Evaluation of a New Ionic Liquid Stationary Phase with PEG Like Selectivity

Supelco, Div. of Sigma-Aldrich
Bellefonte, PA 16823 USA
Overview of Presentation

- Overview of Ionic Liquids
- Selectivity Evaluations
- Selectivity Ranking/ Assignment
- SLB-IL60
- Applications
- Conclusions
Ionic Liquids: Definition and Uses

- Ionic liquids are a class of solvents with low melting points that consist of organic cations associated with (inorganic or organic) anions.

- Ethyl ammonium nitrate \((\text{EtNH}_3^+)(\text{NO}_3^-)\), which has a melting point of 12 °C, was described in 1914 by P. Walden.

- Today, they are used as solvents, electrically conducting fluids, and sealants.
Ionic Liquids: Example Structure

• **Benefits**
  - Greater stability compared to polysiloxane polymers and polyethylene glycols
    - Lower column bleed, longer life, and higher thermal limits
    - More resistant to damage from moisture/oxygen
  - Numerous combinations of cations and anions are possible allowing for “tailored” selectivity, application, or function
    - Dicationic (*shown*) or polycationic
    - Cations, linkages, and/or anions can be changed
    - Pendant groups can be added to cations and/or linkages

1,9-di(3-vinylimidazolium) nonane bis(trifluoromethyl) sulfonyl imidate
Common Anions for Ionic Liquid Phases

\[
\begin{align*}
\text{(NTF}_2^-) & \quad \text{(OTf}^-) \\
\end{align*}
\]
SLB-IL60
Phase Structure

1,12-Di(tripropylphosphonium)dodecane bis(trifluoromethylsulfonyl)imide
Selectivity Evaluations
Ionic Liquid Test Mix
TCEP Column, 110 °C

1. n-Tridecane
2. Toluene
3. Ethylbenzene
4. p-Xylene
5. Isopropylbenzene (Cumene)
6. 1,2,4-Trimethylbenzene
7. 1,2,4,5-Tetramethylbenzene (Durene)
8. Cyclohexanone
Ionic Liquid Columns, 110 °C Isothermal

1. n-Tridecane
2. Toluene
3. Ethylbenzene
4. p-Xylene
5. Isopropylbenzene (Cumene)
6. 1,2,4-Trimethylbenzene

SLB-IL59

SLB-IL60
Ionic Liquid Columns, 110 °C Isothermal

SLB-IL100

1. n-Tridecane
2. Toluene
3. Ethylbenzene
4. p-Xylene
5. Isopropylbenzene (Cumene)
6. 1,2,4-Trimethylbenzene

SLB-IL111

© 2013 Sigma-Aldrich Co. All rights reserved.
GC Column Polarity Scale and Naming System
McReynold’s Number Probes

- **Benzene (X)** - Aromatics, olefins
- **Butanol (Y)** - Alcohols, nitriles, acids
- **2-Pentanone (Z)** - Ketones, ethers, aldehydes, esters, epoxides, dimethyl amino derivatives
- **Nitropropane (U)** - Nitro and nitrile compounds
- **Pyridine (S)** - Bases, N-heterocycles
- **2-Methyl-2-pentanol (H)** - Branched chain compounds, alcohols
- **1-Iodobutane (I)** - Halogen compounds
- **2-Octyne (K)** - Acetylenic compounds
- **1,4- Dioxane (L)** - Ethers, polyols
- **cis-Hydrindane (M)** - Polycyclic compounds, steroids
Description of Our Procedure

- Each column is characterized with a series of five probes plus several n-alkane markers to determine the retention index for each probe:
  - Benzene
  - Butanol
  - 2-Pentanone
  - Nitropropane
  - Pyridine

- McReynolds Constants are then calculated using the retention index data of the column relative to the retention index data for the same five probes on squalane, the most non-polar GC stationary phase.

- The five McReynolds Constants are summed to obtain Polarity (P) values, which are then normalized to SLB-IL100 (set at P=100) to obtain Polarity Number (P.N.) values.

