Electronic Supplementary Information

Direct Determination of Ionic Transference Numbers in Ionic Liquids by Electrophoretic NMR

Martin Gouverneur, Jakob Kopp, Leo van Wüllen+, Monika Schönhoff*

A. Experimental setup and pulse sequence

Scheme S1. Self-built eNMR electrode configuration for 5 mm NMR tubes. The cell has a length of 2.1 cm. The contacts are housed in a Teflon cap, in which the 5 mm NMR tube can be fixed with a Teflon screw.

Scheme S2. Double stimulated echo pulse sequence with alternating polarity of the electric field to compensate convection artefacts.
B. Raw data of phase shifts for electrophoretic mobility determination

The raw data of the phase shift for the ionic liquids are displayed in Figures S1 to S7. The applied voltage and drift time are given for every ion species. Due to the automatic determination of the phase shift, the values of the phase are not absolute, but relative to a reference spectrum.

Figure S1. Phase shift in dependence on the gradient strength of EmimBF\(_4\) for a) cation (\(^1\)H) and b) anion (\(^{19}\)F). Errors are estimated to \(\pm 3^\circ\).

Figure S2. Phase shift in dependence on the gradient strength of EmimTFSI for a) cation (\(^1\)H) and b) anion (\(^{19}\)F). Errors are estimated to \(\pm 3^\circ\).

**Figure S3.** Phase shift in dependence on the gradient strength of P14TFSI for a) cation (1H) and b) anion (19F). Errors are estimated to ±3°.

**Figure S4.** Phase shift in dependence on the gradient strength of BMATFSI for a) cation (1H) and b) anion (19F). Errors are estimated to ±3°.

**Figure S5.** Phase shift in dependence on the gradient strength of BmPipTFSI for a) cation (1H) and b) anion (19F). Errors are estimated to ±3°.

Figure S6. Phase shift in dependence on the gradient strength of BmimPF₆ for a) cation (¹H) and b) anion (¹⁹F). Errors are estimated to ±3°.

Figure S7. Phase shift in dependence on the gradient strength of BmimTFSI for a) cation (¹H) and b) anion (¹⁹F). Errors are estimated to ±3°. The red line follows from a linear regression.

C. Tabulated mobilities

Table S1. Electrophoretic mobilities of cations and anions in the investigated IL in this study at 295 K.

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>EmimBF₄</th>
<th>EmimTFSI</th>
<th>BmimTFSI</th>
<th>P₄TFSI</th>
<th>BMATFSI</th>
<th>BmPipTFSI</th>
<th>BmimPF₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>µ⁺ [10⁻⁹m³V⁻¹s⁻¹]</td>
<td>9.6 ± 0.9</td>
<td>13 ± 1</td>
<td>5.2 ± 0.5</td>
<td>3.5 ± 0.4</td>
<td>2.2 ± 0.2</td>
<td>1.4 ± 0.2</td>
<td>1.2 ± 0.2</td>
</tr>
<tr>
<td>µ⁻ [10⁻⁹m³V⁻¹s⁻¹]</td>
<td>13 ± 1</td>
<td>9.6 ± 0.9</td>
<td>6.7 ± 0.7</td>
<td>3.4 ± 0.3</td>
<td>2.6 ± 0.3</td>
<td>1.9 ± 0.2</td>
<td>1.7 ± 0.2</td>
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