

## Redox Ionic Liquid Phases: Ferrocenated Imidazoliums

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Investigations of tailor-made<sup>1</sup> ionic liquids (ILs, imidazolium and other organic molten salts with melting points usually <100 °C) are active topics in both academic and industrial research.<sup>2,3</sup> Electrochemical interest in pyridinium and imidazolium ILs dates to 1975,<sup>4</sup> and their investigation continues today.<sup>5a-c</sup> Properties such as good ionic conductivities, large electrochemical stability window, and low volatility, have been emphasized in a variety of studies, including electroplating, dye-sensitized solar cells,<sup>6</sup> fuel cells, lithium batteries, and supercapacitors.<sup>5a,d</sup>

Our laboratory has for several years probed mass and electron transport phenomena in undiluted forms of another class of ILs, namely, room temperature melts formed by hybrids of redox materials and polyethers.<sup>7</sup> Combinations of poly(ethylene glycol)s (PEG) with redox entities, or their counterions, comprise a completely general route to redox melts, including even an example of a DNA melt.<sup>7c</sup> The ionic conductivities of these melts, although they are highly viscous, are sufficient to carry out microelectrode voltammetry of the redox sites in the undiluted melt. The redox sites are so concentrated and redox site diffusion so slow that charge transport typically occurs by electron hopping between oxidized and reduced forms of the redox sites. The electron hopping is equivalent to an electron self-exchange reaction,<sup>8</sup> which opens a window to study electron transfer dynamics in semisolid phases. A primary motivation in these studies has been to gain experimental information for a range of redox systems and ultimately to understand the factor(s) that control their electron transfer rates in semisolid phases.

The present work extends the chemical diversity of intrinsically electroactive IL phases to redox molten salts based on ferrocene tethered to imidazolium ions. These materials, in which the ferrocene concentrations exceed 2 M, differ from solutions of ferrocenes in ILs,<sup>9</sup> which are insufficiently concentrated for electron hopping to be an important process. Ferrocene has been previously attached to dialkyl imidazolium salts<sup>10</sup> but without electrochemical investigation of the concentrated phase. In reports<sup>6,11</sup> of the sole previously known intrinsically electroactive imidazolium IL phase, the electroactivity was supplied by its counterions, namely, an iodide/triiodide mixture. Electron hopping was evident in the results.

We have prepared the ferrocenated ILs listed in Table 1; the structural skeleton is shown at the top. They were prepared as bromide salts by refluxing *N*-alkyl-substituted imidazole and appropriate ferrocene-appended alkyl bromide (~2 equiv) in toluene under Ar atmosphere. Their PF<sub>6</sub><sup>-</sup> and BF<sub>4</sub><sup>-</sup> salts were obtained by ion metathesis with 1.3(±0.1) equiv of NH<sub>4</sub><sup>+</sup>PF<sub>6</sub><sup>-</sup> or Na<sup>+</sup>BF<sub>4</sub><sup>-</sup> in a mixed solvent dichloromethane:ethanol:acetone (1:1:1). All synthesized ILs were characterized for purity and completion of ion metathesis by appropriate analytical techniques, including IR, <sup>1</sup>H NMR, UV-vis, and mass spectroscopy. Selected data are provided in Supporting Information.

To achieve a semisolid state yet retain ionic conductivity sufficient for electrochemical voltammetry, it is desirable that the IL phases be highly viscous fluids (not crystalline), preferably at

