Innowacja w GC: ciecze jonowe jako fazy stacjonarne

SEMINARIUM ANALITYCZNE SIGMA-ALDRICH

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Overview

Structure of a Polysiloxane Polymer Phase

- **Drawbacks**
  - Active hydroxyl (-OH) groups at the polymer termini allow a back-biting reaction
    - Resulting in phase degradation
    - Contributing to column bleed
  - Chemistry modifications are limited to pendent group changes

\[
\begin{align*}
&\text{HO} &\text{Si} &\text{O} &\text{Si} &\text{O} &\text{H} \\
&R_1 & & & & & R_3 \\
&R_2 & & & & & R_4 \\
\end{align*}
\]

\( R = \) methyl, phenyl, fluoropropyl, and/or cyanopropyl (polarity increases from left).

\( x,y = \) percentage in the overall polymer composition.
Overview
Structure of a Polyethylene Glycol Phase

\[
\text{HO} \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{O} \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{O} \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{OH}
\]

• Drawbacks
  – Limited to 280 °C maximum temperature
  – Active hydroxyl (-OH) groups at the polymer termini allow a back-biting reaction
    ▪ Resulting in phase degradation
    ▪ Contributing to column bleed
  – Very limited chemistry modifications possible

\[ n = \text{number of monomer repetitions to make the overall polymer.} \]

Carbowax 20M (commonly used to make these) has a MW of 20,000.
Definition, Early Literature, and Use

• 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 \((\text{C}_2\text{H}_5\text{NH}_3^+)\text{(NO}_3^-)\), which has a melting point of 12 °C, was described in 1914

• Today, they are used as solvents, electrically conducting fluids, and sealants
Structure of an Ionic Liquid Phase

- Numerous combinations of cations, anions and linkers are possible allowing for “tailored” selectivity or application
  - Dicationic (shown) or polycationic
  - Cations (imidazolium, phosphonium, pyrrolidinium, …), anions (NTf₂⁻, triflat, tetrafluoroborate, hexafluorophosphate, …), and linkages (alkanes, polyethylenglycols, different lengths, …) can be changed
  - Pendant groups can be added to cations and/or linkages

Phase used to make the SLB-IL100

1,9-di(3-vinylimidazolium) nonane bis(trifluoromethyl) sulfonyle imide
Ionic Liquids in GC

• Several properties make ionic liquids desirable as GC stationary phases:
  – Very low volatility…
    ▪ should result in columns with lower bleed and longer life
  – Remain in the liquid state over a wide temperature range…
    ▪ should result in columns with extended temperature ranges
  – No active hydroxyl (-OH) groups at their termini…
    ▪ should result in columns resistant to damage from moisture/oxygen
  – Are inherently highly polar…
    ▪ should result in columns with higher polarity that have lower elution temperatures
      plus an increased selectivity for polarizable analytes
  – Have the broadest range of physical-chemical solvation interactions of any solvent…
    ▪ should result in columns with unique selectivity
  – High viscosity…
    ▪ should be easy to coat columns
Polarity scale for GC phases

Above scale: Position/Maximum temperature classical GC phases.
Below scale: Position/Maximum temperature of Ionic Liquid GC phases.
Ionic Liquid GC Columns from Sigma-Aldrich

Application areas include:

**Food & Beverage Applications**
- Fatty Acid Methyl Esters (FAMEs) by degree of unsaturation cis/trans
- Fatty Acid Methyl Ester (FAME) isomers

**GCxGC Applications**
- As the polar column for orthogonal separations

**Petroleum Applications**
- Fatty Acid Methyl Ester (FAME)
- Profile of B20 Biodiesel
- Benzene and other aromatics in gasoline

For more information, visit sigma-aldrich.com/il-gc
Selectivity Evaluations
Test Mix Peak IDs and Conditions

• Peak IDs (listed in boiling point order)
  – Toluene
  – Ethylbenzene
  – p-Xylene
  – Isopropylbenzene (Cumene)
  – Cyclohexanone
  – 1,2,4-Trimethylbenzene
  – 1,2,4,5-Tetramethylbenzene
  – n-Tridecane (C13)

• Conditions
  – columns: 30 m x 0.25 mm I.D., 0.20 µm
  – oven: 110 °C
  – inj.: 250 °C
  – det.: FID, 250 °C
  – carrier gas: helium, 26 cm/sec
  – injection: 1.0 µL, 100:1 split
  – sample: each analyte at various concentrations in isooctane
Test Mix on Ionic Liquid Columns
30 m Columns, 110 °C Isothermal

SLB-IL59
SLB-IL61
SLB-IL76
SLB-IL82
SLB-IL100
SLB-IL111
SLB®-IL60: Unique Selectivity

