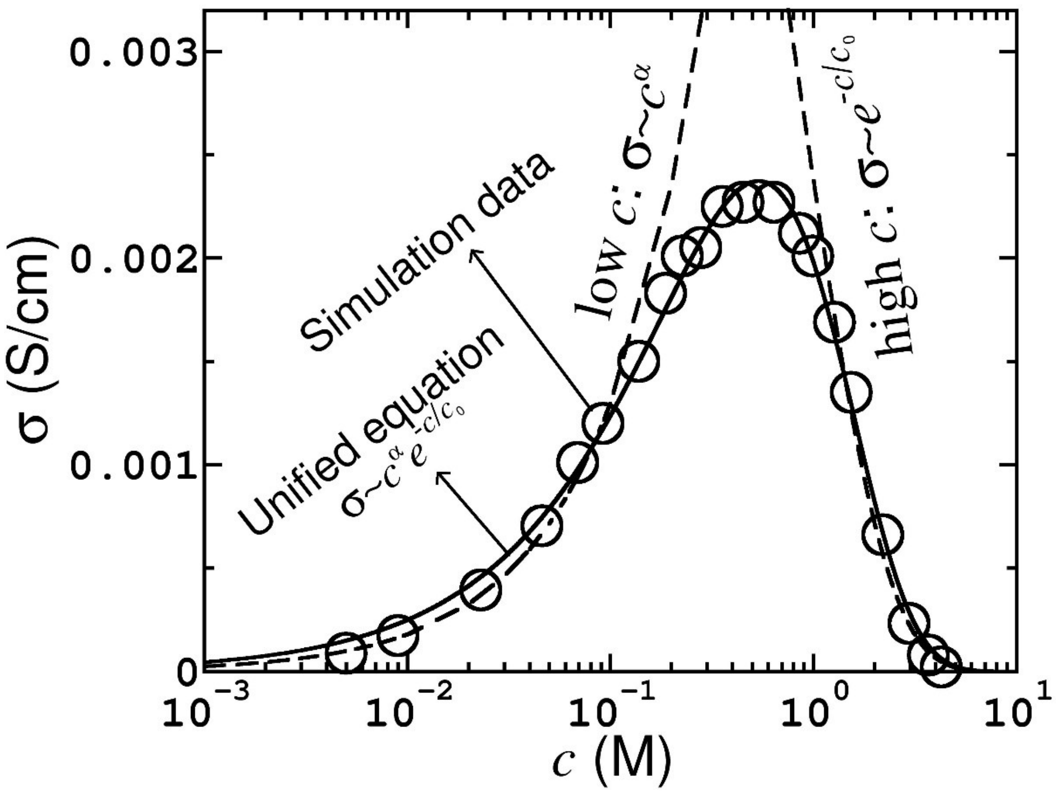
$$\sigma \sim \eta^{-1} \text{ and } \eta \sim e^{c/c_0}$$

$$\Rightarrow \sigma \sim e^{-c/c_0} \text{ ---------- (B)}$$

Ions move by means of formation and breaking of ion-pairs -> *Structural* transport mechanism