**Table 1.** Intrinsically Electroactive Ionic Liquids<sup>a</sup>

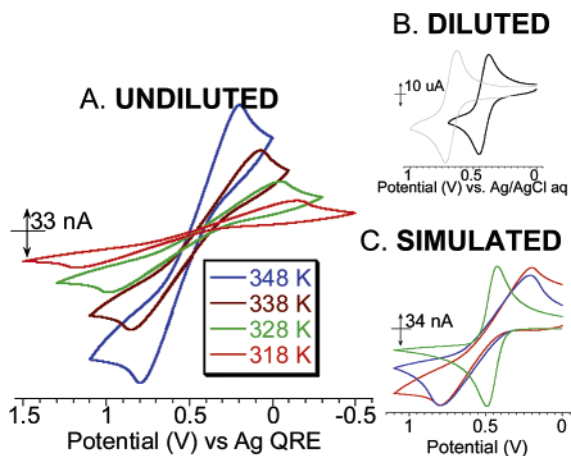
	linker	side chain	$\eta$ , cP (25 °C) <sup>b</sup>
<b>1</b>	C <sub>4</sub> H <sub>8</sub>	CH <sub>3</sub> or C <sub>4</sub> H <sub>9</sub>	na <sup>c</sup>
<b>2</b>	C <sub>6</sub> H <sub>12</sub>	CH <sub>3</sub> or C <sub>4</sub> H <sub>9</sub>	8.5 × 10 <sup>3</sup>
<b>3</b>	COO-C <sub>3</sub> H <sub>6</sub>	CH <sub>3</sub> or C <sub>4</sub> H <sub>9</sub>	1.4 × 10 <sup>7</sup>
<b>4</b>	COO-C <sub>6</sub> H <sub>12</sub>	CH <sub>3</sub> or C <sub>4</sub> H <sub>9</sub>	5.8 × 10 <sup>5</sup>
<b>5</b>	COO-C <sub>11</sub> H <sub>22</sub>	CH <sub>3</sub> or C <sub>4</sub> H <sub>9</sub>	1.6 × 10 <sup>5</sup>
<b>6</b>	COO-C <sub>2</sub> H <sub>4</sub> OC <sub>2</sub> H <sub>4</sub>	CH <sub>3</sub> or C <sub>4</sub> H <sub>9</sub>	5.4 × 10 <sup>5</sup>
<b>7</b>	COO-C <sub>3</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub> OCH <sub>3</sub>	na <sup>c</sup>
<b>8</b>	COO-C <sub>6</sub> H <sub>12</sub>	C <sub>2</sub> H <sub>4</sub> OCH <sub>3</sub>	na <sup>c</sup>

<sup>a</sup> X = Br<sup>-</sup>, PF<sub>6</sub><sup>-</sup>, or BF<sub>4</sub><sup>-</sup>. All ILs listed are either fluid or glassy materials except for **1**·CH<sub>3</sub>·Br, **2**·CH<sub>3</sub>·Br, and **2**·CH<sub>3</sub>·PF<sub>6</sub>, which are solids.  
<sup>b</sup> All viscosities are for X = PF<sub>6</sub><sup>-</sup> and side chain = C<sub>4</sub>H<sub>9</sub>. <sup>c</sup> Not measured.

room temperature. Our early syntheses focused on ferrocenes appended by simple alkyl linkers (products **1** and **2**). Some bromide salts with methyl side chains (**1**·CH<sub>3</sub>·Br and **2**·CH<sub>3</sub>·Br) proved to be electrochemically unusable solids at room temperature, but butyl imidazolium derivatives (**1**·C<sub>4</sub>H<sub>9</sub> and **2**·C<sub>4</sub>H<sub>9</sub>) were sufficiently fluid for voltammetric studies as illustrated below. Introducing ester linkages (**3**–**8**) diminished the fluidity, but less so for longer alkyl linkers. Having a previous<sup>7</sup> appreciation of how short PEG chains improve fluidity in redox melts, a single ethyleneoxide segment was introduced in **6**–**8**, giving an appreciably enhanced IL fluidity. The hybridization of longer PEG chains with imidazolium ILs<sup>12</sup> should be a potent tool to manipulate fluidities for electrochemical and other purposes. Table 1 gives viscosities ( $\eta$ ) for a selection of the ferrocenated ILs. The measured viscosities were Newtonian (see Supporting Information) and paralleled electrochemically measured ionic conductivities as seen before.<sup>13</sup> A plot of inverse viscosity versus conductivity is, however, nonlinear.<sup>14</sup>

