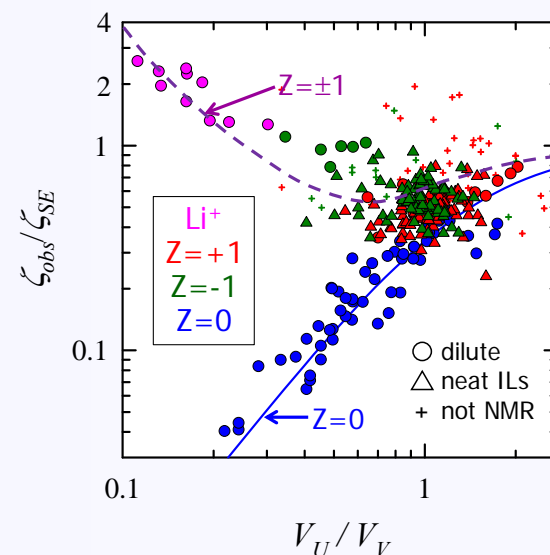
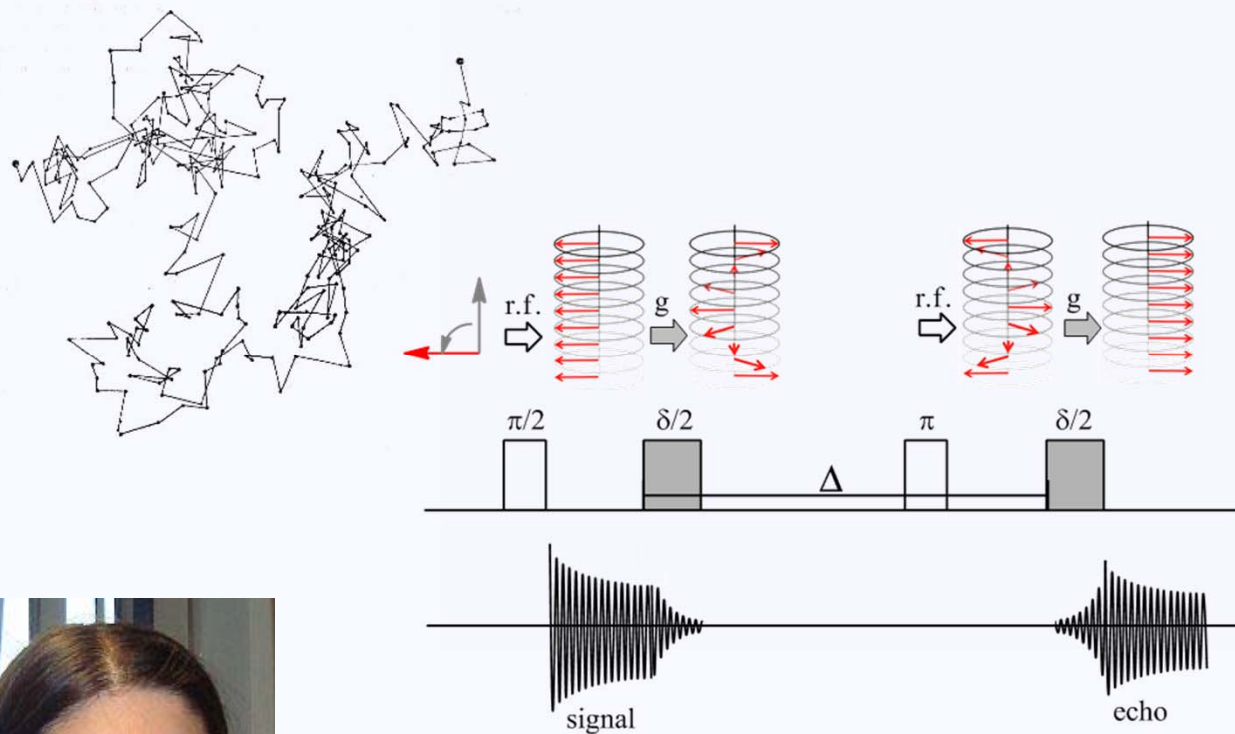
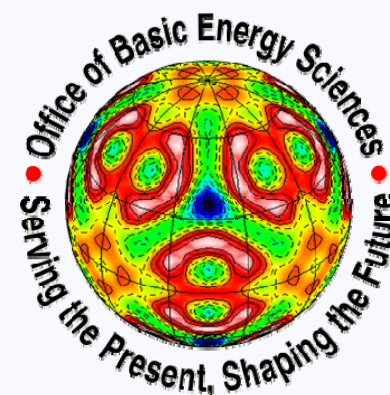


# Solute Translational Diffusion in Ionic Liquids



Anne Kaintz & Mark Maroncelli,  
Department of Chemistry,  
The Pennsylvania State University

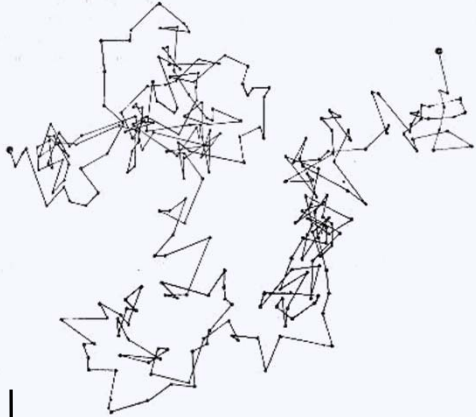


# Motion, Friction, & Hydrodynamic Models

Einstein Relation:

$$D = k_B T / \zeta$$

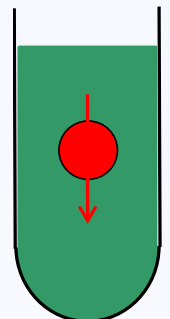
diffusion coefficient      friction constant



Stokes Law for Spherical Object:

$$\zeta_{sphere} = 6\pi\eta R$$

solvent viscosity      object radius



Stokes-Einstein-(Sutherland):

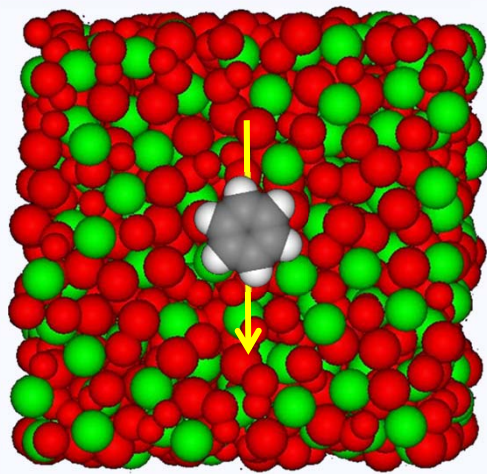
$$D_{SE} = \frac{k_B T}{6\pi\eta R}$$

- 6π for stick, 4π for slip boundary conditions
- shape is a minor effect

Rotational Equivalent:

$$D_{SED} = \frac{k_B T}{6\eta V}$$

- 6 for stick, 0 for slip BCs
- shape is critical
- observable more complex



are hydrodynamic models useful?

# Terminology & Perspective

**Self Diffusion:** diffusion of a molecule in its own liquid

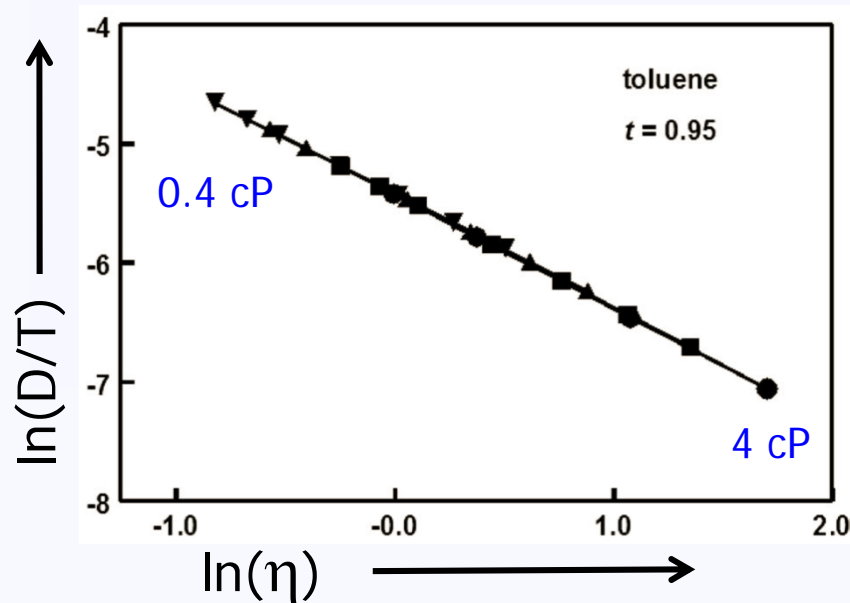
**Tracer Diffusion:** diffusion of an infinitely dilute solute in a solvent

**Empirical Focus:**  $\frac{\zeta_{obs}}{\zeta_{SE}} = \frac{D_{SE}}{D_{obs}}$

# Self-Diffusion: Viscosity Scaling

Harris, *JCP* **131**, 054503 (2009); Harris & Kanakubo, *Faraday Disc.* **154**, 425 (2012)