Unified equation for ionic conductivity

$$\sigma(c) \sim c^{\alpha} e^{-c/c_0}$$

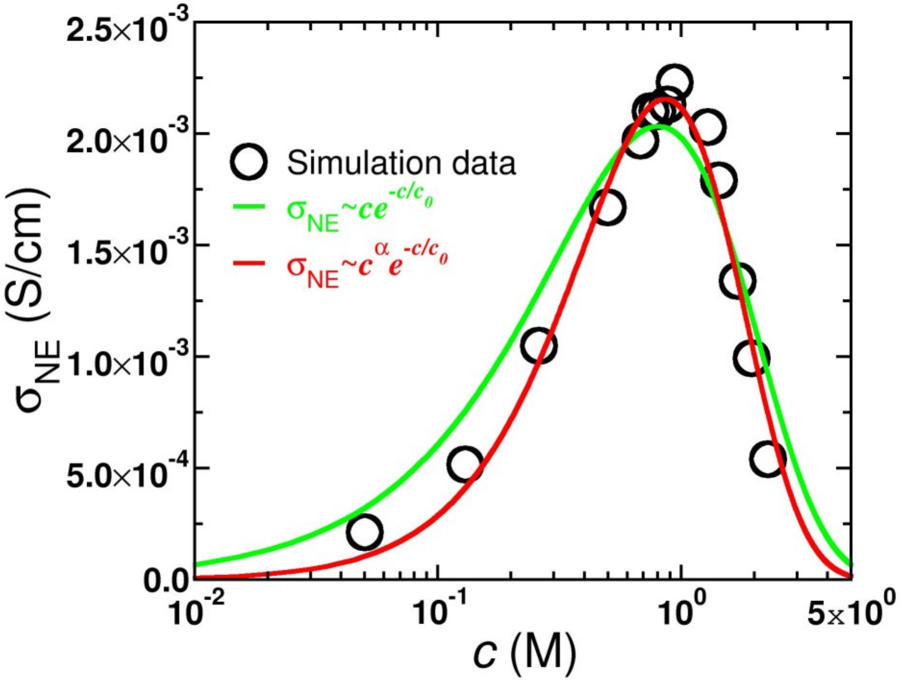


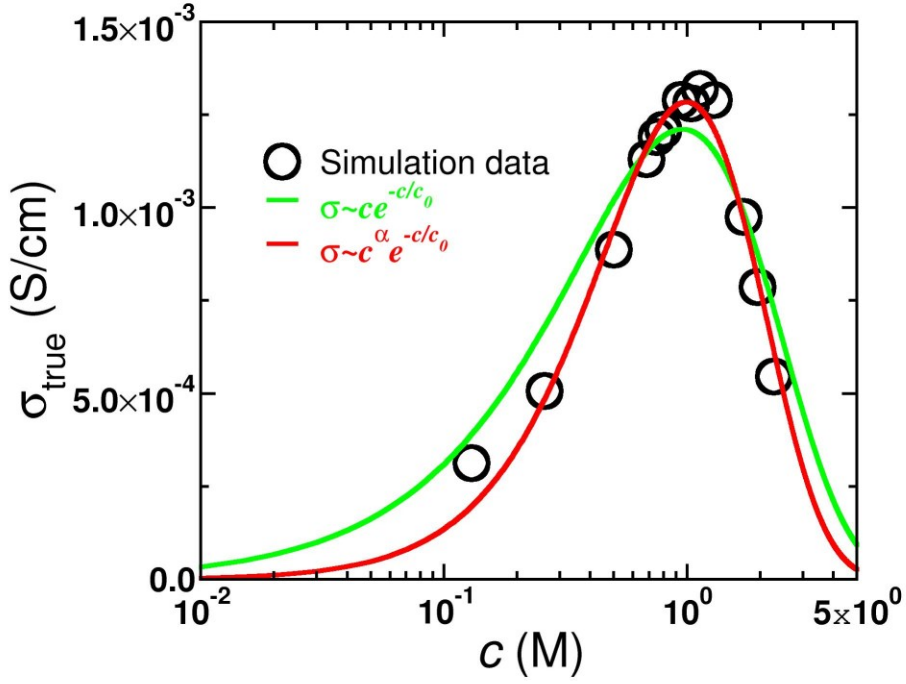
ACS Macro Lett., 2025

- Low *c*: minimal ion-ion correlations. *Vehicular mechanism*
- Intermediate *c*: vehicular + structural diffusion
- High *c*: high ion-pair relaxations and viscosity dominates. *Structural diffusion*

Unified equation for PEO-$NaPF_6$ electrolytes

(Hema, Sipra, Akash, et al., submitted, 2025)





The unified equation explains ionic conductivity across a wide range of salt concentrations!

Conclusions

- Diffusion decreases with *c* but σ increases at low *c* and then decreases at high *c* due to increased ion-ion correlations.

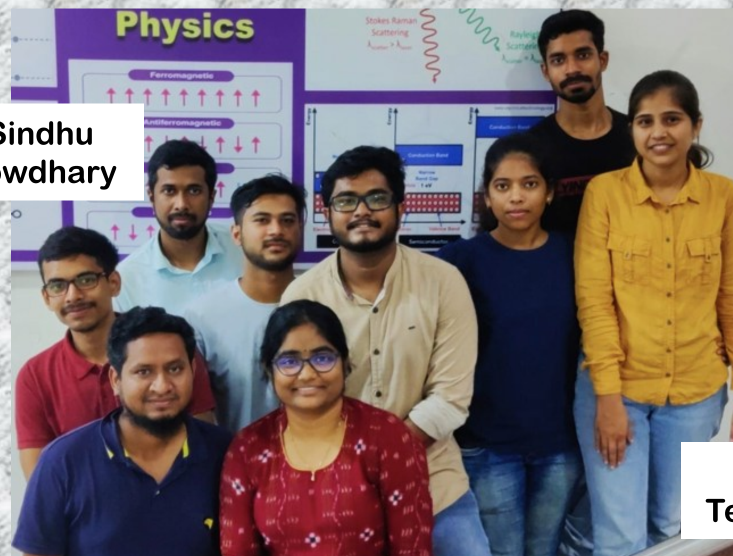
- Viscosity and ion-pair relaxation times are related to each other via $\eta \sim \tau_c^{1/2}$ at low *c* and $\eta \sim \tau_c$ at high *c*.

- $\sigma \sim c^{\alpha}$ at low *c* and $\sigma \sim \eta^{-1} \sim e^{-c/c_0}$ at high *c* leading to a unified equation that explains ionic conductivity across a wide range of salt concentrations, via, $\sigma(c) \sim c^{\alpha} e^{-c/c_0}$.

- Our extensive simulations and analyses conclude that *vehicular transport mechanism* is dominant at low *c* and *structural transport mechanism* at high *c*.

Pectin-EC-LiTFSI electrolytes: *Nanoscale* 2024
Pectin-IL electrolytes: *J. Chem. Phys.* 2023
Viscosity of pectin-IL electrolytes: *J. Mol. Liq.* 2024
EC-LiTFSI electrolytes: *ACS Macro Lett.*, 2025, *Phys. Chem. Chem. Phys.* 2025

Acknowledgements



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Pectin-EC-LiTFSI electrolytes: *Nanoscale* 2024
Pectin-IL electrolytes: *J. Chem. Phys.* 2023
Viscosity of pectin-IL electrolytes: *J. Mol. Liq.* 2024
EC-LiTFSI electrolytes: *ACS Macro Lett.* 2025, *PCCP* 2025

Thanks for your time and attention!