Examples of microelectrode cyclic voltammetry (CV) of undiluted **8** ferrocenated IL and of dilute solutions of **1** and **3** are shown in Figure 1A and B, respectively. The dilute solution CV is unremarkable, showing well-defined Fc<sup>1+/0</sup> waves with formal potentials typical of alkylated (**1**) and carboxylated (**3**) ferrocenes. ILs with Br<sup>-</sup> impurity display an additional wave at 0.97 V. Voltammetry, such as that of undiluted IL **8**, shown for a series of temperatures in Figure 1A, is a target of the investigation. Similar results are obtained with BF<sub>4</sub><sup>-</sup> counterions. The large separations between the oxidation and reduction peak potentials in Figure 1A are attributed to a large uncompensated resistance (*iR*<sub>UNC</sub>) effect. The CV digital simulation in Figure 1C matches the experimental CV quite well; its *iR*<sub>UNC</sub> content (approximated as being constant through the CV) is based on an experimental ionic conductivity.<sup>15</sup>

Potential step chronoamperometric measurements of the charge transport diffusion constants can nonetheless be effected with microelectrodes, as we have shown in previous resistive melts.<sup>7</sup>



**Figure 1.** (A) CV (10 mV/s) of undiluted **8**. PF<sub>6</sub> at 12.5 μm radius Pt microdisk electrode, in vacuum at indicated temperatures. (B) CV of 1-CH<sub>3</sub>-PF<sub>6</sub> (right curve) and carboxylated 3-CH<sub>3</sub>-PF<sub>6</sub> (left curve) in dilute CH<sub>2</sub>Cl<sub>2</sub> solution with 0.2 M Bu<sub>4</sub>NClO<sub>4</sub> electrolyte. (C) Digital simulation (blue curve, includes *i*<sub>R<sub>UNC</sub></sub> effect, see Supporting Information) CV (10 mV/s) of undiluted **8**. PF<sub>6</sub> at 75 °C, compared to experimental result (red curve). The green curve is ideal CV with no *i*<sub>R<sub>UNC</sub></sub> effect.

The linear Cottrell plot from chronoamperometry of IL **8** in Figure 1 gives an apparent diffusion coefficient (*D*<sub>APP</sub>) of  $5.2 \times 10^{-11}$  cm<sup>2</sup> s<sup>-1</sup> at 25 °C, with a thermal activation barrier *E*<sub>A</sub> = 73 kJ/mol (data from 75 to 25 °C). Given the >2 M ferrocene redox site concentration of **8**, we anticipate that the value of *D*<sub>APP</sub> is dominated by the rate of diffusive electron hopping (*D*<sub>E</sub>) between ferrocene and ferrocenium sites, as opposed to physical diffusion (*D*<sub>PHYS</sub>) of the bulky ferrocenated imidazolium cations. Direct evidence for this is obtained from chronoamperometry of a small amount of an iso-structural cobaltocenium imidazolium surrogate (same as IL 4-C<sub>4</sub>H<sub>9</sub> but with Co as the metal)<sup>7b,14</sup> dissolved in otherwise undiluted ILs 4-C<sub>4</sub>H<sub>9</sub> and **8** in the two experiments that both show *D*<sub>APP</sub> of the cobaltocenium surrogate diffusant to be >10-fold smaller than the *D*<sub>APP</sub> of ILs 4-C<sub>4</sub>H<sub>9</sub> and **8**. This result is also consistent with comparisons of *D*<sub>APP</sub> to counterion diffusivities obtained from ionic conductivity measurements. A calculation of the apparent Fc<sup>1+/0</sup> electron self-exchange rate constant (*k*<sub>EX</sub>) from the Dahms–Ruff equation<sup>8,16</sup> based on the above *D*<sub>APP</sub> and ignoring physical diffusion gives *k*<sub>EX</sub> =  $1.7 \times 10^4$  M<sup>-1</sup> s<sup>-1</sup> at 25 °C for IL **8**.

The intrinsically electroactive ILs described here differ from earlier reports<sup>6,11</sup> in that the (ferrocene) redox moiety is directly linked to the imidazolium center, rather than being its counterion. This points to an enlarged generality of structural design of electroactive ILs. The charge transport properties of the ferrocenated ILs and other physical data will be described in a separate report<sup>14</sup> as will be results from current work appending other electroactive groups, including nanoparticles, to ILs.

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**Supporting Information Available:** Synthesis, selected spectral data of ferrocenated ionic liquids, and viscosity and cyclic voltammetry measurement details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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