## D/T vs $\eta$ - Toluene



- in most liquids T or P variation of  $\eta$  leads to near hydrodynamic behavior:

$$D/T = A\eta^{-p} \text{ with } p \cong 1$$

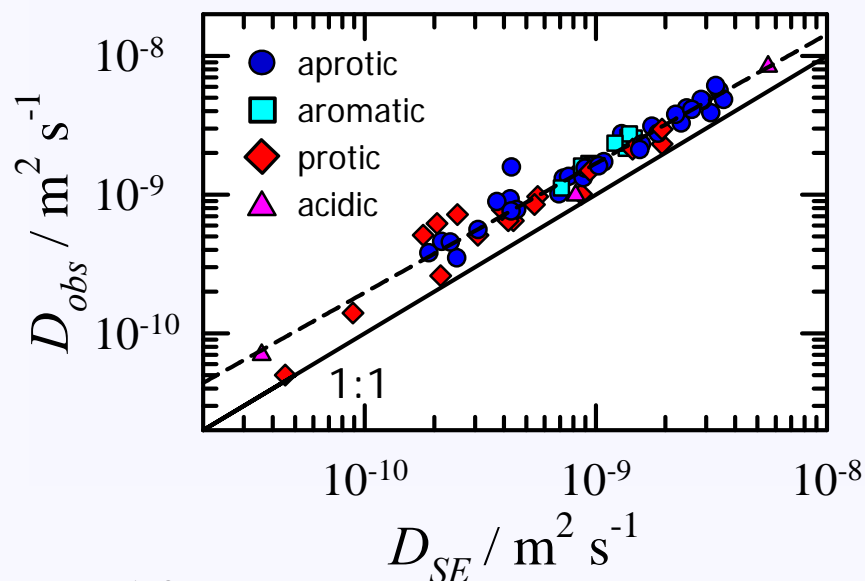
## Exponent $p$ in a Variety of Liquids

Liquid	$t$	Liquid	$t$
Hard sphere	0.97 <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	0.95 <sub>1</sub>
Lennard-Jones	0.92 <sub>1</sub>	<i>c</i> -C <sub>6</sub> H <sub>12</sub>	0.92 <sub>7</sub>
Xe	0.94 <sub>3</sub>	<i>c</i> -C <sub>6</sub> H <sub>11</sub> CH <sub>3</sub>	0.96 <sub>1</sub>
CH <sub>4</sub>	0.91	<i>n</i> -C <sub>6</sub> H <sub>14</sub>	0.90 <sub>9</sub>
CCl <sub>4</sub>	1.00 <sub>5</sub>	<i>n</i> -C <sub>8</sub> H <sub>18</sub>	0.88 <sub>9</sub>
Si(CH <sub>3</sub> ) <sub>4</sub>	0.99 <sub>5</sub>	<i>n</i> -C <sub>16</sub> H <sub>34</sub>	0.87 <sub>6</sub>
CHCl <sub>3</sub>	0.92 <sub>0</sub>	CO <sub>2</sub>	0.98 <sub>2</sub>
C <sub>5</sub> H <sub>10</sub>	0.87 <sub>8</sub>	CH <sub>3</sub> CN	0.84 <sub>7</sub>
C <sub>6</sub> H <sub>6</sub>	0.89 <sub>0</sub>	HCONHCH <sub>3</sub>	0.94 <sub>4</sub>
C <sub>6</sub> D <sub>6</sub>	0.94 <sub>2</sub>	C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>12</sub> OOC <sub>6</sub> H <sub>5</sub>	1.00 <sub>0</sub>
C <sub>5</sub> D <sub>5</sub> N	0.93 <sub>0</sub>		

Substance <sup>a</sup>	$t(D_+)$	$t(D_-)$
[BMIM][BF <sub>4</sub> ]	0.85 <sub>2</sub>	0.89 <sub>8</sub>
[OMIM][BF <sub>4</sub> ]	0.88 <sub>8</sub>	0.88 <sub>8</sub>
[BMIM][PF <sub>6</sub> ]	0.88 <sub>3</sub>	0.92 <sub>0</sub>
[HMIM][PF <sub>6</sub> ]	0.84 <sub>5</sub>	0.86 <sub>8</sub>
[OMIM][PF <sub>6</sub> ]	0.86 <sub>0</sub>	0.94 <sub>8</sub>
[BMIM][Tf <sub>2</sub> N]	0.92 <sub>5</sub>	0.93 <sub>3</sub>
[Pyr <sub>14</sub> ][Tf <sub>2</sub> N]	0.93 <sub>7</sub>	0.93 <sub>3</sub>
[P <sub>2225</sub> ][Tf <sub>2</sub> N]	0.96 <sub>3</sub> <sup>b</sup>	0.94 <sub>1</sub>
[N(C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> ][B(C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> ]	—	—

# Self-Diffusion: Conventional Liquids

## D in 64 Common Solvents

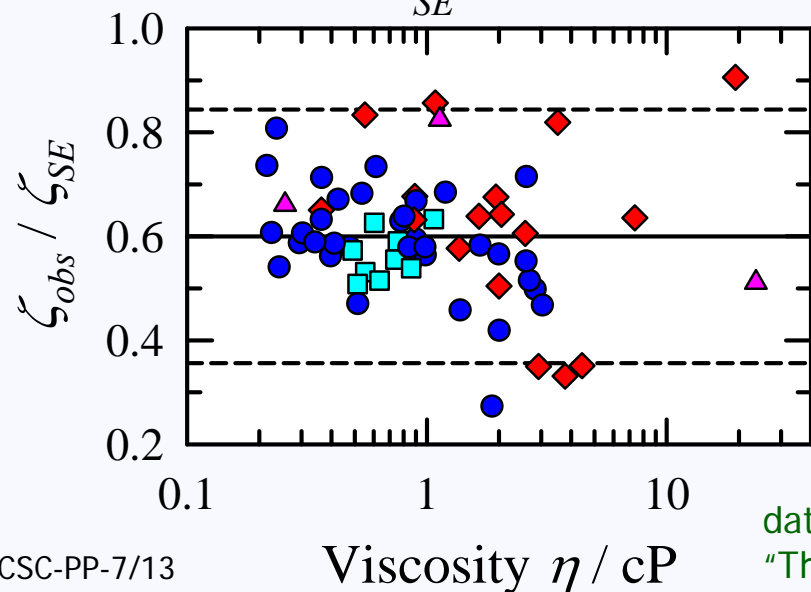


How accurate are SE predictions?

$$D_{SE} = \frac{k_B T}{6\pi\eta R_U}$$

assume solute (=solvent) radius related to vdW volume:

$$R_U = (4V_U / 3\pi)^{1/3}$$



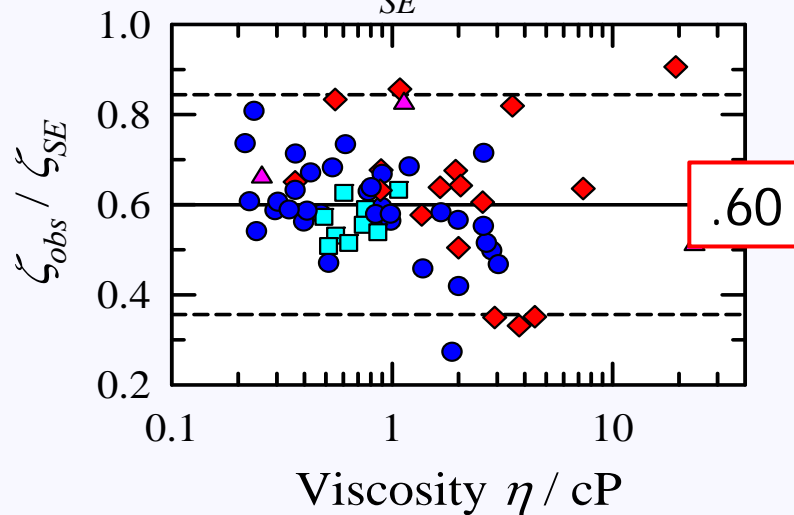
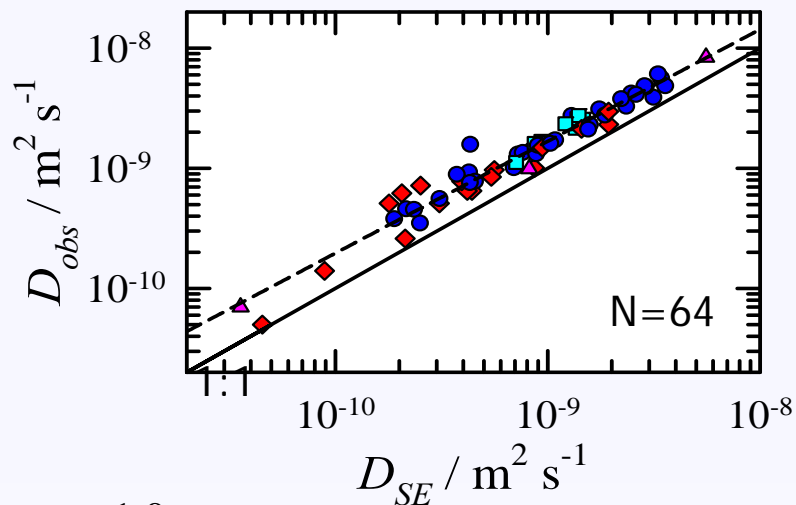
$$\frac{\zeta_{obs}}{\zeta_{SE}} = .60 \pm .24_{(2\sigma)}$$

➤ SE is remarkably accurate (average w. slip BC is ~1) !