Figure 1. FAMEs

- Column 1: TRG 3, 30 m x 0.25 mm LD, 0.25 µm
- Column 2: SLB-8.40, 30 m x 0.25 mm LD, 0.20 µm (2965-U)
- Oven: 70°C, 1°C/min to 225°C
- Inj. Temp: 250°C
- Carrier gas: helium, 1.2 mL/min
- Det.: FID, 260°C
- Injection: 1 µL, 100:1 split
- Liner: 6.0 mm LD, split/splitless type, single taper wool packed Polysilane™ design
- Sample: Supelco 37 Component FAME Mix (47885-U) + C22:0 as internal standard in methylene chloride
SLB®-IL60:
 Improved Resolution
SLB®-IL60: Lower FID Bleed

Figure 1. FID Bleed Chromatograms

- PEG columns: 30 m x 0.25 mm I.D., 0.25 μm
- SLB-IL60 column: 30 m x 0.25 mm I.D., 0.20 μm (29555-U)
- Oven: 50 °C (2 min), 15 °C/min to column programmed temperature limit (10 min)
- Inj. Temp.: 250 °C
- Carrier gas: helium, 1 ml/min
- Detector: FID, at column programmed temperature limit
- Injection: 1 μl, splitless
- Liners: 4 mm ID, split/splitless type, single taper wool packed FocusLin™ design
- Sample: methylene chloride
Comparison of GC-MS TIC Bleed

Commercial WAX column #1 (max temp of 260 °C)

Commercial WAX column #2 (max temp of 280 °C)

SLB-IL76 (max temp of 270 °C)

SLB-IL59 (max temp of 300 °C)

All TICs are on the same Y-scale
SLB®-IL60: Better High Temperature Stability

Figure 1. FID Bleed Levels (pA) During Thermal Stress Test

![Bar chart showing FID bleed levels during thermal stress test.](image)

Figure 2. FID Bleed Levels (pA) Before/After Thermal Stress Test

![Bar chart showing FID bleed levels before and after thermal stress test.](image)
SLB®-IL60: Better High Temperature Stability

Figure 3. Selectivity Before/After Thermal Stress Test

- **Column 1:** PEG 3, 30 m x 0.25 mm I.D., 0.25 µm
- **Column 2:** SLB-IL60, 30 m x 0.25 mm I.D., 0.20 µm (29505-U)
- **Oven:** 155 °C (25 min) for PEG 3, 190 °C (25 min) for SLB-IL60
- **Injection:** 1 µL, 1000 split
- **Detector:** FID, 250 °C
- **Carrier gas:** helium, 20 cm/sec for PEG 3, helium, 25 cm/sec for SLB-IL60
- **Sample:** polar column test mix (47303), 9 analytes, each at 500 µg/mL in methylene chloride
SLB®-IL60: Stability to Loss of Carrier Gas Flow

Figure 1. Performance Before/After Stop Flow Test

- **Column:** SLB-IL60, 30 m x 0.25 mm I.D., 0.20 µm (29505-10)
- **Oven:** 130°C (25 min)
- **Injector Temp.:** 350°C
- **Carrier Gas:** Helium, 25 cm³/min
- **Detector:** FID, 250°C
- **Injection:** 1 µL, 1001 split
  - Liner: 4 mm I.D., split/splitless type, single taper wool packed FocusLiner™ design
- **Sample:** Polar column test mix (47302), 9 analytes, each at 500 µg/mL in methylene chloride

1. 2-Octanone
2. n-Pentadecane
3. 1-Octanol
4. n-Hexadecane
5. n-Heptadecane
6. n-Octadecane
7. 2,6-Dimethylphenol
8. 2,6-Dimethylaniline
9. n-Heptane

Chart showing performance before, after 1st hour, and after 2nd hour.
Air as Carrier Gas - Experimental Design

• Columns
  • Carbowax column, 30 m x 0.25 mm I.D., 0.25 µm
  • SLB-IL59 column, 30 m x 0.25 mm I.D., 0.20 µm

• Conditions
  • oven: 50 °C (2 min.), 4 °C/min. to 200 °C (15 min.)
  • inj.: 250 °C
  • det.: 250 °C
  • carrier gas: compressed air, 16 psi constant
  • injection: 1µL, 50:1 split
  • sample: Programmed Test Mix
Air as Carrier Gas - Carbowax Column

200 °C Ending Oven Temperature!

1st injection

After 100 injections

After 200 injections
Air as Carrier Gas – Ionic Liquid column

After 120 injections

After 220 injections

After 320 injections

After 420 injections

After 520 injections

After 620 injections

200 °C Ending Oven Temperature!
Summary

• GC phases based on Ionic Liquids:
  – have a different selectivity compared to conventional phases
  – allow for shorter analysis times
  – provide lower bleeding and long lifetime
  – offer a broader temperature range compared to conventional polar phases
  – improve multidimensional separations (orthogonal selectivity and high thermal stability of polar phase)
# Ordering Information

<table>
<thead>
<tr>
<th>Part Number</th>
<th>Description</th>
<th>Dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td>SLB-IL59</td>
<td>SLB®-IL59 Capillary GC Column</td>
<td>L x I.D. 15 m x 0.10 mm, df 0.08 μm</td>
</tr>
<tr>
<td>SLB-IL60</td>
<td>SLB-IL60 Capillary GC Column</td>
<td>L x I.D. 30 m x 0.25 mm, df 0.20 μm</td>
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<td>SLB-IL61</td>
<td>SLB-IL61 Capillary GC Column</td>
<td>L x I.D. 15 m x 0.10 mm, df 0.08 μm</td>
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<tr>
<td>SLB-IL76</td>
<td>SLB-IL76 Capillary GC Column</td>
<td>L x I.D. 15 m x 0.10 mm, df 0.08 μm</td>
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</tbody>
</table>

