Solvation & Solute Dynamics in Ionic Liquids
Mark Maroncelli, Penn State

1. Translation & Rotation
2. Solvation Dynamics
3. Reaction Kinetics & Heterogeneity
4. Effect of Nanostructure?

![Diagram of solvation dynamics in ionic liquids with molecular structures and graphs showing friction ratio changes with volume ratio and frequency plots.]
(Room Temperature) Ionic Liquids

Lowering $T_f$:

- charge delocalization
- size mismatch
- low symmetry
- conformational disorder

Cation Families:
- imidazolium $\text{Im}_{n1}^+$
- pyrrolidinium $\text{Pr}_{n1}^+$
- phosphonium $\text{P}_{1234}^+$
- ammonium $\text{N}_{1234}^+$

Common Anions:
- $\text{BF}_4^-$, $\text{PF}_6^-$, $\text{CF}_3\text{SO}_3^-$
- $\text{DCA}^-$
- $\text{Tf}_2\text{N}^-$

Typical Properties:
- Low Volatility
- High Thermal Stability
- Intrinsically Conductive
- Wide Electrochemical Window
- Solubility/Phase Control

Our Interests:
- Distinctive solvation/chemistry?
- New lessons to be learned?
1. The Simplest Dynamics: Solute Translation & Rotation

Anne Kaintz
Juan Carlos Araque
Chris Rumble
Ion Self-Diffusion Coefficients & Friction

Stokes-Einstein (Sutherland)

Hydrodynamic Prediction:

\[ D_{SE} = \frac{k_B T}{6\pi \eta R} \] \( \zeta_{SE} = \) friction on sphere of radius \( R \)

Friction Ratio:

\[ \frac{\zeta_{obs}}{\zeta_{SE}} = \frac{D_{SE}}{D_{obs}} \] measure of the coupling between the diffusor and solvent bath

- SE predictions are reasonably accurate for estimating ion self diffusion in ILs
- nearly identical situation exists in conventional solvents

Ion D in 32 ILs (298 K)

data from Watanabe, Matsumoto, Martinelli, ...
Diffusion of Aromatic Hydrocarbons in ILs

PFG-NMR measurements of simple aromatic hydrocarbons in a homologous series of ILs

\[ \text{[Pr}_{n1}\text{][Tf}_2\text{N]} ~ n=3, 4, 6, 8, 10 \]

- Departure from SE predictions increases with decreasing solute and increasing solvent size
- Shape is also a factor: Bz > Na > Py > An > Bp (oblate ~ prolate)

Neutral Solutes Diffusing in ILs

- **nonpolar solutes**
  
  - ![Nonpolar Solutes](image)

- **polar solutes**
  
  - ![Polar Solutes](image)
  
  - literature data:
    - 323 solute/solvent pairs, 37 solutes, 56 ILs
  
  - small gaseous solutes:
    - CO, CO₂, C₂H₄, C₄H₁₀, ...

- **large solutes**
  
  - ![Large Solutes](image)

Friction Ratio \( \zeta_{\text{obs}} / \zeta_{\text{SE}} \)

- Friction Ratio vs. Volume Ratio \( V_U / V_V \)
  
  - \( \{1 + a(V_U / V_V)^{-p}\} \)
  
  - marked departures from SE predictions
  
  - primary determinant is U/V size ratio

lit. data from: Noble, Baltus, Scovazzo, Kimura, Hardacre, Compton, License, Halpiot, Lagroste, Hussey, ...
Charged (±1e) Solute Diffusion in ILs

- \( \zeta_{\text{obs}}/\zeta_{\text{SE}} \approx 1 \) for ions (helpful for \( \Lambda \eta \) interpretations)
- Large difference in \( \zeta_{\text{obs}}/\zeta_{\text{SE}} \) for small ions compared to neutral solutes
- The “solventberg” limit well-documented for Li⁺
  - Analogous but weaker trends also seen in conventional solvents
  - Mismatch between solute and solvent in size or interactions responsible for marked departures from SE predictions
Transport Mechanisms from MD

\[ \text{CH}_4 \quad \text{NH}_4^+ \]

\[[\text{Pr}_{41}][\text{Tf}_2\text{N}]\]

\[ \text{CH}_4 \quad 600\text{ps trajectory} \quad \text{NH}_4^+ \quad 600\text{ps trajectory} \]

Friction Ratio $\zeta_{\text{obs}}/\zeta_{\text{SE}}$

\[ \text{Volume Ratio } V_u/V_v \]

