Znamenskiy V.S., Kobrak M.N.  
Simulation of the polarization response of room-temperature ionic liquids  
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What are Room-Temperature Ionic Liquids?

- Salts that are molten at room-temperature
- Recent interest spurred by the discovery of RTILs that are stable under ambient conditions

**Common Cations:**

\[
\begin{align*}
&\begin{array}{c}
R_1 \\
N^+ \\
R_4 \\
N \\
R_3 \\
R_2
\end{array} \\
&\begin{array}{c}
R_1 \\
N \\
R_2
\end{array}
\]

**Common Anions:**

\[
\begin{align*}
&PF_6^- \\
&BF_4^- \\
&Cl^- \\
&NO_3^-
\end{align*}
\]
Properties of RTILs

**Physical Properties:**
- Nonvolatile
- Nonflammable
- Nontoxic(?)
- Wide Liquidus Temperature Range

\[ \text{Good properties for synthesis and separations} \]

- Conductive
- Wide Electrochemical Window

\[ \text{Good properties for electrochemistry} \]

**Solvation Properties:**
- RTILs behave as moderately polar organic solvents
Applications of RTILs

**Synthesis:**
- “Classic” organic chemistry
  - Diels-Alder, Heck, Suzuki, *etc.*
- Novel reactions
  - (*e.g.* Synthesis of an extended coordination network, Jin *et al.* Chem. Comm. 2872 (2002))

**Separations and Analysis:**
- Liquid-liquid extractions
  - (simple, crown-ether, solvent-optimized)
- MALDI matrix for mass spectrometry
- Continuous loop bioreactor (membrane)

**Electrochemistry:**
- Electroplating
- Voltaic cells
Structural Features of RTILs

- Most known species monovalent
- Cation/anion sizes mismatched
- Charge asymmetrically distributed in cation
- Both ions highly polarizable

1-butyl-3-methylimidazolium hexafluorophosphate (BMIM[PF₆])
Polarity of molecular solvents is connected to molecular structure by the dipole moment.
Polarity of ionic solvents is not understood.

### Match Game
Identify which solute is most soluble in each solvent

<table>
<thead>
<tr>
<th>Solute</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>Water</td>
</tr>
<tr>
<td>Phenol</td>
<td>1-propanol</td>
</tr>
<tr>
<td>Napthalene</td>
<td>Benzene</td>
</tr>
<tr>
<td></td>
<td>BMIM[Pf$_6$]</td>
</tr>
</tbody>
</table>
**Mechanism of Solvation**

**Molecular Liquids:**
- **Specific interactions:** Hydrogen-bonding
- **Nonspecific interactions:** Electrostatic effects

*What can we say about RTILs?*
The Chemical Environment of Fused Salts

- Most models based on a "solid lattice with holes" model
  - Temkin model
  - Quasi-lattice model
  - Crystallite Model
  - Hole Model
  - Liquid Free-volume Model
  - Significant structure Model
- Experimental NMR and optical measurements support this view

Spontaneous Ionization in a Metal-Fused Salt Solution
Stillinger et al. (JCP 32 1837 (1960)): Ion in a fused salt is surrounded by alternating layers of positive and negative charge

Cation-cation and cation-anion radial distribution functions for a model fused salt

Characterizing the Polarity of RTILs

- Theoretical definition of polarity: None
- Empirical scales for polarity:
  - Dielectric constant
  - Partitioning between bilayers
  - Solvatochromism of probe molecules
Partitioning of Solute Species

- Simple solubility experiments
- Reverse-phase chromatography

Comparison of partition coefficients for organic compounds in biphasic BMIM[PF$_6$]/H$_2$O and octan-1-ol/H$_2$O systems (from Huddleston et al. Chem. Comm. 1765 (1998))
Solvatochromism

- Based on the difference in dipole moment between chromophore electronic states
- Polarity scales and linear free energy relationships built on specific molecules
Solvent Polarity from Simulation

- Need to connect polarity to ionic behavior
- Must simulate an empirical measure of polarity

Simulate the solvatochromism of betaine-30 in BMIM[PF$_6$]
Solute and Solvent Structures
Simulation Details

- Force Field
  - Short-ranged forces: OPLS
  - Coulomb forces: Ewald summation
  - United atom treatment of CH\textsubscript{n}
- 200 ion pairs/1 betaine-30
- ~700 ps equilibration time
- NPT ensemble
Calculation of the Absorption Spectrum

\[
Z = \Delta E_s - \Delta E_v = V_{SS}^e - V_{SS}^o
\]
Time-Dependence of The Spectral Shift

Z vs. Time for Four Trajectories

Z vs. Time for Four Trajectories (Averaged Over 5 ps Intervals)
Time-Averaged Z-distribution

Distribution of Z for Betaine–30 in BMIM[PF₆]

Relative Probability (arb.)