Our procedure was proposed by Prof. Luigi Mondello (University of Messina, Italy).
**Experimentally Determined Polarity Numbers**

<table>
<thead>
<tr>
<th>Column</th>
<th>Benzene</th>
<th>n-Butanol</th>
<th>2-Pentanone</th>
<th>Nitropropane</th>
<th>Pyridine</th>
<th>P</th>
<th>P.N.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPB-Octyl</td>
<td>17</td>
<td>-20</td>
<td>6</td>
<td>19</td>
<td>6</td>
<td>28</td>
<td>1</td>
</tr>
<tr>
<td>Equity-1</td>
<td>11</td>
<td>10</td>
<td>33</td>
<td>60</td>
<td>16</td>
<td>130</td>
<td>3</td>
</tr>
<tr>
<td>SLB-5ms</td>
<td>33</td>
<td>30</td>
<td>55</td>
<td>91</td>
<td>43</td>
<td>252</td>
<td>6</td>
</tr>
<tr>
<td>SPB-20</td>
<td>76</td>
<td>79</td>
<td>104</td>
<td>167</td>
<td>109</td>
<td>535</td>
<td>12</td>
</tr>
<tr>
<td>Equity-1701</td>
<td>82</td>
<td>131</td>
<td>150</td>
<td>233</td>
<td>136</td>
<td>732</td>
<td>16</td>
</tr>
<tr>
<td>SPB-35</td>
<td>175</td>
<td>113</td>
<td>151</td>
<td>225</td>
<td>175</td>
<td>839</td>
<td>19</td>
</tr>
<tr>
<td>SPB-50</td>
<td>154</td>
<td>134</td>
<td>176</td>
<td>266</td>
<td>218</td>
<td>948</td>
<td>21</td>
</tr>
<tr>
<td>SPB-225</td>
<td>233</td>
<td>342</td>
<td>342</td>
<td>501</td>
<td>375</td>
<td>1793</td>
<td>40</td>
</tr>
<tr>
<td>PAG</td>
<td>276</td>
<td>459</td>
<td>320</td>
<td>508</td>
<td>428</td>
<td>1991</td>
<td>45</td>
</tr>
<tr>
<td>SUPELCOWAX 10</td>
<td>334</td>
<td>509</td>
<td>375</td>
<td>601</td>
<td>505</td>
<td>2324</td>
<td>52</td>
</tr>
<tr>
<td>SLB-IL59</td>
<td>338</td>
<td>505</td>
<td>549</td>
<td>649</td>
<td>583</td>
<td>2624</td>
<td>59</td>
</tr>
<tr>
<td>SLB-IL60</td>
<td>362</td>
<td>492</td>
<td>525</td>
<td>679</td>
<td>564</td>
<td>2622</td>
<td>59</td>
</tr>
<tr>
<td>SLB-IL61</td>
<td>371</td>
<td>551</td>
<td>516</td>
<td>624</td>
<td>648</td>
<td>2710</td>
<td>61</td>
</tr>
<tr>
<td>SP-2330</td>
<td>469</td>
<td>663</td>
<td>608</td>
<td>859</td>
<td>712</td>
<td>3311</td>
<td>75</td>
</tr>
<tr>
<td>SLB-IL76</td>
<td>456</td>
<td>690</td>
<td>643</td>
<td>845</td>
<td>745</td>
<td>3379</td>
<td>76</td>
</tr>
<tr>
<td>SP-2331</td>
<td>495</td>
<td>674</td>
<td>622</td>
<td>856</td>
<td>735</td>
<td>3382</td>
<td>76</td>
</tr>
<tr>
<td>SP-2560</td>
<td>510</td>
<td>724</td>
<td>652</td>
<td>913</td>
<td>773</td>
<td>3572</td>
<td>81</td>
</tr>
<tr>
<td>SLB-IL82</td>
<td>532</td>
<td>676</td>
<td>701</td>
<td>921</td>
<td>808</td>
<td>3638</td>
<td>82</td>
</tr>
<tr>
<td>TCEP</td>
<td>622</td>
<td>871</td>
<td>772</td>
<td>1072</td>
<td>957</td>
<td>4294</td>
<td>97</td>
</tr>
<tr>
<td>SLB-IL100</td>
<td>602</td>
<td>853</td>
<td>884</td>
<td>1017</td>
<td>1081</td>
<td>4437</td>
<td>100</td>
</tr>
<tr>
<td>SLB-IL111</td>
<td>766</td>
<td>930</td>
<td>957</td>
<td>1192</td>
<td>1093</td>
<td>4938</td>
<td>111</td>
</tr>
</tbody>
</table>

P (Polarity) = sum of the first 5 McReynolds Constants.
P.N. (Polarity Number) = Polarity (P) normalized to SLB-IL100 (set at P=100).
Why SLB-IL60?

