

# INVESTIGATION OF THE SELECTIVITY OF POLYIONIC IONIC LIQUID STATIONARY PHASES FOR CAPILLARY GAS CHROMATOGRAPHY

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## Abstract

Ionic liquids are a class of nonmolecular ionic solvents with low melting points. These liquids are a unique combination of cations and anions and can provide a variety of different selectivities when used as stationary phases in capillary gas chromatography. We have recently begun evaluating the selectivity and thermal stability of a number of different ionic liquid cation and anion combinations. Selectivity was determined and compared using various isothermal and temperature programmed test mixes. Thermal stability was determined by examining column performance during incremental (destructive) and long-term stability testing at various upper temperatures. Particular cation and anion combinations appear to provide the selectivity similar to polar polyethylene glycol and highly polar cyanosilicone phases while possibly providing higher maximum temperature stability.

## Introduction

Ionic liquids have received considerable interest as new green solvent systems in the areas of organic reactions<sup>1</sup> and separation technologies<sup>2,3</sup> along with a number of other areas. These materials are a class of non-molecular solvents which consist of essentially organic cations and anions. They have been found to possess negligible volatility, non-flammability, high thermal stability, and low melting points. There are numerous combinations of cations and anions possible, so tailoring the material to a specific application or function is a potential benefit of these materials.

Recently, a series of geminal dicationic ionic liquids have been prepared for use as stationary phases in capillary gas chromatography.<sup>4</sup> These materials are known to provide higher thermal stability for gas chromatography, broader liquid working ranges and broader selectivity ranges than monocationic ionic liquids.<sup>5</sup>

The purpose of this study is to investigate the selectivity of three different dicationic ionic liquids containing the same anion but differing in the cation or the alkyl chain linking the cations.

## Materials and Methods

Ionic Liquid stationary phases were prepared by Dr. Daniel W. Armstrong at the University of Texas @ Arlington.

All capillary columns were prepared at Supelco using the provided Ionic Liquid phases. 30 meter x 0.25 mm I.D. x 0.25  $\mu$ m df capillary columns were prepared using the following Ionic Liquids:

1,9-di(3-vinyl-imidazolium) nonane bis(trifluoromethyl) sulfonyl imidate (IL3), 1,5-di(3-butyl-imidazolium) pentyl bis(trifluoromethyl) sulfonyl imidate (IL10), 1,9-di(tri-propyl-phosphonium) nonane bis(trifluoromethyl) sulfonyl imidate (IL6).

The ionic liquid capillary columns were evaluated using a variety of standard test mixes under isothermal and temperature programmed conditions. The various test mixes used were designed to evaluate the efficiency, inertness, and selectivity of the ionic liquid phases. The test mixes used include:

### Naphthalene test mix

**Nonpolar and polar test mixes** containing a homologous series of n-alkanes along with the active probes 2-octanone, 1-octanol, 2,6-dimethylphenol, and 2,6-dimethylaniline.

### Grob mix

### C7 to C30 n-alkane mix

### Rapeseed oil FAMES

**37 component FAME** mix that mimics the fatty acid composition of grain, vegetable oils, dairy, and fish oils.

**BTEX mix** - Benzene, toluene, ethylbenzene and p, m, o-xylene.

**TCEP mix** designed to evaluate selectivity of a TCEP capillary column for the analysis of mineral spirits. We will only demonstrate the results for a few of the test standards.

## Results and Discussion

**Naphthalene Test Mix** The columns were first evaluated using naphthalene as the test probe @ 100 °C to determine the  $k'$  and efficiency.

(n=4)

	<b><math>k'</math> (Naphthalene)</b>	<b>Plates/meter</b>
IL 3	8.37 +/- 0.08	3545 +/- 170
IL 10	10.03 +/- 0.09	3847 +/- 150
IL 6	11.56 +/- 0.10	4000 +/- 75

## Rapeseed Oil Fame Analysis

Rapeseed oil is a simple vegetable oil that contains a series of saturated and unsaturated fatty acids ranging from C14 through C24 in carbon number. The composition of the mix is:

