Environmental Sustainability of Cellulose-Supported Solid Ionic Liquids for CO₂ Capture

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Supporting information

S1. Estimation of raw material requirements

Table S1 Raw materials used in the synthesis of the SoILs and their precursors

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>MW (g·mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[N₁₈₈₈][Ac]</td>
<td>C₂₇H₅₇NO₂</td>
<td>427</td>
</tr>
<tr>
<td>[N₁₈₈₈][OH]</td>
<td>C₂₅H₅₂NO</td>
<td>385</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>CH₃COOH</td>
<td>60</td>
</tr>
<tr>
<td>Water</td>
<td>H₂O</td>
<td>18</td>
</tr>
<tr>
<td>[N₁₈₈₈]I</td>
<td>C₂₅H₅₅NI</td>
<td>495</td>
</tr>
<tr>
<td>Trioctylamine</td>
<td>C₂₄H₅₁N</td>
<td>353</td>
</tr>
<tr>
<td>Methyl iodide</td>
<td>CH₃I</td>
<td>142</td>
</tr>
<tr>
<td>1-octanol</td>
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<tr>
<td>Ammonia</td>
<td>NH₃</td>
<td>17</td>
</tr>
<tr>
<td>[N₄₄₄₄][Ac]</td>
<td>C₁₈H₃₀NO₂</td>
<td>301</td>
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<tr>
<td>[N₄₄₄₄][OH]</td>
<td>C₁₆H₃₇NO</td>
<td>259</td>
</tr>
<tr>
<td>[N₄₄₄₄]Br</td>
<td>C₁₆H₃₆NBr</td>
<td>322</td>
</tr>
<tr>
<td>Tributylamine</td>
<td>C₁₂H₂₇N</td>
<td>185</td>
</tr>
<tr>
<td>1-bromobutane</td>
<td>C₆H₅Br</td>
<td>137</td>
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<td>1-butanol</td>
<td>C₄H₉OH</td>
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<tr>
<td>[N₈₈₈₈][Br]</td>
<td>C₃₂H₉₃Br</td>
<td>546</td>
</tr>
<tr>
<td>1-bromo-octane</td>
<td>C₄H₁₇Br</td>
<td>193</td>
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<tr>
<td>[Bmim]Br</td>
<td>C₈H₁₅N₂Br</td>
<td>219</td>
</tr>
<tr>
<td>1-methylimidazole</td>
<td>C₄H₆N₂</td>
<td>82</td>
</tr>
</tbody>
</table>

S1.1. Production of [N₁₈₈₈][Ac]

\[
[N₁₈₈₈][OH] + CH₃COOH \rightarrow [N₁₈₈₈][Ac] + H₂O
\]

\[
1000 \text{ g } [N₁₈₈₈][Ac] \times \frac{1 \text{ mol } [N₁₈₈₈][Ac]}{427 \text{ g } [N₁₈₈₈][Ac]} \times \frac{1 \text{ mol } [N₁₈₈₈][OH]}{1 \text{ mol } [N₁₈₈₈][Ac]} \times \frac{385 \text{ g } [N₁₈₈₈][OH]}{1 \text{ mol } [N₁₈₈₈][OH]} = 901.6 \text{ g } [N₁₈₈₈][OH]
\]

\[
1000 \text{ g } [N₁₈₈₈][Ac] \times \frac{1 \text{ mol } [N₁₈₈₈][Ac]}{427 \text{ g } [N₁₈₈₈][Ac]} \times \frac{1 \text{ mol } CH₃COOH}{1 \text{ mol } [N₁₈₈₈][Ac]} \times \frac{60 \text{ g } CH₃COOH}{1 \text{ mol } CH₃COOH} = 140.5 \text{ g } CH₃COOH
\]

\[
1000 \text{ g } [N₁₈₈₈][Ac] \times \frac{1 \text{ mol } H₂O}{1 \text{ mol } [N₁₈₈₈][Ac]} \times \frac{18 \text{ g } H₂O}{1 \text{ mol } H₂O} = 42.1 \text{ g } H₂O
\]

[N₁₈₈₈][OH] is produced from [N₁₈₈₈][I] using an anion exchange resin (AER):

\[
[N₁₈₈₈][I]_{\text{AER}} \rightarrow [N₁₈₈₈][OH]
\]

For the production of [N₁₈₈₈][Ac] we need 1 mole of [N₁₈₈₈][OH] or 1 mole of [N₁₈₈₈][I]; therefore:

\[
901.6 \text{ g } [N₁₈₈₈][OH] \times \frac{1 \text{ mol } [N₁₈₈₈][OH]}{385 \text{ g } [N₁₈₈₈][OH]} \times \frac{1 \text{ mol } [N₁₈₈₈][I]}{1 \text{ mol } [N₁₈₈₈][OH]} \times \frac{495 \text{ g } [N₁₈₈₈][I]}{1 \text{ mol } [N₁₈₈₈][I]} = 1159.2 \text{ g } [N₁₈₈₈][I]
\]