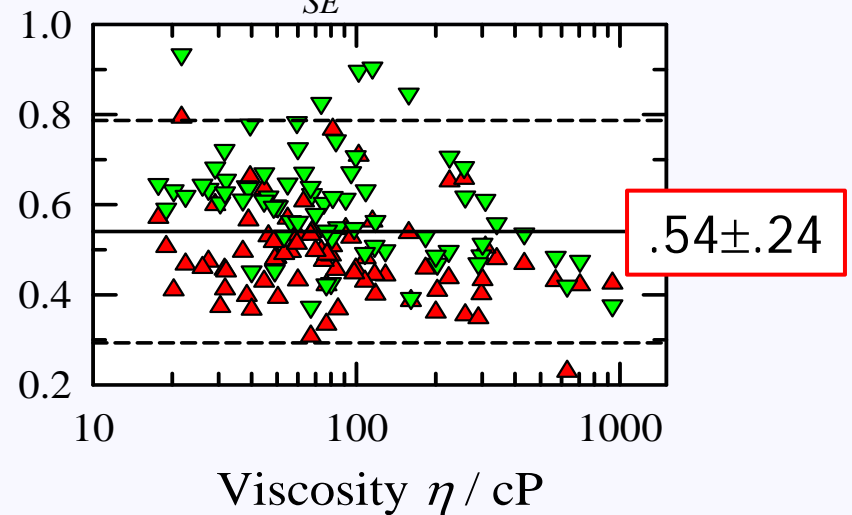
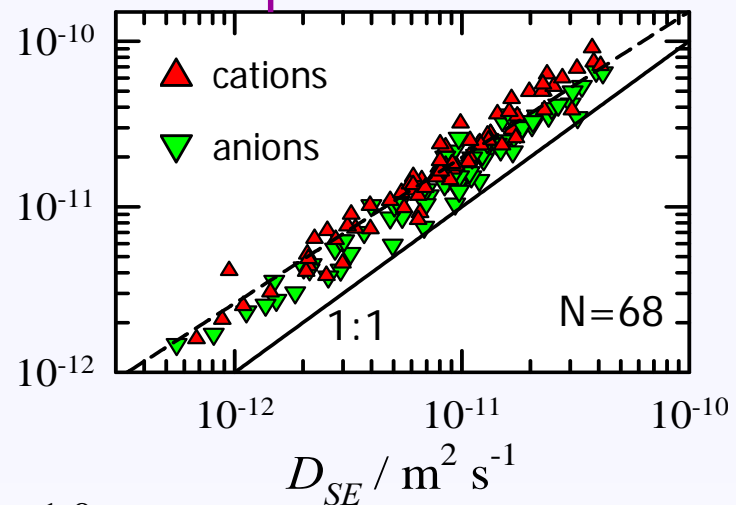
data from Y. Marcus,  
"The Properties of Solvents" (1998)

# Similar Accuracy in Ionic Liquids

## Conventional Solvents



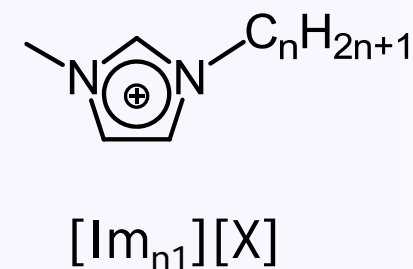
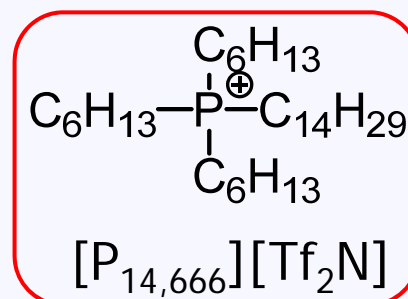
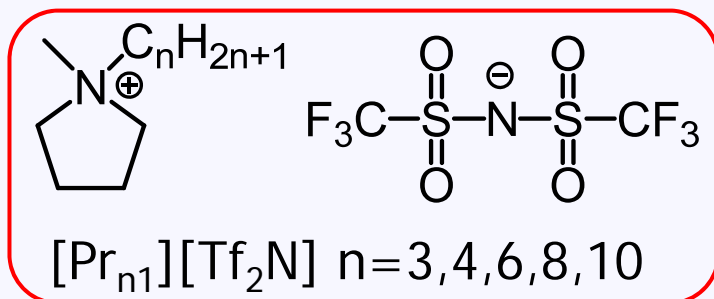
## Ionic Liquids



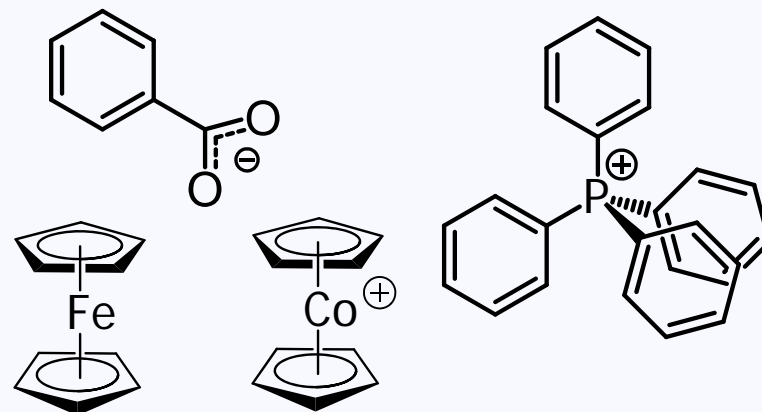
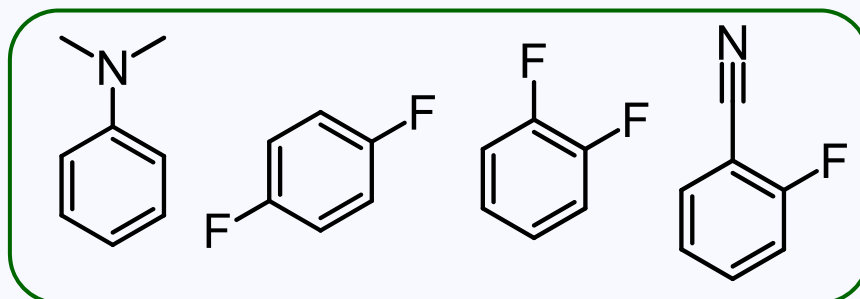
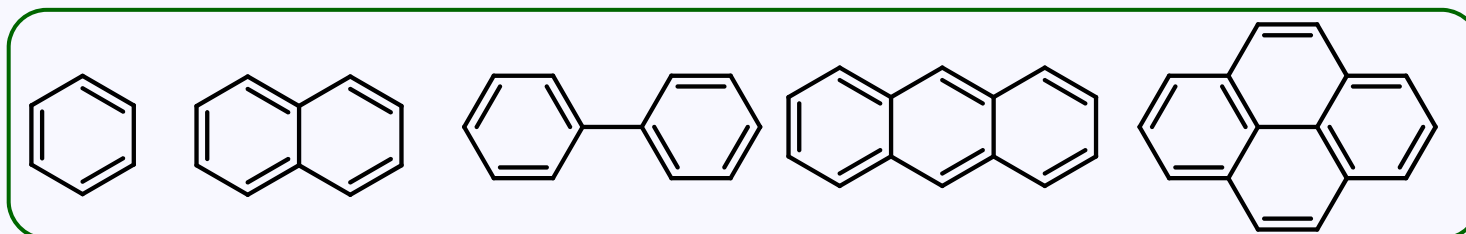
# Our Work: Solute Diffusion in ILs