C&DiCE 2015
Trajectory-Resolved Structure

- jumps are associated with low density (and low polarity = “soft”) and caging with high density (and polarity = “stiff”) regions of the liquid
- CH$_4$ explores both regions more effectively than NH$_4^+$
CH$_4$ exchanges with nonpolar tails -- Coulomb lattice unperturbed

NH$_4^+$ exchanges anions in its 1$^{st}$ shell -- Coulomb lattice must rearrange
Solute & Ion Rotation

Fluorescence Measurements

Rotation time $<\tau_{rot}> / s$

$\eta/T / (\text{cP K}^{-1})$

$\tau_{rot}^{(L)} = \frac{6\eta V_{hyd}}{L(L+1)k_B T}$

$V_{vdW}/V_{hyd}$ from Dielectric Measurements

<table>
<thead>
<tr>
<th>Cat/An</th>
<th>DCA$^{-}$</th>
<th>BF$_4^{-}$</th>
<th>PF$_6^{-}$</th>
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</thead>
<tbody>
<tr>
<td>Im$_{21}^{+}$</td>
<td>220</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>Im$_{41}^{+}$</td>
<td>83</td>
<td>310</td>
<td>110</td>
</tr>
</tbody>
</table>

Recent NMR & Fluorescence Data

- $V_{vdW}/V_{hyd}$
  - 65
  - 22
  - 25

- $V_{vdW}/V_{hyd}$
  - 4
  - 2

- Rotation of large solutes not unusual
- Im$^{+}$ cations and other small molecules may show more interesting dynamics

Jin et al., JPCB 111, 7291 (2007)
2. More Complicated Dynamics: The Solvation Response

Min Liang

Xin-Xing Zhang
The Spectral / Solvation Response

- **S0** and **S1**
- Solvation Coordinate
- Energy
- Time

- **Dynamic Stokes Shift**
- of Emission Spectra
- \[ S_v(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)} \]

- basic property of polar liquids
- determines friction on charge motion

- \( \nu(t) \) peak frequency

- \( \nu(0) \)
- \( \nu(\infty) \)
- spectral or solvation response function

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C&DiCE 2015
S(t) in Ionic Liquids

- upconversion (FLUPS) & time-correlated single photon counting (TCSPC) experiments combined to capture the full response over 80 fs – 40 ns

- ~100-fold slower than dipolar solvents (η also 100-fold larger)
- strongly bimodal decay
- broadly distributed in time
Dissecting the Solvent Response

\[ S_v(t) = f_G \exp\left\{ -\frac{1}{2} \omega_G^2 t^2 \right\} + (1 - f_G) \exp\left\{ -(t / \tau)^\beta \right\} \]

- mechanism is primarily solvent translation
- #1: 30-40% inertial motions
  \( \Rightarrow \) displacements of 1st shell ions
- #2: the rest is overdamped & highly coupled ion motions
  \( \Rightarrow \) subtle displacements of ions over <1\( \sigma \)

Solvation & Dielectric Relaxation

- dielectric continuum predictions are qualitatively correct in ILs
- but too fast by factors of 3-4
- similar results in IL + dipolar solvent mixtures

Some S(t) Comparisons

Why Continuum Predictions are too Fast

- molecular solvation entails charge redistribution in response to non-uniform fields; basic dynamics captured in \( \Phi_{qq}(k,t) \) of the neat solvent

\[
\Phi_{qq}(k,t) \propto \left< \rho_q(\vec{k})\rho_q(-\vec{k},t) \right>
\]

\( \varepsilon(\omega) \) captures only \( k=0 \) (\( \lambda=\infty \)) dynamics

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solvation involves entire spectrum \( k=0-\infty \)

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solvent response is slower at \( k>0 \) thus dielectric predictions are too fast

Solvation & Conductivity

The D.C. model predicts integral solvation times \( <\tau_{\text{solv}} > \) to be inversely proportional to conductivity \( \sigma_0 \)

\[
<\tau_{\text{solv}} > \equiv \int_0^\infty S(t)dt = \frac{\varepsilon_\infty + \frac{1}{2} \varepsilon_c}{4\pi\sigma_0}
\]

\( \sim \text{const.} \)

\( \geq \tau_{\text{solv}} \) as predicted, \( <\tau_{\text{solv}} > \) and \( \sigma_0 \) are strongly correlated

\( \geq \tau_{\text{solv}} \) prediction is an average of 3-fold too fast

\( \geq \tau_{\text{solv}} \) (\( \sigma \) is easy)