S1.1.1. Production of [N₈₈₈₈][I]

(C₉H₁₇)₃N⁺ CH₃I → [N₈₈₈₈]
S1.1.2. Production of \((C_8H_{17})_3N\)

\[3C_8H_{17}OH + NH_3 \rightarrow (C_8H_{17})_3N + 3H_2O\]

\[
1000 \frac{[N_{1888}][I]}{g} \times 1 \frac{mol}{[N_{1888}][I]} \times 1 \frac{mol \ (C_8H_{17})_3N}{1 \ mol \ (C_8H_{17})_3N} \times 353 \frac{g \ (C_8H_{17})_3N}{1 \ mol \ (C_8H_{17})_3N} = 713.1 \ g \ (C_8H_{17})_3N
\]

\[1000 \frac{[N_{1888}][I]}{g} \times 1 \frac{mol \ CH_3I}{495 \ [N_{1888}][I]} \times 1 \frac{mol \ CH_3I}{1 \ mol \ CH_3I} \times 142 \frac{g \ CH_3I}{1 \ mol \ CH_3I} = 286.9 \ g \ CH_3I\]

S1.1.2.1. Production of \([N_{4444}]([Ac])\)

\[[N_{4444}][OH] + CH_3COOH \rightarrow [N_{4444}][Ac] + H_2O\]

\[
1000 \frac{[N_{4444}][Ac]}{g} \times 1 \frac{mol \ [N_{4444}][Ac]}{301 \ [N_{4444}][Ac]} \times 1 \frac{mol \ [N_{4444}][OH]}{1 \ mol \ [N_{4444}][Ac]} \times 259 \frac{g \ [N_{4444}][OH]}{1 \ mol \ [N_{4444}][OH]} = 860.47 \ g \ [N_{4444}][OH]
\]

\[
1000 \frac{[N_{4444}][Ac]}{g} \times 1 \frac{mol \ CH_3COOH}{1 \ mol \ [N_{4444}][Ac]} \times 60 \frac{g \ CH_3COOH}{1 \ mol \ CH_3COOH} = 199.34 \ g \ CH_3COOH
\]

\[
1000 \frac{[N_{4444}][Ac]}{g} \times 1 \frac{mol \ H_2O}{301 \ [N_{4444}][Ac]} \times 18 \frac{g \ H_2O}{1 \ mol \ H_2O} = 59.80 \ g \ H_2O
\]

\([N_{4444}][OH]\) is produced from \([N_{4444}][Br]\) using an Anion Exchange Resin (AER):

\[N_{4444}[Br] \rightarrow N_{4444}[OH]\]

For the production of \([N_{4444}][Ac]\) we need 1 mole of \([N_{4444}][OH]\) or 1 mole of \([N_{4444}][Br]\); therefore:

\[860.47 \ g \ [N_{4444}][OH] \times \frac{1 \ mol \ [N_{4444}][OH]}{259 \ g \ [N_{4444}][OH]} \times 322 \frac{g \ [N_{4444}][Br]}{1 \ mol \ [N_{4444}][OH]} = 1069.77 \ g \ [N_{4444}][Br]\]

S1.2. Production of \([N_{4444}][Ac]\)

\[(C_4H_9)_3N + C_4H_9Br \rightarrow [N_{4444}][Br]\]

\[
1000 \frac{[N_{4444}][Br]}{g} \times 1 \frac{mol \ (C_4H_9)_3N}{322 \ [N_{4444}][Br]} \times 1 \frac{mol \ (C_4H_9)_3N}{1 \ mol \ (C_4H_9)_3N} \times 185 \frac{g \ (C_4H_9)_3N}{1 \ mol \ (C_4H_9)_3N} = 574.53 \ g \ (C_4H_9)_3N
\]

\[1000 \frac{[N_{4444}][Br]}{g} \times 1 \frac{mol \ C_4H_9Br}{322 \ [N_{4444}][Br]} \times 1 \frac{mol \ C_4H_9Br}{1 \ mol \ C_4H_9Br} \times 137 \frac{g \ C_4H_9Br}{1 \ mol \ C_4H_9Br} = 425.46 \ g \ C_4H_9Br\]