- PFG-NMR measurements of solute D at near infinite dilution

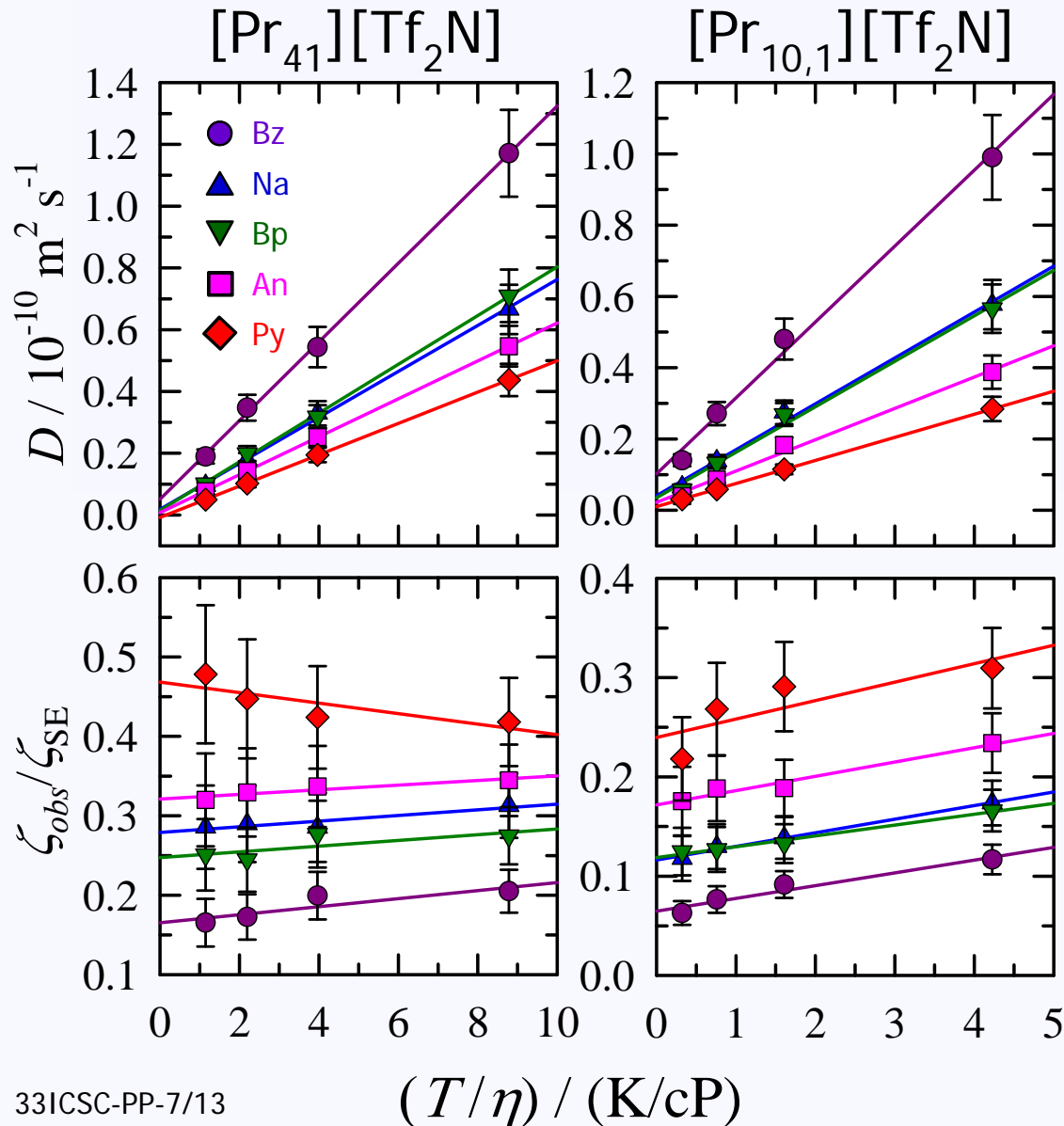
Ionic Liquids



Solutes



# Temperature Dependence

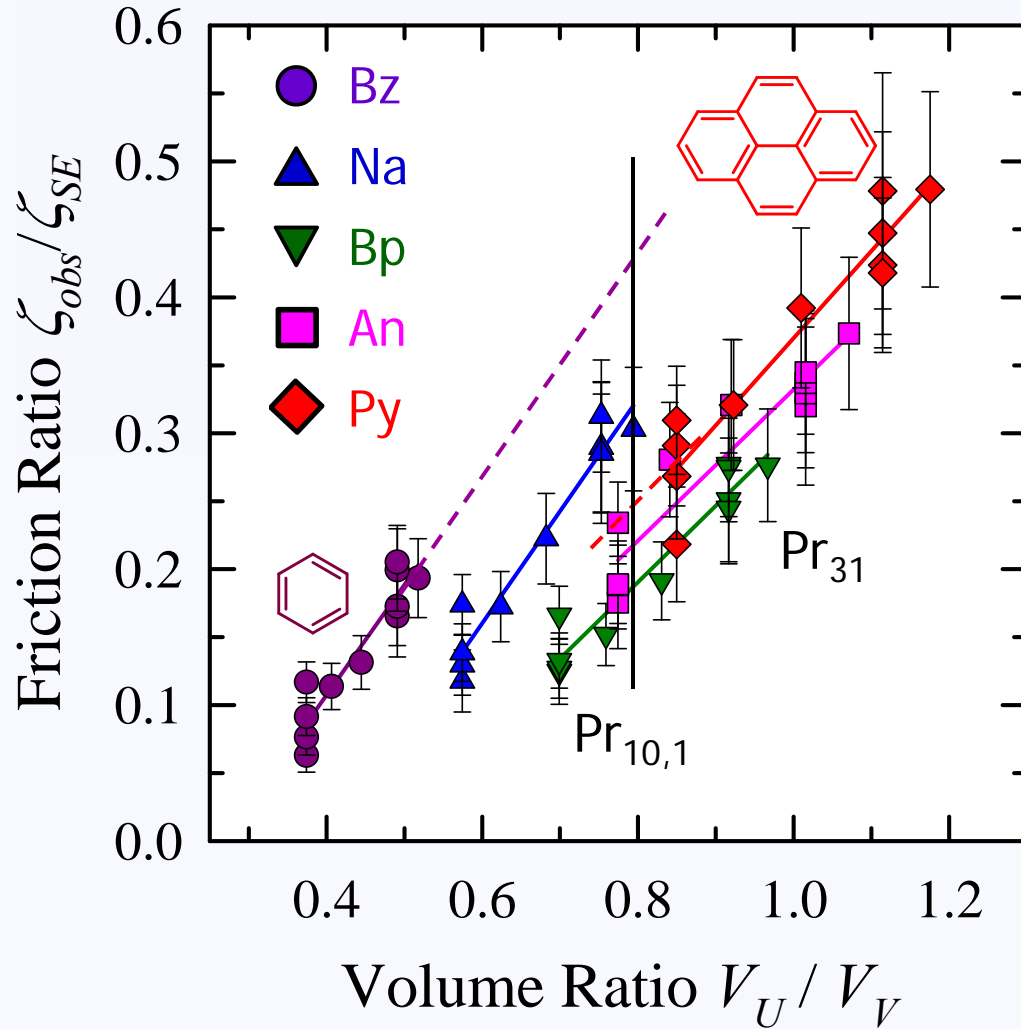


- for a single solute-solvent pair  $D$  is nearly  $\propto T/\eta$
- fit to  $\propto \eta^{-p}$  with  $p \sim 0.9$
- $\zeta \uparrow$  with solute  $\uparrow$  size but not as fast as  $R_U$
- $\zeta_{\text{obs}}/\zeta_{\text{SE}} \downarrow$  with  $\uparrow$  cation size



# Size Dependence

## Aromatics in [Prn<sub>1</sub>][Tf<sub>2</sub>N] Series

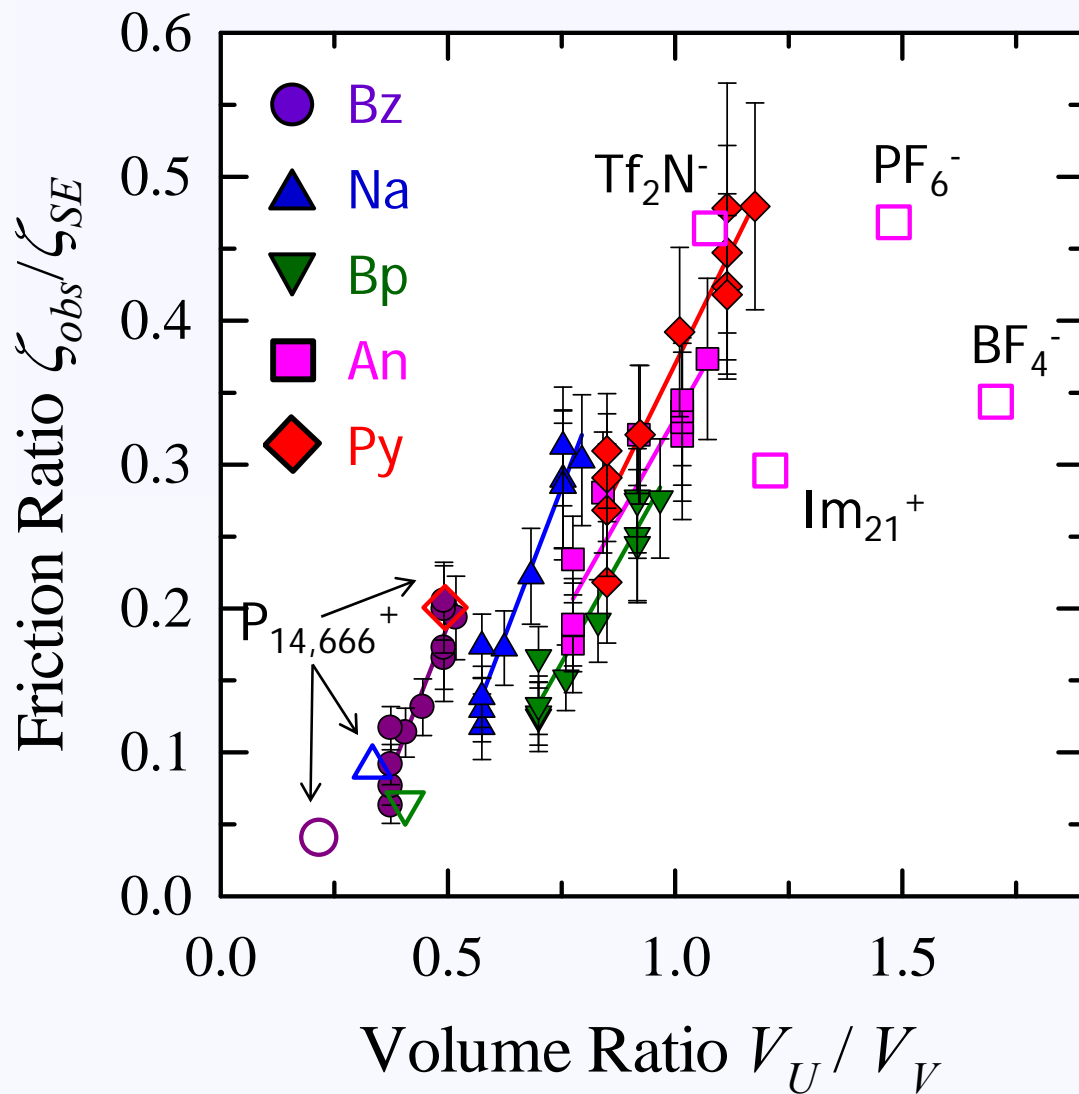


- for a single solute  $\zeta_{obs}/\zeta_{SE}$  ~ linear with solute/solvent volume ratio  $V_U/V_V$
- not a single correlation
- for fixed  $V_U/V_V$   $\zeta_{obs}/\zeta_{SE}$  possibly related to solute shape

