Selective Ion Transport across a Lipid Bilayer in a Protic Ionic Liquid- Supplementary Information

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\begin{figure}[h]
  \centering
  \includegraphics[width=0.8\textwidth]{cartridge.png}
  \caption{Cartridge with six wells and tethaPod\textsuperscript{TM} reader (SDx). Solvent is applied to the circular wells (bottom of the cartridge in the image) where it flows across the electrodes and the membranes, and gathers in the wider reservoir (oval-shaped at the top of the cartridge in the image).}
\end{figure}
Figure S2. Phase angle and impedance plots of EtAF and EDTA-Tris with and without membranes. Data from triplicate membranes made with EtAF is shown to demonstrate the consistency of bilayer formation. Data is also shown for when there are no lipids in the system, only EDTA-Tris or EtAF. This demonstrates the significant change in the Bode plots that occurs as a result of the presence of a bilayer.

Table S1. Average parameters of AM199 membranes made in either EDTA-Tris buffer or EtAF.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>EDTA-Tris</th>
<th>EtAF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyte Conductance (mS)</td>
<td>2.98</td>
<td>2.3</td>
</tr>
<tr>
<td>Series Capacitance (nF)</td>
<td>150.8</td>
<td>405.0</td>
</tr>
<tr>
<td>Constant Phase Element</td>
<td>0.9</td>
<td>0.8</td>
</tr>
<tr>
<td>Membrane Conductance (µS)</td>
<td>0.3</td>
<td>1.5</td>
</tr>
<tr>
<td>Membrane Capacitance (nF)</td>
<td>21.9</td>
<td>26.0</td>
</tr>
</tbody>
</table>
Figure S3. Membrane capacitance of an AM199 membrane exposed to varying concentrations of EtAF. Data for the membrane in EDTA-Tris buffer before and after exposure to EtAF are labelled 0 and 105%. Error bars are based on the standard deviation of triplicate samples.

Figure S4 shows the change in solvent and membrane conductance at different concentrations of ethylammonium formate (EAF). The solvent conductance shows much the same pattern as that of EtAF (Figure 2), and consistent with other ILs where peak conductance is a result of a balance between viscosity and ion concentration. As with EtAF, the conductance of the membrane increased consistently with increasing EAF concentration (the value at 70 vol% is likely anomalous, possibly the result of an air-bubble or other interruption). However, most importantly, the membrane conductance value in EDTA-Tris before (labelled 0% in Figure S4) and after (labelled 105% in Figure S4) exposure to EAF are significantly different (0.178 μS compared to 2.834 μS). This indicates that the membrane has been irreversibly altered by the presence of EAF. For this reason, further studies in EAF were not carried out.
Figure S4. Solvent and membrane conductance of an AM199 membrane exposed to varying concentrations of ethylammonium formate (EAF). Data for the membrane in EDTA-Tris buffer before and after exposure to EtAF are shown at 0 and 105% respectively. Error bars are based on 5% error reported by the tethaQuick software. Red arrow highlights the change in membrane conductance in EDTA-Tris buffer after exposure to EAF.

Figure S5. Phase angle and impedance plots of AM199 membranes exposed to different volumes of EtAF (from 0 to 100 vol%) in EDTA-Tris buffer. Error based on standard deviation from triplicate samples.
Figure S6. Phase angle and impedance plots of an AM199 membrane exposed to EtAF at either pH 5.4 or 6.9, compared to membranes in EDTA-Tris buffer.

Figure S7. Phase angle and impedance plots of AM199 membranes before and after exposure to valinomycin. Data without valinomycin is plotted with solid lines while data after addition of valinomycin is plotted with dashed lines. Measurements for duplicate wells shown.
Figure S8 shows how the different parameters change under different solvent conditions, with, and without valinomycin. The series capacitance (Figure S8A) changed very little throughout the experiment, although the value for the aqueous KCl buffer was slightly higher in the presence of valinomycin than without, possibly due to the movement of valinomycin through the membrane causing perturbations to the diffusion of potassium through the reservoir between the membrane and the gold electrode.

On the other hand, the membrane capacitance (Figure S8B) showed a large change for both the aqueous KCl buffer and the EtAF+KCOOH before and after addition of valinomycin. This is probably due to movement of valinomycin through the membrane which disrupts the structure—probably thinning the bilayer—which manifests as an increase in membrane capacitance.

The solvent conductance (Figure S8C) did not significantly change across the entire series, in keeping with the results in Figure 2 which showed the electrolyte conductance of 100 % EtAF was very similar to that of the EDTA-Tris aqueous buffer.

The constant phase elements remained unchanged across the entire series, even with changing solvents and addition of valinomycin (Figure S8D).
Figure S8. Series capacitance, membrane capacitance, solvent conductance and constant phase element of an AM199 membrane under different solvent conditions with/without valinomycin. Error bars based on 5% reported by thetaQuick software.

Data Availability: Raw data is available on request.