Δ E_s (kcal/mol)
Calculated and Experimental Absorption Spectra

Absorption Spectrum of Betaine–30 in BMIM[PF₆]
Local Structure About Betaine-30 Oxygen Atom

O (Betaine–30) – [BMIM]
Radial Distribution Function

![Graph showing radial distribution function with peaks at different radii.]

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\[
g(r) = C \int_{0}^{1} \rho(r') \rho(r-r') dr'
\]

Where:
- \( g(r) \) is the radial distribution function.
- \( C \) is a constant.
- \( \rho(r) \) is the density at \( r \).
- \( r \) is the distance from the center of mass.

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Different components:
- Center of Mass
- Ring
- Side–Chain

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\[ r (\text{Å}) \]

---

\[ g(r) \]

---

20
Local Structure About Betaine-30 Oxygen Atom
Z-Component of O-Solvent Interaction

Mente and Maroncelli: Z-Contributions from Specific Betaine O-Solvent Interactions
Extremal Z-Component Spectra For Betaine-Solvent Interaction

Z–Contribution Spectra of Extremal BMIM$^+$ and PF$_6^-$

![Graph showing relative probability versus Z (kcal/mol)]
Sample Configuration of Largest Z-Contributors
Z-Components of Extremal Betaine-Solvent Interactions

Z–Contribution Spectra of Extremal Ions

![Graph showing relative probability vs. Z (kcal/mol)]
Spatial Distribution of Extremal Z-Contributors
Contribution to $Z$ as a Function of Solute-Solvent Distance
Contribution to $Z$ as a Function of Solute-Solvent Distance
Hypothesis:
- Large fraction of polarization due to reorganization of ions neighboring chromophore
- Long-range contribution to polarization less significant
  - Individual interactions very strong
  - Collective solute-solvent interactions cancel out on average (statistical effect)
- Concept of “solvation shell” applies to RTILs, but arises from different effects
Time-Resolved Fluorescence

- Fluorescence spectrum is difference between ground and excited state energies when solvent is equilibrated to the excited state configuration.
- If system is excited by an ultrashort pulse, fluorescence spectrum changes in time until equilibrium is reached.

\[ \Delta G \]

Fluorescence

Absorption

\[ Z \]

\[ e \]

\[ o \]
Time-Resolved Fluorescence in Molecular Liquids

- Response occurs on two timescales
- Timescales correspond roughly to rotational and translational motion of solvent

How does this work in Ionic Liquids?
Experimental Time-Resolved Fluorescence in Ionic Liquids

Results from Ingram et al. (Maroncelli group)

Studied t.r. fluorescence of 4-aminophthalimide in BMIM[PF₆]

0, 50, 100, 200 ps
.5, 1, 2, 5, 10 ns
Experimental Observations

- Two timescales observed
- Widely separated (sub-picosecond vs. nanosecond)

Can get at solvent motion via simulation. (Caveat: Betaine-30 does not fluoresce)
Time-Resolved Fluorescence Data

Fluorescence Response for Four Trajectories

![Graph showing time-resolved fluorescence data with four trajectories.](image-url)
Time-Resolved Fluorescence Data

Fluorescence Response for Four Trajectories
Calculated vs. Theoretical Decay Constants

Fit to Fluorescence Response
Experiment and Theory

Experimental Data from Ingram et al. on 4-aminophthalimide (~50 kcal/mol)

\[ Z_{\text{max}} = Z_{\text{inf}} + A \exp[-(t/B)^c] \]
Nature of Time-Resolved Response

**Hypothesis:**
- Short-time response due to local motion of ions about chromophore
- Long-time response due to collective reorganization of solvent
  - Involves relatively large distances
  - Occurs slowly by weakly-biased random walk
Conclusions

- Solvation shell concept applies to RTILs, but arises from statistical cancellations at large distances
- Time-resolved fluorescence response consists of rapid response by inner shell, followed by slow diffusion of other ions (weakly driven by solute dipole)
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