	$\kappa$	
Bz	+1	oblate
Na	-.40	
Py	-.69	
An	-.91	
Bp	-.94	-1=prolate

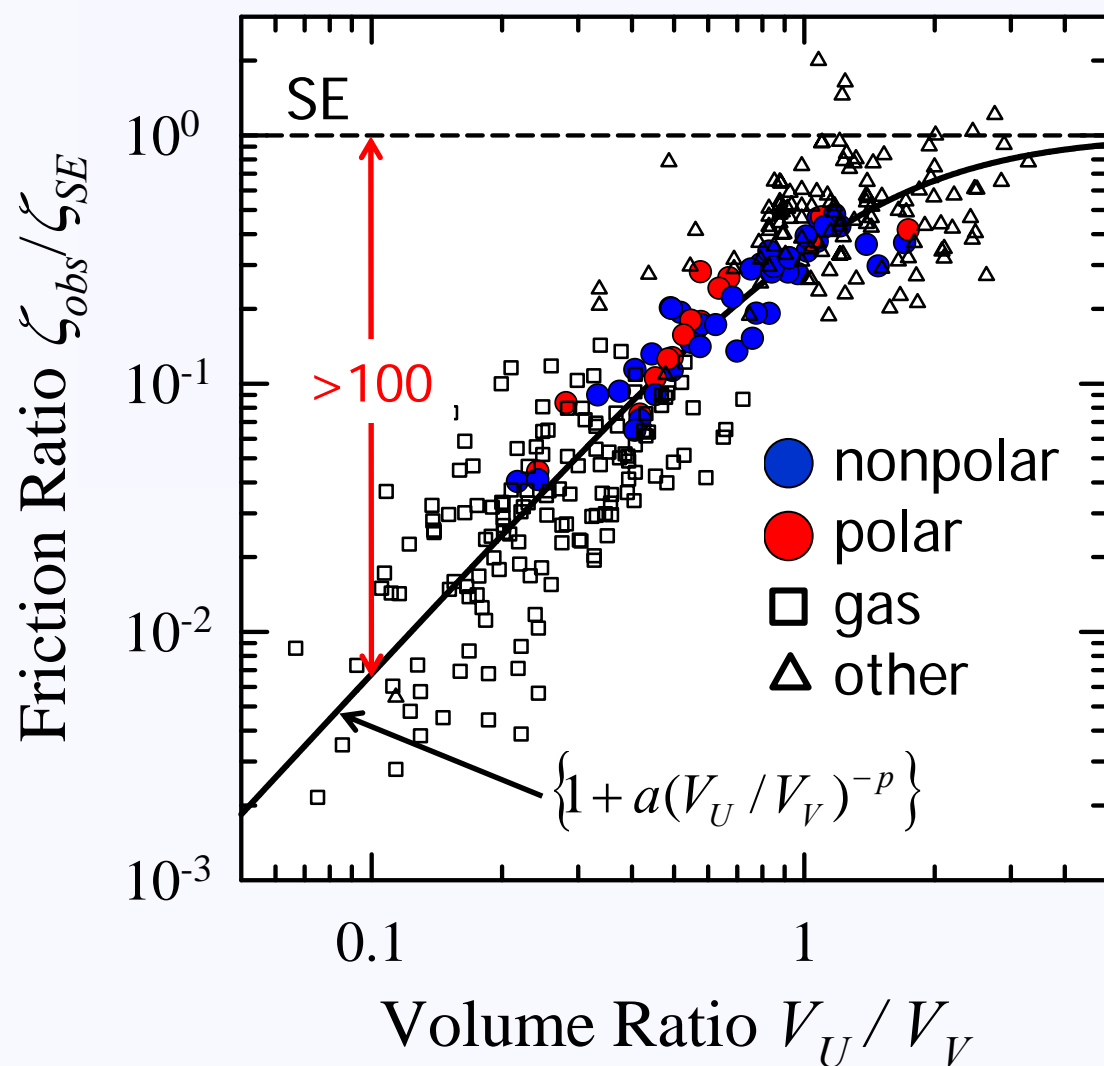
↑  $\zeta_{obs}/\zeta_{SE}$

# It's not that Simple...

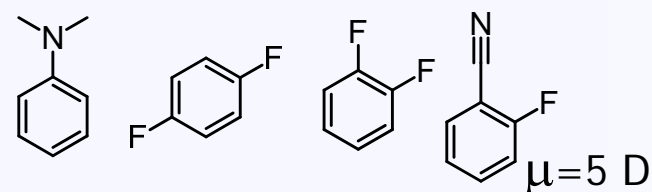


- in  $[P_{14,666}][Tf_2N]$  extends the same correlation
- $\zeta_{SE} > 50\zeta_{obs}$  for benzene in  $[P_{14,666}][Tf_2N]$
- anthracene in other ILs deviates

# Adding Polar Solutes & Literature Data



- polar solutes (this work)

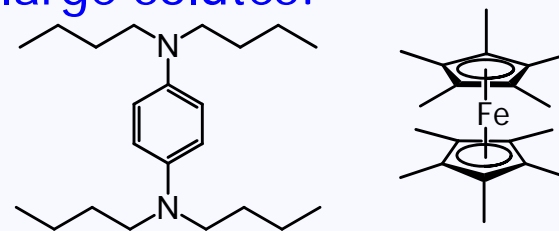


- literature data:  
323 solute/solvent pairs,  
37 solutes, 56 ILs

- small gaseous solutes:

$\text{CO}$ ,  $\text{CO}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_4\text{H}_{10}$ , ...

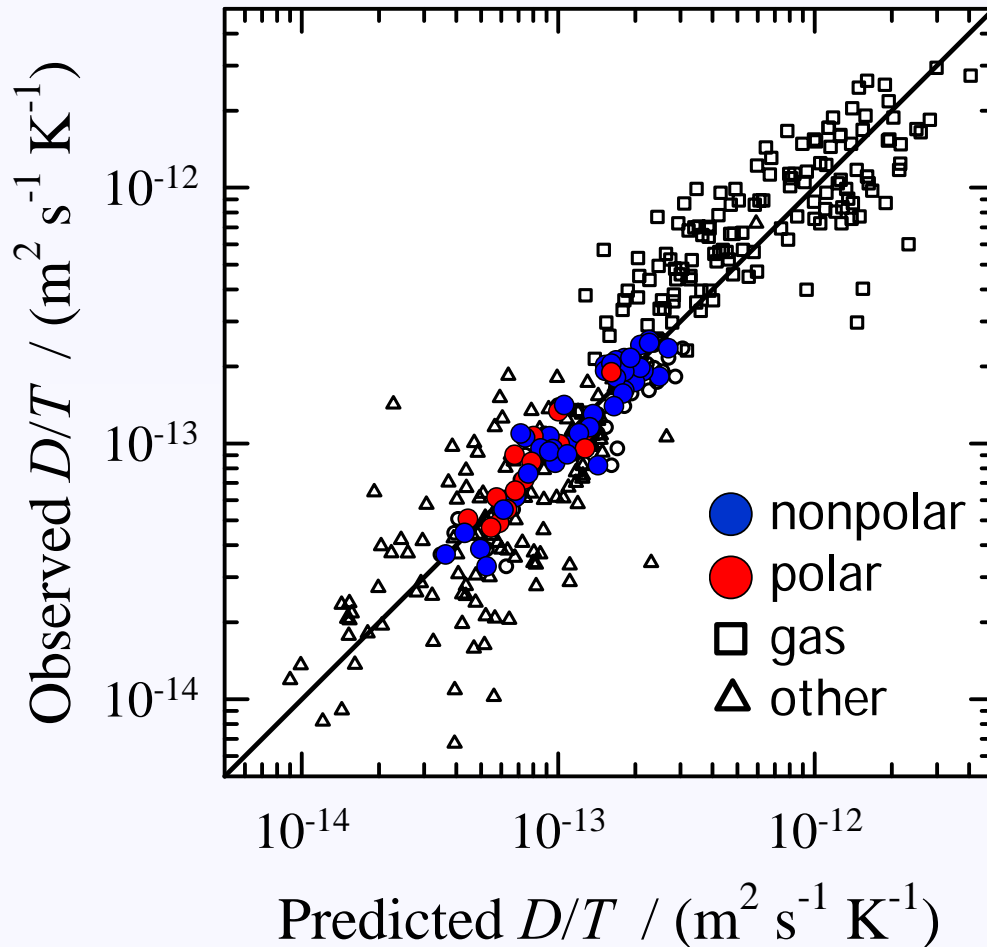
- large solutes:



lit. data from: Baltus, Scovazzo, Kimura,  
Hardacre, Compton,  
License, Halpiot, Lagroste, Hussey, ...