<b>1. Myristic (C14:0)</b>	<b>1.0%</b>
<b>2. Palmitic (C16:0)</b>	<b>4.0%</b>
<b>3. Stearic (C18:0)</b>	<b>3.0%</b>
<b>4. Oleic (C18:1n9c)</b>	<b>60.0%</b>
<b>5. Linoleic (C18:2)</b>	<b>12.0%</b>
<b>6. Linolenic (C18:3)</b>	<b>5.0%</b>
<b>7. Arachidic (C20:0)</b>	<b>3.0%</b>
<b>8. cis-11-Eicosenoic (C20:1)</b>	<b>1.0%</b>
<b>9. Behenic (C22:0)</b>	<b>3.0%</b>
<b>10. Erucic (C22:1)</b>	<b>5.0%</b>
<b>11. Lignoceric (C24:0)</b>	<b>3.0%</b>

The sample is methylated and analyzed as fatty acid methyl esters (FAMES). The elution pattern of the saturated versus unsaturated FAMES of the same carbon number is very indicative of the polarity of the phase. Nonpolar columns will elute the unsaturated FAMES prior to its saturated counterpart. Polar columns like a polyethylene glycol phase will elute the saturated FAMES first followed by the monoene, diene, triene, and high poly-unsaturates of the same carbon number, with minimal to no overlap of the carbon chain lengths.

Highly polar columns containing greater than 90% cyanopropyl substitution in the polymer backbone will elute the saturated and unsaturated FAMES in a pattern similar to the polar columns but there will be an overlap of the carbon chain lengths. Typically, the triene and higher polyunsaturates will elute after the saturated FAME of a longer carbon number chain length. The key area to evaluate is the elution pattern of the C18 carbon chain lengths relative to the C20 chain lengths. The saturated C18 FAME elutes first followed by the monoene (C18:1) and diene (C18:2). The next eluting FAME is the C20 saturate (C20:0) followed the C18:3 triene and then the C20 monoene (C20:1).

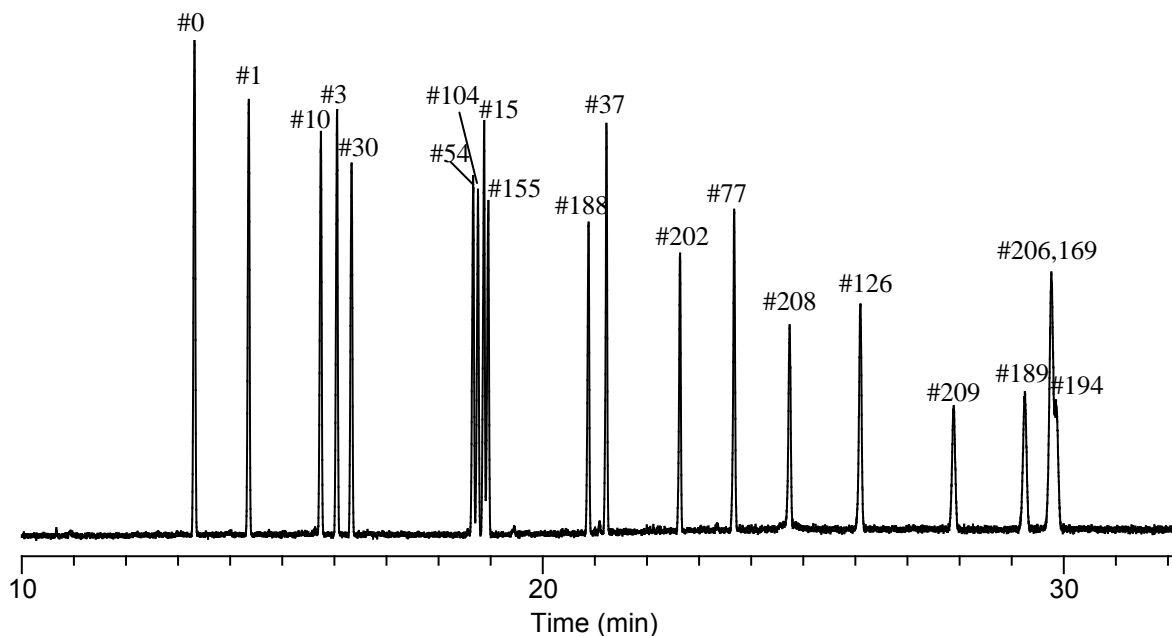
## PCB Congeners on the SLB-IL100

PCB congeners are hydrophobic, and when analyzed on a non-polar capillary column, such as a poly(5% diphenyl/95% dimethylsiloxane), retention increases with the degree of chlorination, with more overlap between the elution ranges as chlorination increases. The deca-chlorinated congener (decachlorobiphenyl), being the heaviest and most hydrophobic, elutes last.