- Improved inertness over SLB-IL59
- Complimentary selectivity to PEG phases
- Higher maximum temperature than PEG phases
- Lower bleed than PEG phases
**Improved Inertness**

*C1-C12 n-Alcohols - 110 °C isothermal*

- Severe tailing
- C9-C12 alcohols adsorbed
Complimentary Selectivity to Wax

SLB-IL60

Wax

1. 2-Octanone
2. n-C15
3. n-Octanol
4. n-C16
5. n-C17
6. n-C18
7. 2,6-Dimethylphenol
8. 2,6-Dimethylaniline
9. n-C20
Higher Max Temp and Lower Bleed than Wax

SLB-IL60, $T_f = 300 \, ^\circ C$

- Wax #1, $T_f = 280 \, ^\circ C$
  - FID bleed at published temp. program max
  - Area Under the Curve (AU) = 8.3pA

- Wax #2, $T_f = 300 \, ^\circ C$
  - Area Under the Curve (AU) = 29.3pA
  - 129pA
Applications

• BTEX and n-alkanes
• Solvents on the SLB-IL60
• Fatty Acid Methyl Esters
BTEX + C9 to C14 n-alkanes

60 °C Isothermal

IL columns by increasing polarity numbers

SLB-IL59/
SLB-IL60

Significantly less retention of aliphatics

SLB-IL76

Significantly less retention of aliphatics
BTEX + C9 to C14 n-alkanes

60 °C Isothermal

Most polar IL column

C13 elutes before toluene

SLB-IL111
Chlorinated solvents on the SLB-IL60 & Wax

SLB-IL60

All resolved – yet faster elution

Wax

1. 1,1-Dichloroethylene
2. trans-1,2-Dichloroethylene
3. Methylene chloride
4. 1,1-Dichloroethane
5. Carbon tetrachloride
6. 1,1,1-Trichloroethane
7. Chloroform
8. Trichloroethylene
9. 1,2-Dichloroethane
10. Tetrachloroethene
11. 1,1,1,2-Tetrachloroethane
12. 1,1,2,2-Tetrachloroethane

SLB-IL60: 30 m x 0.25 mm I.D. x 0.20 µm
Wax: 30 m x 0.25 mm I.D. x 0.25 µm
Oven: 40 °C (4 min.), 8 °C/min. to 200 °C
Helium, 30 cm/sec, set at 120 °C
Ester & Ether solvents on the SLB-IL60 & Wax

SLB-IL60: 30 m x 0.25 mm I.D. x 0.20 µm
Wax: 30 m x 0.25 mm I.D. x 0.25 µm
Oven: 40 °C (4 min.), 8 °C/min. to 200 °C
Helium, 30 cm/sec, set at 120 °C

1. Methyl formate
2. Ethyl formate
3. Methyl acetate
4. Tetrahydrofuran
5. Ethyl acetate
6. Isopropyl acetate
7. n-Propyl acetate
8. 1,4-Dioxane
9. Isobutyl acetate
10. n-Butyl acetate
11. Isoamyl acetate
12. n-Amyl acetate
13. 2-Butoxyethano
C: contaminant (2-Methylbutyl acetate)
Cis / trans FAMES on SLB-IL60 vs. PEG Type Phase