# No Accurate Correlations Found

## Neutral Solutes in ILs



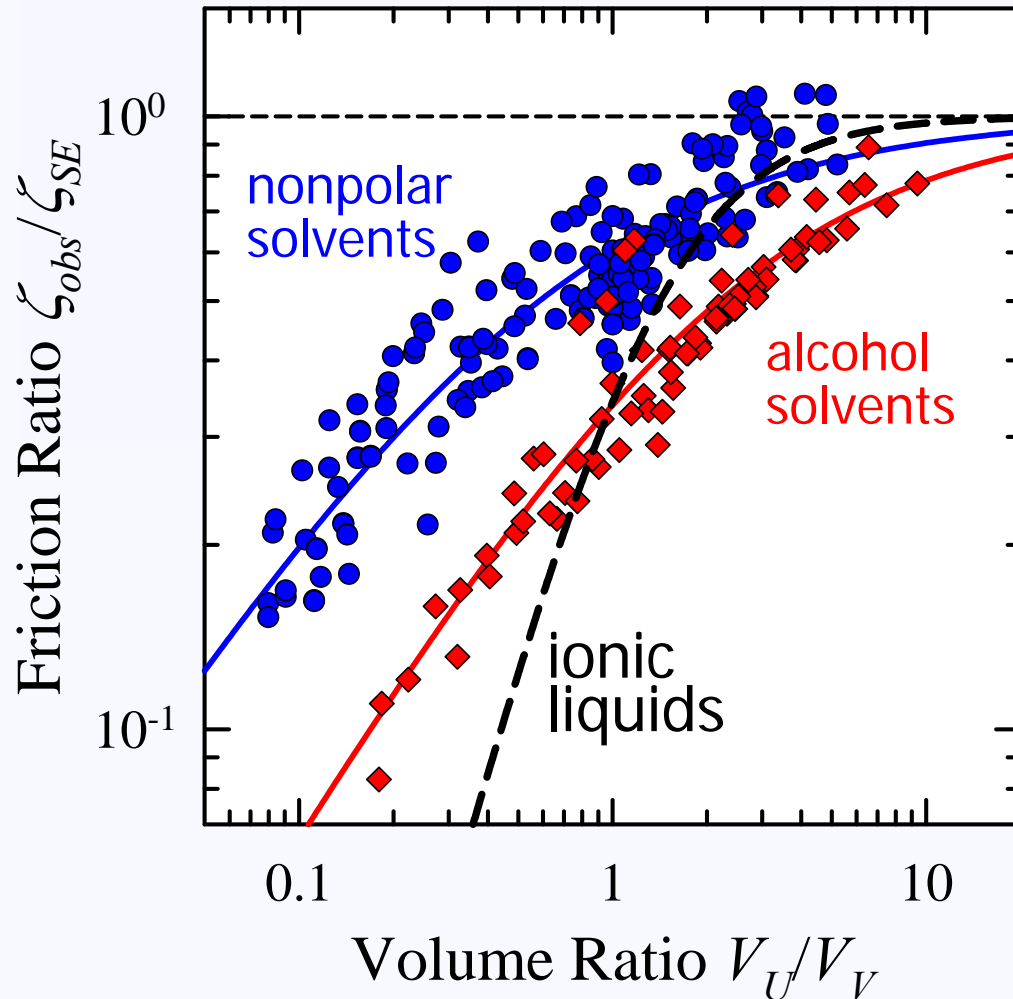
- tried to correlate  $\zeta_{\text{obs}}/\zeta_{\text{SE}}$  or  $D_{\text{obs}}$  to various solute and solvent properties
- best result (shown) was
$$\ln(D/T) = -23.14 - 1.77 \ln V_U + 0.84 \ln V_V - 0.52 \ln \eta$$

- standard error  $\pm 0.54 \leftrightarrow$   
~55% average error

➤ no more predictive than single variable correlation with  $V_U/V_V$

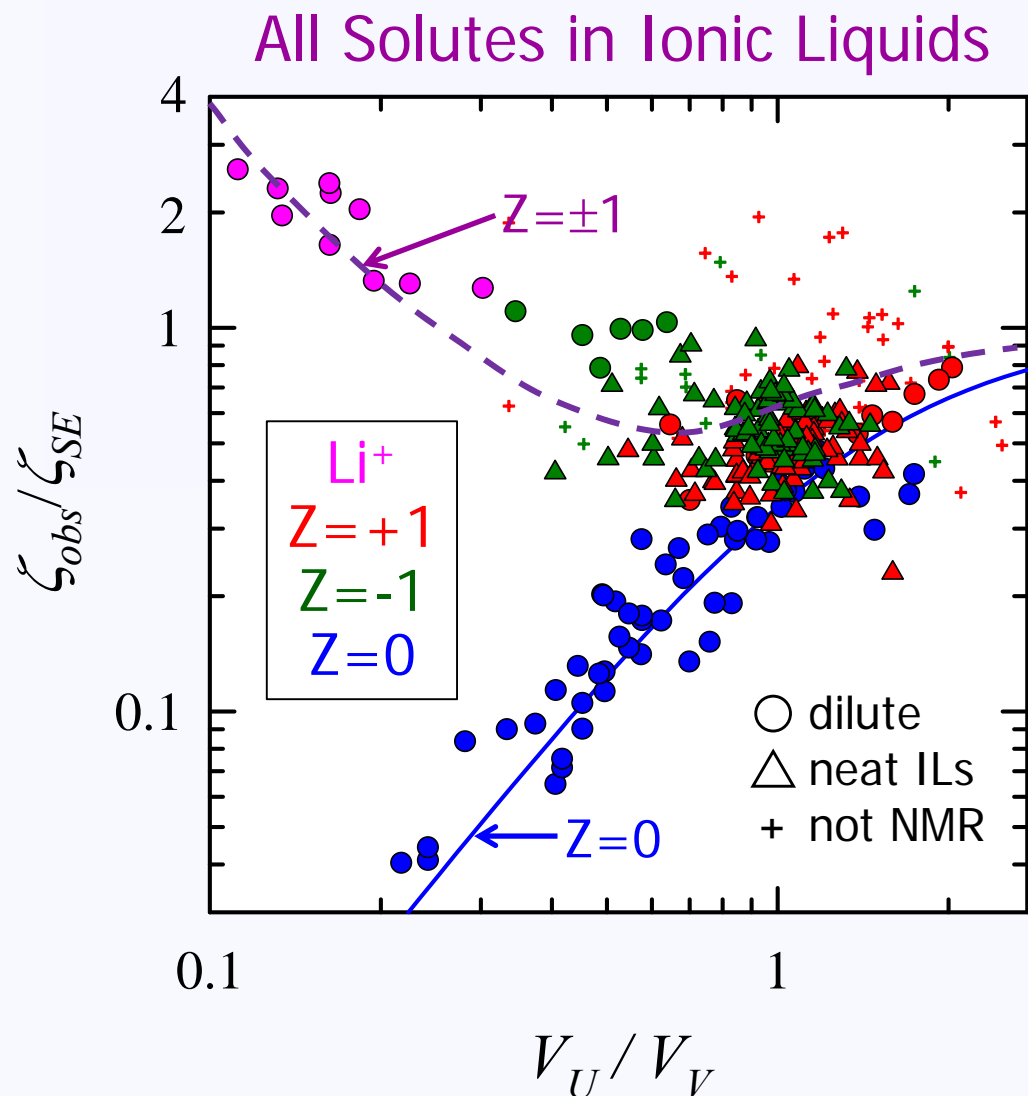
# Similar in Conventional Solvents

## Neutral Aprotic Solute Data



- $\zeta_{obs}/\zeta_{SE}$  is also primarily correlated to  $V_U/V_V$  in conventional solvents
- stronger V-V than U-V interactions lead to greater departure from SE predictions (smaller  $\zeta_{obs}/\zeta_{SE}$ )
- $V_U/V_V$  dependence much steeper in ILs