The \( \varepsilon(\omega) \leftrightarrow \sigma_0 \) Connection:

\[
\hat{\varepsilon}(\omega) = \hat{\varepsilon}_{\text{corr}}(\omega) + i \frac{4\pi\sigma_0}{\omega}
\]

expts. divergence removed

conductivity & permittivity reflect identical dynamics

\[
\hat{\sigma}(\omega) = i \omega \frac{\hat{\varepsilon}(\omega)}{4\pi} \left\langle \tilde{M} \cdot \tilde{M}(t) \right\rangle
\]

\[
\left\langle \tilde{J} \cdot \tilde{J}(t) \right\rangle
\]

C153 in 34 Ionic Liquids

\( \text{Resistivity } \sigma^{-1} / \Omega \text{ m} \)

Zhang et al., JPC Lett. 4, 1205 (2013).
3. Even More Complicated: Reaction Kinetics

Min Liang

Lillian Li

Minako Kondo
1. Intramolecular Charge Transfer

Biphenyl Acridinium (BPAC\(^+\))

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<th>LE</th>
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TR Emission in [N\(_{3111}\)][Tf\(_2\)N]

Reaction and Solvation Times

- [N\(_{3111}\)][Tf\(_2\)N]
- [Im\(_{21}\)][Tf\(_2\)N]
- [Im\(_{41}\)][PF\(_6\)]
- [N\(_{3111}\)][Tf\(_2\)N]
- [P\(_{14,666}\)][Tf\(_2\)N]

- reaction in ILs continues trend established by dipolar solvents

2. Isomerization

An empirical correlation:

\[ \ln \tau = a + b \ln(\frac{\eta}{T}) + cf(\varepsilon) \]

- Observed time, \( \tau_{obs} / \text{ps} \)
- Calculated time, \( \tau_{clc} / \text{ps} \)
- Relative intensity

Rates in ILs correlate with those in dipolar solvents.

REE & Kinetic Heterogeneity

- heterogeneous kinetics should be the norm for ps processes given the slow solvation / structural relaxation times of ILs
Other Examples

**TICT Reaction of DMABN**

![TICT Reaction of DMABN](image1)

**ESPT in DEAHF**

![ESPT in DEAHF](image2)


Possible Interpretations

Distinct Local Dynamics

- reaction senses "dynamic heterogeneity" - the fact that local packing effects cause different regions to have different fluidities

Distinct Local Energies

- different solute-solvent interaction energies affect PES for reaction

Nanoscopic Domains

- solutes are distributed among nanoscopic domains of different polarity and/or fluidity


4. Aside: Where’s the Effect of Nanoscopic Structure?

Jacob Schesser
Solvation in $[\text{P}_{14,666}][\text{X}]$ ILs

Further Recent Attempts

- anthracene & bianthryl in [Im$_{n1}$][Tf$_2$N] (n=2-12), & [P$_{14,666}$][Tf$_2$N]+n-hexane

**Anthracene Absorption Spectra**

**Anthracene Solvatochromic Shifts**

in 74 organic solvents:

$$\nu - \nu_{\text{gas}} = \alpha \left( \frac{n^2 - 1}{n^2 + 2} \right) + \beta \left( \frac{\varepsilon - 1}{\varepsilon + 2} \right) - \left( \frac{n^2 - 1}{n^2 + 2} \right)$$

$$\alpha = 4100 \text{ cm}^{-1}, \beta = 170 \text{ cm}^{-1}$$
Bianthryl ET Reaction Times

TR Emission Spectra

ET Reaction Times

M. Liang, preliminary results

[P14,666][Tf2N] + n-C6 xC6 = 0.8

green=n-C6
red=P14,666+
blue=Tf2N-

ILs + mixtures
dipolar solvents
Summary

Solute Translation & Rotation:
- $D \sim T/\eta$ as expected by hydrodynamic models, but Stokes-Einstein predictions can be wrong by factors of 100 or more (at room $T$)
- diffusion of small neutral versus charged solutes is markedly different
- rotations of small solutes can be far from hydrodynamic expectations

Solvation Dynamics:
- solvation is highly bimodal: $\sim 1/3$ sub-ps and $2/3$ relax over 1 ps- 10 ns
- unlike dipolar solvents, translational solvent motions dominate
- $S(t)$ and $\varepsilon(\omega)$ reflect the same underlying molecular dynamics but dielectric continuum predictions too fast by a factor >4
- solvation closely related to conductivity ($<\tau_{solv}> \propto 1/\sigma_0$)

Fast Reaction Kinetics:
- slow solvation/structural relaxation in ILs leads to heterogeneous reaction kinetics for fast reactions ($\tau < 1$ ns)
- origins of heterogeneity unclear (especially relevance of nanostructure)
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