THE UTILISATION OF IONIC LIQUIDS WITH IONIC LIQUID-LIQUID CHROMATOGRAPHY

ILLC

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A New Form of Chromatography

A general purpose method for the separation of practically all dissolvable compounds
Presentation Order

• Principals of Liquid-Liquid Separations
• Ionic Liquid – Liquid Separations (ILLC)
  • Operation of ILLC Chromatography
    • Metal Separations
What is Liquid-Liquid Chromatography?
A wide range of industrial scale liquid-liquid, countercurrent (CC) extractors are available.
Dr Les Brown with IL-Prep™ Machine
AECS’s IL Prep™ ILLC Machine Installed in QUILL
The J-Type Centrifuge

The flying leads go through both the axis of rotation and the axis of revolution.

No overall rotation of the flying leads.
The coils are subject to double rotation in what is known as planetary motion (like Earth rotation, it rotates own axis as rotates around the sun, this is defined as “J” type.)
Imagine on Earth, at 1 “G” fixed wind causes 10 foot wave in ocean / water interface. Imagine same wind, same ocean, **BUT** 200 “G”? NO WAVE / NO MIXING. At 0.1 “G” FORCE OCEAN & AIR RAPIDLY MIXED.
Ionic Liquid-Liquid Chromatography

Ionic Liquid-Liquid Liquid Extraction = ILLC
Ionic Liquid-Liquid Liquid Extraction = ILLE
QUILL Statement

No ionic liquids were harmed during the making of the films and in all separation processes carried out.
Ionic liquids have not been significantly tested in most forms of liquid-liquid chromatography.
Use of Coils

<table>
<thead>
<tr>
<th>Coil Volume (cm$^3$)</th>
<th>Ionic Phase Needed (cm$^3$)</th>
<th>Comments</th>
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<tbody>
<tr>
<td>12</td>
<td>20</td>
<td>Feasibility testing</td>
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<tr>
<td>34</td>
<td>55</td>
<td>Small separations</td>
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<td>133</td>
<td>175</td>
<td>General separations</td>
</tr>
<tr>
<td>236</td>
<td>300</td>
<td>Extractions and prep scale</td>
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</table>

The ionic phase is the combination of materials that make up the ionic phase, and not the amount of ionic liquid needed.

For a full test and scale up of a separation, at least 0.5 Kg of ionic phase may be required.

All ionic liquids are recycled and reused.
Example of Operation

- Pump ionic liquid phase into coil (stationary phase)
- Start the rotation of the machine
- Pump organic or water phase into coil until no more ionic phase comes out

Flow Rate vs Phase Retention %

- Ionic liquid = $[\text{C}_{12}\text{mim}][\text{NTf}_2]$  
- Mobile phase = hexane  
- Coil = 34 ml, 1.0 mm diameter  
- Speed = 865 rpm

% Ionic phase retention in coil
Example of Operation

Solution of mixture in ionic liquid phase and a second non-ionic phase

Mixture to be separated

Sample vials

Organic or Water Phase

Ionic Phase

Pump

Pump

Fraction Collector
Separation of a Natural Plant Oil

Carried out on Coil 4 (236 cm$^3$), 30 C, @ 2 ml/min
Solvent system = [C$_{12}$mim][NTf$_2$] / Hexane with ionic phase as stationary phase
Copper, Nickel and Cobalt Separations

The dihalides of Cu, Ni, and Co partition differently in a [Phosphonium][Halide] / Water mixture

The equilibrium is $[M(H_2O)_6]^{2+} + 4 X^- = [MX_4]^{2-} + 6 H_2O$  $X = \text{halide}$  $M = \text{Cu, Ni, Co}$

Ni$^{2+}$ strongly prefers the water phase

Co$^{2+}$ is more soluble in the water phase than ionic phase

Cu$^{2+}$ prefers the ionic phase
Separation of copper(II) and cobalt(II)

- Most dense stationary phase = [Phosphonium][Halide] / CH₂Cl₂
- Least dense mobile phase = H₂O
Separation of Copper(II), Nickel(II) and Cobalt(II)

- Least dense stationary phase = [Phosphonium][Halide] / Ethyl Ethanoate
- Most dense mobile phase = H$_2$O
Summary

• ILLC is a new form of chromatography

• Unlike HPLC, there are no off the shelf columns or ionic liquids for specific separations

• The most difficult part of separations is choosing the best solvent system to use

• This requires test tube experiments to determine the solvent distribution ratios of dissolved solutes
A general purpose methodology for the separation of practically all dissolvable compounds.

CCC can even be used to separate sand, grit and powders provided they can fit inside the piping used.
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Any Questions?