C18:1n9 cis / trans FAMEs @ 180 °C

C18:2n6 cis & trans FAME Isomers- 180 °C
Peak list and run conditions for FAMEs

<table>
<thead>
<tr>
<th>Instrument:</th>
<th>GC-FID</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inj. Temp.:</td>
<td>250 °C</td>
</tr>
<tr>
<td>Det. Temp.:</td>
<td>260°C</td>
</tr>
<tr>
<td>Oven:</td>
<td>170 °C, 1 °C/min. to 225°C</td>
</tr>
<tr>
<td>Carrier gas:</td>
<td>helium, 1.2 mL/min constant flow (EPC)</td>
</tr>
<tr>
<td>Injection volume:</td>
<td>1 μL. 100:1 split</td>
</tr>
<tr>
<td>Injection type:</td>
<td>auto</td>
</tr>
<tr>
<td>Sample:</td>
<td>37-Component FAME Mix + C22:5n3</td>
</tr>
<tr>
<td>Liner:</td>
<td>4 mm ID focus liner</td>
</tr>
<tr>
<td>wash solvent:</td>
<td>Methylene chloride</td>
</tr>
</tbody>
</table>

1. C4:0  
2. C6:0  
3. C8:0  
4. C10:0  
5. C11:0  
6. C12:0  
7. C13:0  
8. C14:0  
9. C14:1  
10. C15:0  
11. C15:1  
12. C16:0  
13. C16:1  
14. C17:0  
15. C17:1  
16. C18:0  
17. C18:1n9c  
18. C18:1n9t  
19. C18:2n6c  
20. C18:2n6t  
21. C18:3n6  
22. C18:3n3  
23. C20:0  
24. C20:1n9  
25. C20:2  
26. C20:3n6  
27. C21:0  
28. C20:3n3  
29. C20:4n6  
30. C20:5n3  
31. C22:0  
32. C22:1n9  
33. C22:2  
34. C23:0  
35. C22:5n3 (added)  
36. C24:0  
37. C22:6n3  
38. C24:1n9  

GC analysis conditions are from methods AOAC 991.39 and AOCS CE-1i-07
Fame Elution order-
SLB-IL 60 compared to Wax

<table>
<thead>
<tr>
<th>Compounds</th>
<th>SLB-IL 60</th>
<th>Wax</th>
</tr>
</thead>
<tbody>
<tr>
<td>17: C18:1n9c</td>
<td>16</td>
<td>17</td>
</tr>
<tr>
<td>18: C18:1n9t</td>
<td>17</td>
<td>18</td>
</tr>
<tr>
<td>19: C18:2n6c</td>
<td>19</td>
<td>20</td>
</tr>
<tr>
<td>20: C18:2n6t</td>
<td>20</td>
<td>21</td>
</tr>
<tr>
<td>26: C20:3n6</td>
<td>26</td>
<td>27</td>
</tr>
<tr>
<td>28: C20:3n3</td>
<td>28</td>
<td>29</td>
</tr>
<tr>
<td>35: C22:5n3</td>
<td>35</td>
<td>36</td>
</tr>
<tr>
<td>36: C24:0</td>
<td>36</td>
<td>37</td>
</tr>
<tr>
<td>37: C22:6n3</td>
<td>37</td>
<td>38</td>
</tr>
</tbody>
</table>

Notable elution changes from wax column:
1. C18:1n9t elutes before C18:1n9c
2. C18:2n6t elutes before C18:2n6c
3. C20:3n3 elutes before C20:3n6
4. C22:6n3 elutes before C22:5n3 and C24:0
PUFA 3 Standard

SLB-IL60

Omegawax 250

Same analysis conditions as 37-component mix
Extract of Farm-Raised Atlantic Salmon

Samples prepared using AOCS Official Method Ce 1k-09; BHT added as an antioxidant
Conclusions

• Ionic Liquids are different than traditional polymer GC phases
  • Not susceptible to same stability issues as siloxane and PEG based phases
  • More “parts” to change thus more possible chemistries possible selectivity
  • Higher temp. limit than traditional phase of comparable polarity

• Ionic Liquids extend the polarity range of GC phases
  • SLB-IL111 more polar than any traditional phase

• SLB-IL60 Ionic Liquid Phase offers
  • Improved inertness over SLB-IL59
  • Complimentary selectivity to PEG phases
  • Higher maximum temperature than PEG phase
  • Lower bleed than PEG phases
  • Can be used for a wide variety of applications
Acknowledgements

- Prof. Daniel Armstrong, U. Texas Arlington
- Prof. Luigi Mondello, U. Messina, Messina, Italy
- Supelco R&D Team
- Our customers worldwide
Thank You