Phase: Non-bonded; 1,12-Di(tripropylphosphonium)dodecane bis(trifluoromethylsulfonyl)imide

Temp. Limits: Subambient to 300 °C (Isothermal or programmed)

1731,39 ÷ 2688,39 PLN netto
### Ordering Information

#### SLB-IL82
Phase: Non-bonded; 1,12-Di(2,3-dimethylimidazolium)dodecane bis(trifluoromethylsulfonyl)imide
Temp. Limits: 50 °C to 270 °C (isothermal or programmed)

<table>
<thead>
<tr>
<th>Code</th>
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<th>Length x I.D.</th>
<th>df</th>
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<td>29477-U</td>
<td>SLB-IL82 Capillary GC Column</td>
<td>L x I.D. 15 m x 0.10 mm, df 0.08 µm</td>
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<tr>
<td>29479-U</td>
<td>SLB-IL82 Capillary GC Column</td>
<td>L x I.D. 30 m x 0.25 mm, df 0.25 µm</td>
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#### SLB-IL100
Phase: Non-bonded; 1,9-Di(3-vinylimidazolium)nonane bis(trifluoromethylsulfonyl)imide
Temp. Limits: Subambient to 230 °C (isothermal or programmed)

<table>
<thead>
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<tr>
<td>28882-U</td>
<td>SLB-IL100 Capillary GC Column</td>
<td>L x I.D. 15 m x 0.10 mm, df 0.08 µm</td>
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<td>28883-U</td>
<td>SLB-IL100 Capillary GC Column</td>
<td>L x I.D. 20 m x 0.18 mm, df 0.14 µm</td>
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<tr>
<td>28884-U</td>
<td>SLB-IL100 Capillary GC Column</td>
<td>L x I.D. 30 m x 0.25 mm, df 0.20 µm</td>
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<tr>
<td>28886-U</td>
<td>SLB-IL100 Capillary GC Column</td>
<td>L x I.D. 60 m x 0.25 mm, df 0.20 µm</td>
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<td>28887-U</td>
<td>SLB-IL100 Capillary GC Column</td>
<td>L x I.D. 30 m x 0.32 mm, df 0.26 µm</td>
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<tr>
<td>28888-U</td>
<td>SLB-IL100 Capillary GC Column</td>
<td>L x I.D. 60 m x 0.32 mm, df 0.26 µm</td>
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#### SLB-IL111
Phase: Non-bonded; 1,5-Di(2,3-dimethylimidazolium)pentane bis(trifluoromethylsulfonyl)imide
Temp. Limits: 50 °C to 270 °C (isothermal or programmed)

<table>
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<tr>
<th>Code</th>
<th>Item Description</th>
<th>Length x I.D.</th>
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<td>28925-U</td>
<td>SLB-IL111 Capillary GC Column</td>
<td>L x I.D. 15 m x 0.10 mm, df 0.08 µm</td>
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<td>28927-U</td>
<td>SLB-IL111 Capillary GC Column</td>
<td>L x I.D. 30 m x 0.25 mm, df 0.20 µm</td>
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<td>28928-U</td>
<td>SLB-IL111 Capillary GC Column</td>
<td>L x I.D. 60 m x 0.25 mm, df 0.20 µm</td>
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<tr>
<td>29647-U</td>
<td>SLB-IL111 Capillary GC Column</td>
<td>L x I.D. 100 m x 0.25 mm, df 0.20 µm</td>
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</table>

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To Learn More…

- Visit our ionic liquid GC column landing page (sigma-aldrich.com/il-gc) at the Sigma-Aldrich web site
- Download or request “Supelco Ionic Liquid GC Columns: Applications”
- Download or request “Supelco Ionic Liquid GC Columns: Bibliography”
Related Products
Maximize Performance! Brochure (T407103 JWE)

- 28-page, 4-color, bundling brochure

- Lists common replacement items
  (septa, liners, ferrules, solvents, syringes, vials, purifiers, and much more)

- For several GC makes/models
  (Agilent/HP, PerkinElmer, Shimadzu, Thermo, and Varian)

A ‘must-have’ for all GC labs!
Can be downloaded from <sigma-aldrich.com/gc-learning>.
Resources

Complementary Pieces

- “Introduction to the Technology”
  - What are ionic liquid GC columns?
  - How do they relate to non-ionic liquid GC columns and to one another?
  - Selectivity information
  - Details about each phase

- “Bibliography”
  - Peer-reviewed journal articles leading up to and beyond the seminal 2005 JACS (Journal of the American Chemical Society) article
  - Updated periodically

Both pieces can be downloaded from <sigma-aldrich.com/il-gc-lit>.
Dziękuję za uwagę!