S1.2.1. Production of \([N_{4444}][Br]\)

\[(C_4H_9)_3N + C_4H_9Br \rightarrow [N_{4444}][Br]\]

\[3C_4H_9OH + NH_3 \rightarrow (C_4H_9)_3N + 3H_2O\]

\[
1000 \frac{[C_4H_9][N]}{g} \times 1 \frac{mol \ (C_4H_9)_3N}{185 \ [C_4H_9][N]} \times 3 \frac{mol \ C_4H_9OH}{1 \ mol \ (C_4H_9)_3N} \times 74 \frac{g \ C_4H_9OH}{1 \ mol \ C_4H_9OH} = 1200.0 \ g \ C_4H_9OH
\]

\[
1000 \frac{[C_4H_9][N]}{g} \times 1 \frac{mol \ NH_3}{185 \ [C_4H_9][N]} \times 1 \frac{mol \ NH_3}{1 \ mol \ NH_3} \times 17 \frac{g \ NH_3}{1 \ mol \ NH_3} = 91.89 \ g \ NH_3\]
S1.3. Production of [N₈₈₈₈][Br]

\[(\text{C}_8\text{H}_{17})_3\text{N} + \text{C}_8\text{H}_{17}\text{Br} \rightarrow [\text{N₈₈₈₈}]\text{Br}\]

\[
1000 \text{ g } [(\text{C}_8\text{H}_{17})_3\text{N}] \times \frac{1 \text{ mol } [(\text{C}_8\text{H}_{17})_3\text{N}]}{185 \text{ g } [(\text{C}_8\text{H}_{17})_3\text{N}]} \times \frac{3 \text{ mol } \text{H}_2\text{O}}{1 \text{ mol } [(\text{C}_8\text{H}_{17})_3\text{N}]} \times \frac{18 \text{ g } \text{H}_2\text{O}}{1 \text{ mol } \text{H}_2\text{O}} = 291.89 \text{ g } \text{H}_2\text{O}
\]

S1.4. [Bmim]Br

\[\text{C}_4\text{H}_9\text{N}_2 + \text{C}_4\text{H}_9\text{Br} \rightarrow [\text{Bmim}]\text{Br}\]

\[
1000 \text{ g } [\text{Bmim}]\text{Br} \times \frac{1 \text{ mol } [\text{Bmim}]\text{Br}}{219 \text{ g } [\text{Bmim}]\text{Br}} \times \frac{1 \text{ mol } \text{C}_4\text{H}_9\text{N}_2}{1 \text{ mol } [\text{Bmim}]\text{Br}} \times \frac{82 \text{ g } \text{C}_4\text{H}_9\text{N}_2}{1 \text{ mol } \text{C}_4\text{H}_9\text{N}_2} = 374.7 \text{ g } \text{C}_4\text{H}_9\text{N}_2
\]

\[
1000 \text{ g } [\text{Bmim}]\text{Br} \times \frac{1 \text{ mol } [\text{Bmim}]\text{Br}}{219 \text{ g } [\text{Bmim}]\text{Br}} \times \frac{1 \text{ mol } \text{C}_4\text{H}_9\text{Br}}{1 \text{ mol } [\text{Bmim}]\text{Br}} \times \frac{137 \text{ g } \text{C}_4\text{H}_9\text{Br}}{1 \text{ mol } \text{C}_4\text{H}_9\text{Br}} = 625.3 \text{ g } \text{C}_4\text{H}_9\text{Br}
\]

S2. Estimation of energy requirements

The energy requirements for the production of the SoILs and their precursors have been estimated using the heat of formation of the reactants and products. This methodology is based on the assumption that the heat required by the reactor is equal to the enthalpy of reaction assuming that no work is carried and that the kinetic and potential energy are zero, according to:

\[Q - W = \Delta H + \Delta E_k + \Delta E_p\]

If \(W, \Delta E_k\) and \(\Delta E_p\) are zero, then:

\[Q = \Delta H\]

where:

- \(Q\) reactor heat consumption
- \(W\) work
- \(\Delta H\) enthalpy of reaction
- \(\Delta E_k\) kinetic energy
- \(\Delta E_p\) potential energy

The enthalpy of reaction \(\Delta H\) can be calculated as:

\[
\Delta H = \sum (n \cdot H)_{\text{out}} - \sum (n \cdot H)_{\text{in}}
\]

where:

- \(n\) molecular weight of reactants
- \(H\) specific enthalpy of reactants

The specific enthalpy of reactants is equal to:

\[H = \Delta H_f^0 + \int_{T_1}^{T_2} C_p dT\]

where:

- \(\Delta H_f^0\) heat of formation of reactants
- \(C_p\) calorific value of reactants
- \(T_1, T_2\) reference temperature (25 ºC) and temperature of the reactants, respectively.
### Table S2 Thermodynamic properties of the compounds used in the synthesis of the SoILs and their precursors