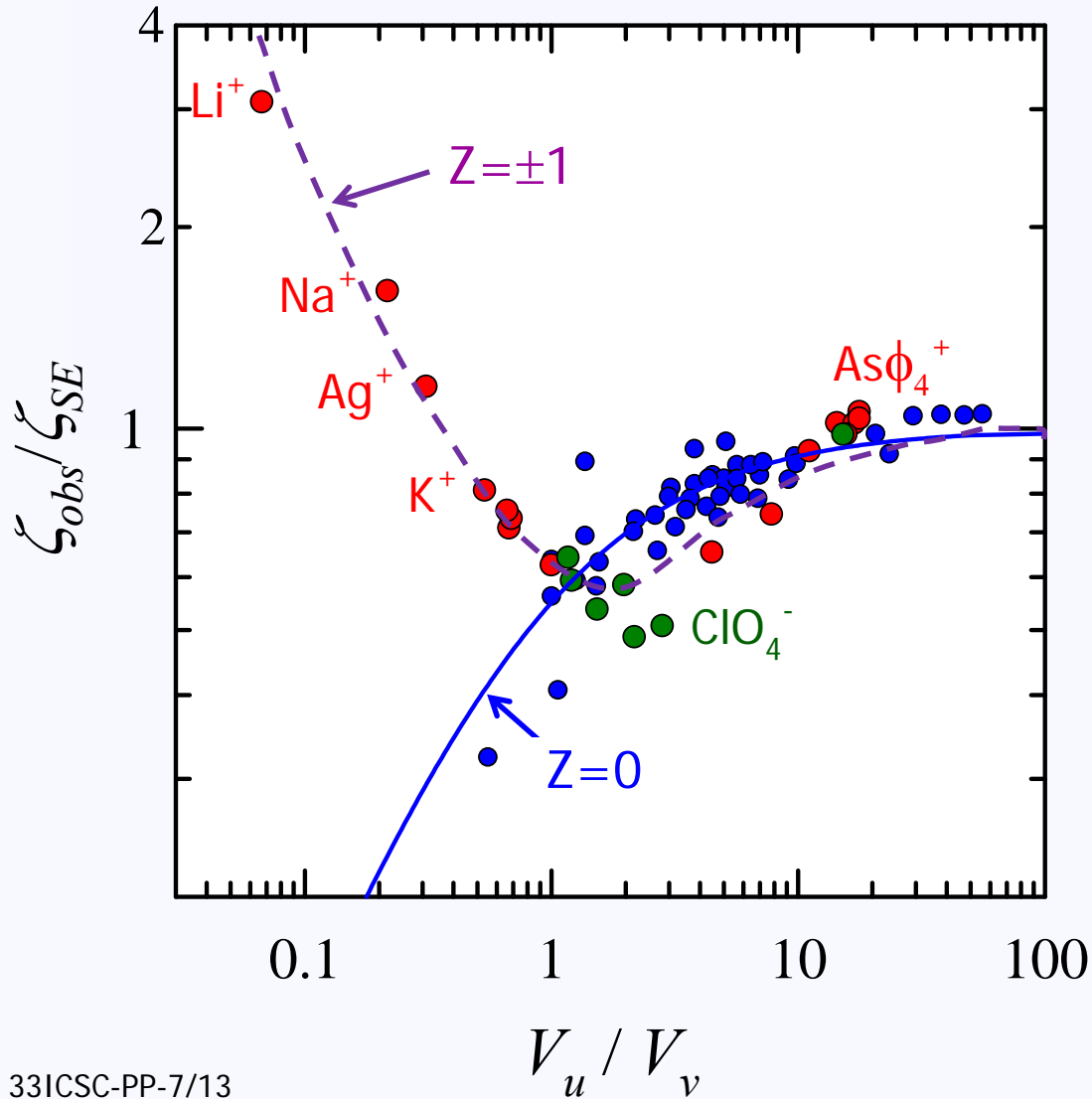
# Charged ( $Z=\pm 1$ ) Solutes in ILs



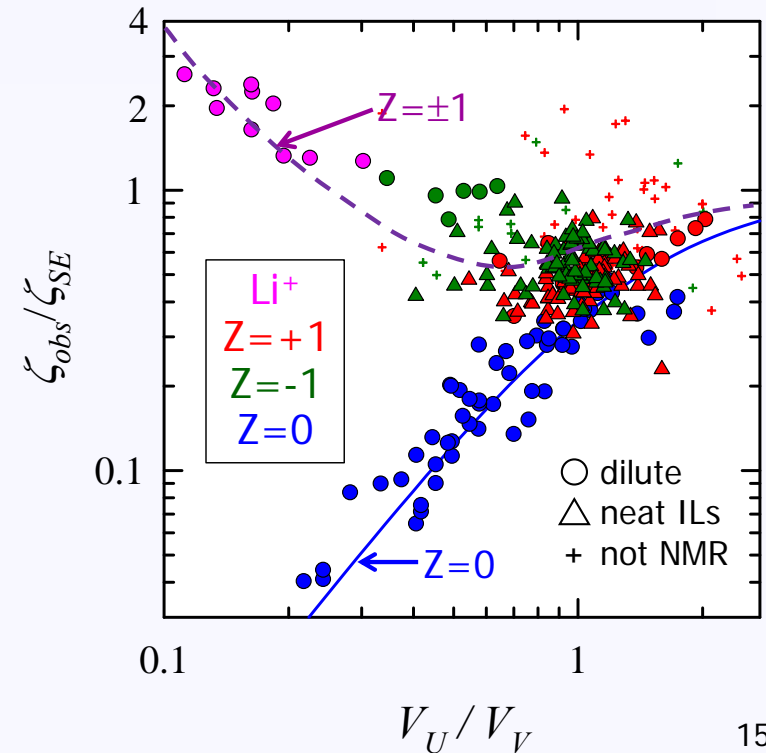
- monovalent ions show  $\zeta_{obs}/\zeta_{SE} \sim 1$  and are similar to neutrals for  $V_U/V_V \sim 1$
- for small  $V_U/V_V$   $\zeta_{obs}/\zeta_{SE}$  of charged solutes is 100× larger than that of neutrals and can exceed unity
- the “solventberg” limit well-documented for  $\text{Li}^+$  solute

# Analogous Behavior in Water

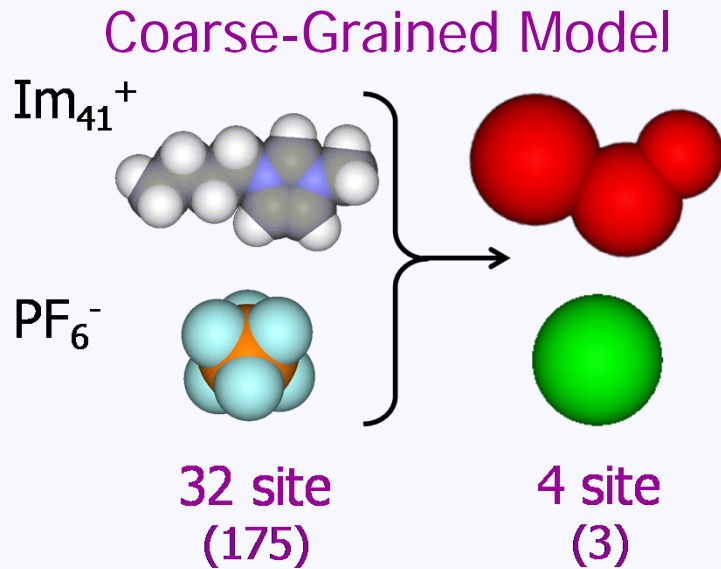
## Solute Diffusion in Water



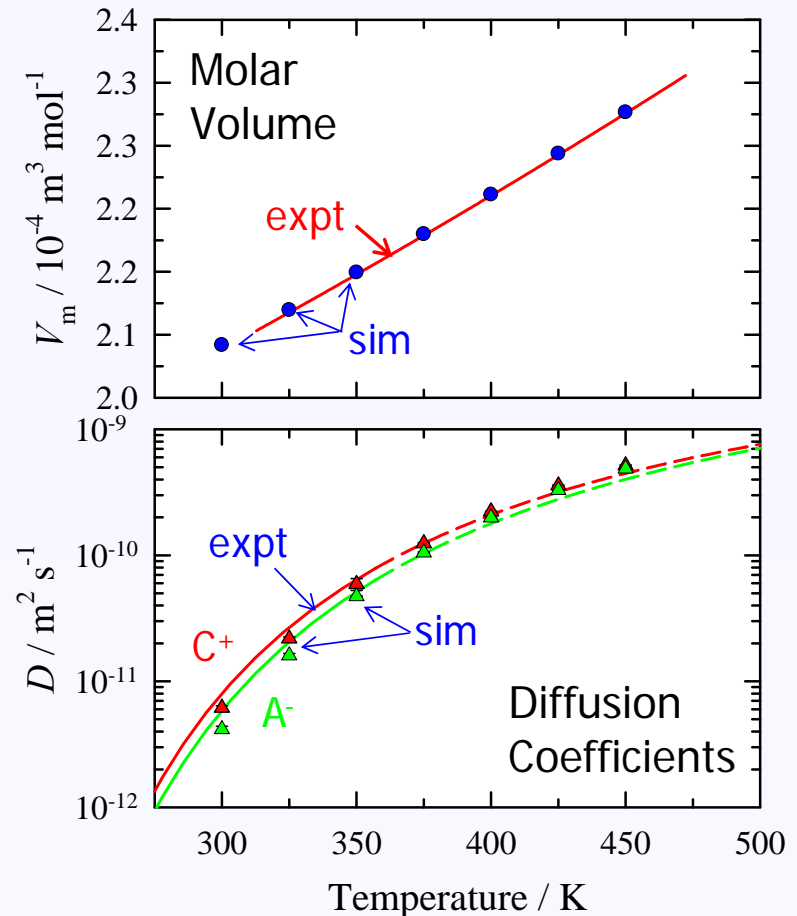
- quite similar differences are observed between neutral and monovalent solutes diffusing in water



# Insights from MD Simulations



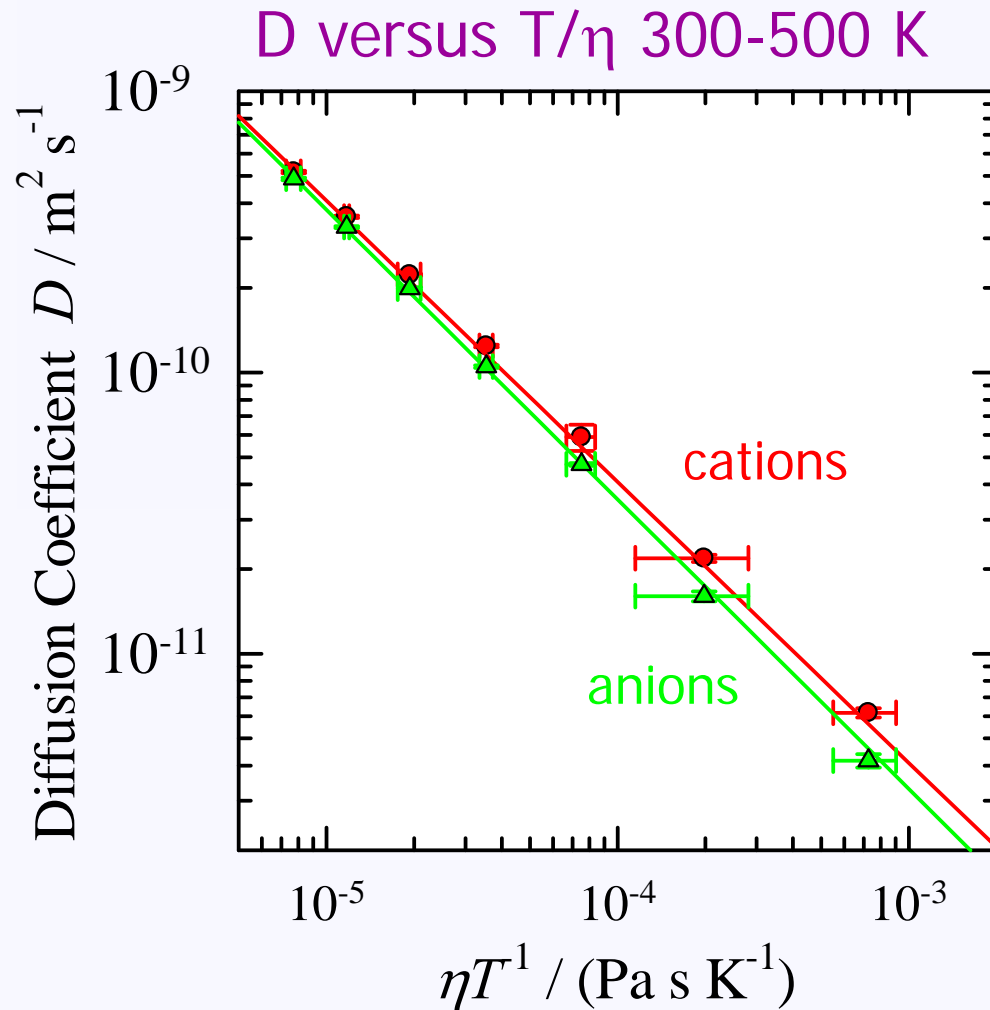
- LJ + q interactions
- group volumes & charges roughly matched to AA model
- cation geometry approximates average over  $\text{Im}_{41}^+$  conformers
- tuned to reproduce  $V_m$  &  $D_i$
- $|q| = 0.78$



- T-dep. viscosity & conductivity
- surface tension (Merlet et al.)