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Cp (kJ·mol⁻¹·K⁻¹)</th>
<th>∆H°f (kJ·mol⁻¹)</th>
<th>Assumptions</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>[N₁₈₈₈][Ac]</td>
<td>C₂₇H₅₉NO₂</td>
<td>-</td>
<td>-615</td>
<td>∆H°f of ammonium acetate used as proxy</td>
<td>Aspen Plus¹</td>
</tr>
<tr>
<td>[N₁₈₈₈][OH]</td>
<td>C₂₅H₅₉NO</td>
<td>-</td>
<td>-498.6</td>
<td>∆H°f of tetra-n-butylammonium iodide used as proxy</td>
<td>NIST²</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>CH₃COOH</td>
<td>-</td>
<td>-484.5</td>
<td></td>
<td>HSC Chemistry³</td>
</tr>
<tr>
<td>Water</td>
<td>H₂O</td>
<td>0.03</td>
<td>-285.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[N₁₈₈₈][I]</td>
<td>C₂₅H₅₉NI</td>
<td>-</td>
<td>-498.6</td>
<td>∆H°f of tetra-n-butylammonium iodide used as proxy</td>
<td>NIST²</td>
</tr>
<tr>
<td>Triocetyamine</td>
<td>C₂₄H₅₁N</td>
<td>0.87</td>
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<tr>
<td>Methyl iodide</td>
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<td>-13.6</td>
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<td>∆H°f of ammonium acetate used as proxy</td>
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<tr>
<td>[N₄₄₄₄][OH]</td>
<td>C₁₆H₃₂NO</td>
<td>-</td>
<td>-540.3</td>
<td>∆H°f of tetra-n-butylammonium bromide used as proxy</td>
<td>NIST⁴</td>
</tr>
<tr>
<td>[N₄₄₄₄][Br]</td>
<td>C₁₆H₃₆NBr</td>
<td>-</td>
<td>-540</td>
<td></td>
<td>NIST⁴</td>
</tr>
<tr>
<td>Tributylamine</td>
<td>C₁₂H₂₂N</td>
<td>0.47</td>
<td>-327</td>
<td></td>
<td>Aspen Plus¹</td>
</tr>
<tr>
<td>1-bromobutane</td>
<td>C₄H₉Br</td>
<td>0.17</td>
<td>-148</td>
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<td>Aspen Plus¹</td>
</tr>
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<td>1-butanol</td>
<td>C₄H₉OH</td>
<td>0.26</td>
<td>-327</td>
<td></td>
<td>Aspen Plus¹</td>
</tr>
<tr>
<td>[N₈₈₈₈][Br]</td>
<td>C₃₂H₃₉Br</td>
<td>-</td>
<td>-540.3</td>
<td>∆H°f of tetra-n-butylammonium bromide used as proxy</td>
<td>NIST⁴</td>
</tr>
<tr>
<td>1-bromoocatane</td>
<td>C₉H₁₇Br</td>
<td>-</td>
<td>-245.2</td>
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<td>Aspen Plus¹</td>
</tr>
<tr>
<td>[Bmim]Br</td>
<td>C₈H₁₅N₂Br</td>
<td>0.35</td>
<td>-178</td>
<td></td>
<td>Cp: Aspen Plus¹</td>
</tr>
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<td>1-methylimidazole</td>
<td>C₄H₇N₂</td>
<td>0.19</td>
<td>70.7</td>
<td>∆H°f: Paulechka et al.⁵</td>
<td>Aspen Plus¹</td>
</tr>
</tbody>
</table>
**S3. Comparison of SoILs**

**Figure S1.** Life cycle environmental impacts of the pure SoILs considered in the study.
(The impacts expressed per kg of pure adsorbent. For impacts nomenclature see Section 3.1 in the paper. Some impacts have been scaled to fit – to obtain the original values, multiply by the factor shown on the x-axis.)
S4. Sensitivity analysis

Figure S2. Sensitivity analysis for the assumptions on the raw materials used in the production of the SoILs with 70% cellulose loading
(The graph bars represent the impacts in the base case and the error bars the impacts for the ± variation in impacts of the proxy raw materials. For impacts nomenclature, see Section 3.1 in the paper. Some impacts have been scaled to fit – to obtain the original values, multiply by the factor shown on the x-axis.)
Figure S3. Sensitivity analysis for the assumptions on the raw materials used in the production of the SoILs with 80% cellulose loading
(The graph bars represent the impacts in the base case and the error bars the impacts for the ± variation in impacts of the proxy raw materials. For impacts nomenclature, see Section 3.1 in the paper. Some impacts have been scaled to fit – to obtain the original values, multiply by the factor shown on the x-axis.)
Fig. S4 Sensitivity analysis for the assumptions on the energy required in the production of the SoILs with 75% cellulose loading.

(The graph bars represent the impacts in the base case and the error bars the impacts for the ± variation in impacts of the proxy raw materials. For impacts nomenclature, see Section 3.1 in the paper. Some impacts have been scaled to fit – to obtain the original values, multiply by the factor shown on the x-axis.)
References