# Comparison to Hydrodynamics



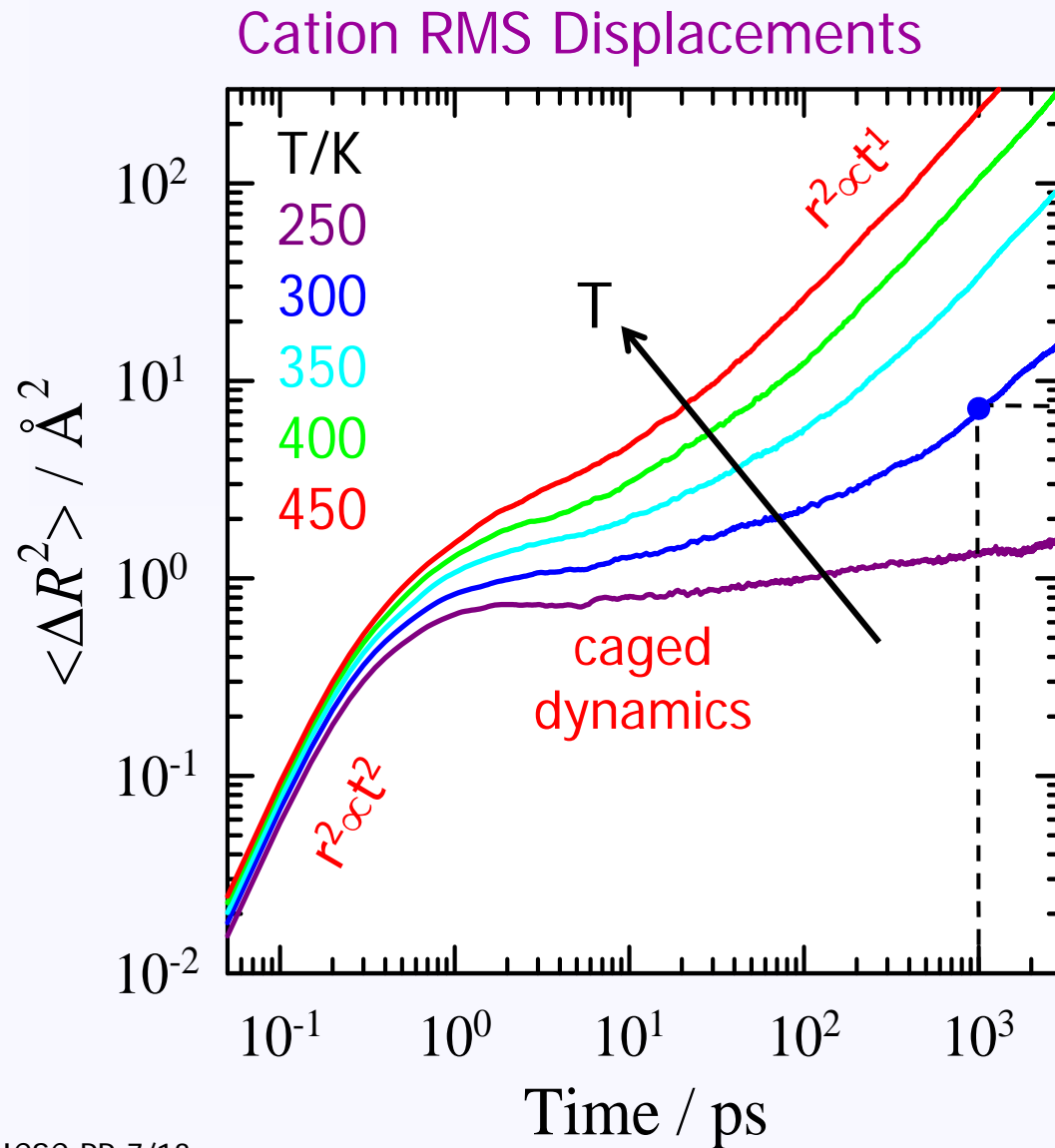
- for both cations and anions

$$\frac{D}{T} \propto \eta^{-p}$$

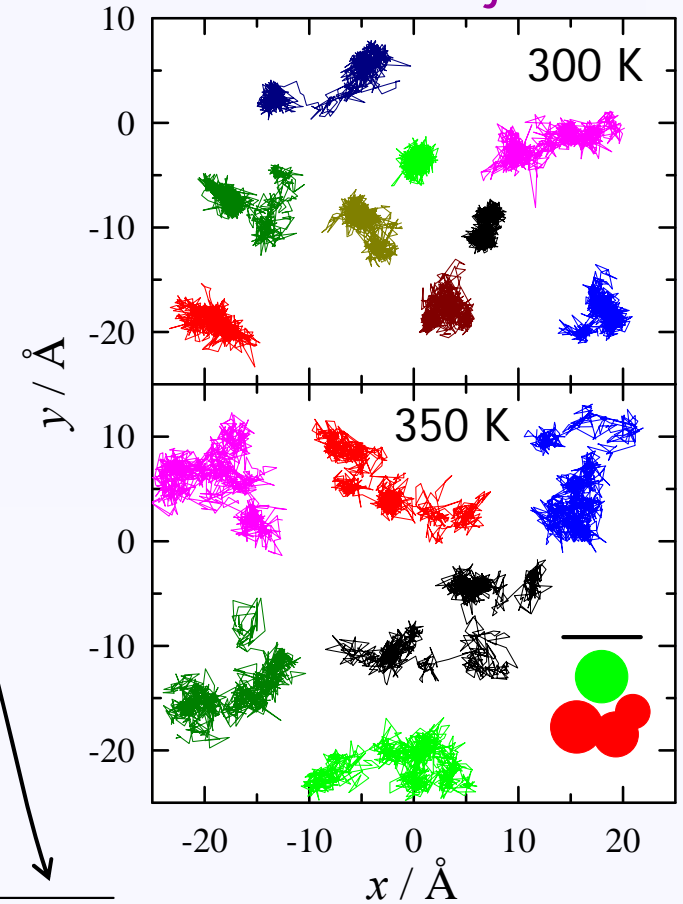
with  $p=1.0$

	$\zeta_{\text{obs}} / \zeta_{\text{SE}}$	$\zeta_{q=1} / \zeta_{q=0}$
cation	1.1	3.4
anion	1.0	2.9

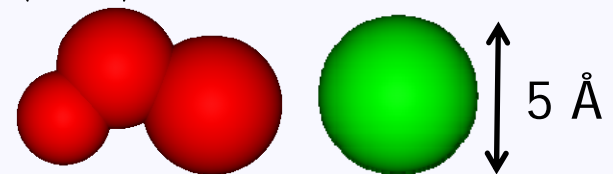
# Translational Caging



## 5 ns Cation Trajectories



$$\sqrt{\langle \Delta R^2 \rangle} = 2.5 \text{\AA}$$



## Summary & Conclusions

- ❑ the hydrodynamic Stokes-Einstein (SE) equation,  $D=k_B T/6\pi\eta R$ , provides good estimates for self-diffusion of molecules in dipolar liquids and ions in ionic liquids ( $\zeta_{\text{obs}}/\zeta_{\text{SE}} \sim 0.6 \pm 0.2$ ); in such systems the diffusing species has similar size and interactions with the “solvent” species
- ❑ neutral solutes diffusing in ionic liquids can show quite large departures from SE predictions ( $\zeta_{\text{obs}}/\zeta_{\text{SE}} < .01$ ); the primary variable controlling  $\zeta_{\text{obs}}/\zeta_{\text{SE}}$  here is the relative size of solute and solvent species,  $V_U/V_V$
- ❑ charged ( $Z=\pm 1$ ) solutes do not depart from SE predictions at low  $V_U/V_V$  like  $Z=0$  solutes; for sufficiently small ions  $\zeta_{\text{obs}}/\zeta_{\text{SE}} > 1$  due to “solventberg” formation
- ❑ parallel behavior is observed for  $Z=0, \pm 1$  solute diffusion in ionic liquids and in conventional solvents
- ❑ simple and predictive models not available for either solvent class

# Acknowledgements



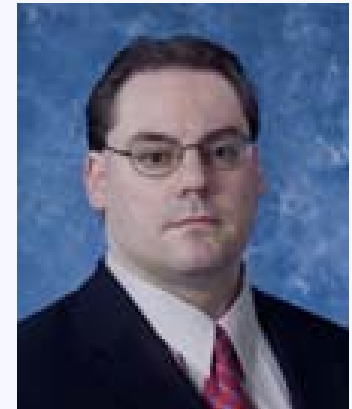
Anne Kaintz



Chris Rumble



Durba Roy



Gary Baker  
U. Missouri