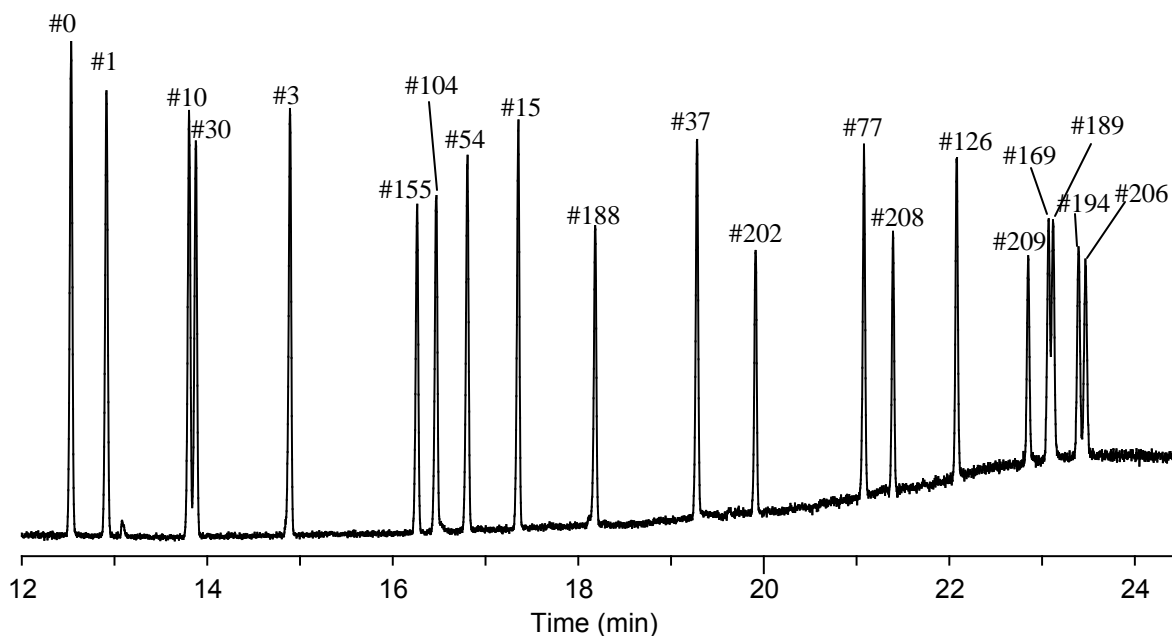
By contrast, on a highly polar column such as the SP-2331, the elution pattern is quite different. The analysis of a mixture of mono-chlorinated through deca-chlorinated congeners on the SP-2331 is presented in figure 3. The deca-chlorinated congener, #209, actually elutes prior to several other congeners. While dispersive interaction is the primary mechanism exhibited by non-polar columns, separation using a polysiloxane phase with a high biscyanopropyl content such as the SP-2331 will be governed by additional mechanisms such as strong dipole-induced dipole interactions. As a result, the deca-chlorinated congener is not as retained on this phase. The same mixture on the SLB-IL100, under the same analysis conditions, is presented in figure 4. Notice that, similar to the SP-2331, #209 elutes prior to several other congeners. However, the higher polarity of the SLB-IL100 has resulted in shorter elution time than the SP-2331 for all congeners. In addition to a shorter elution time, some elution order differences were observed between the two columns, as summarized in table 2. The structure of PCB congeners suggests that they are capable of dipole and  $\pi$  interactions. While dipole-induced dipole interactions are likely the predominant contributor

to selectivity for the SP-2331, the ionic liquid used in the SLB-IL100 has the additional capability of interacting with the congeners'  $\pi$  electrons, thus providing it with different selectivity than the SP-2331.

**Figure 1. PCB Congener standard, mono thru deca, on the SP-2331**



**Figure 2. PCB Congener standard, mono thru deca, on the SLB-IL100.**



### Run conditions for figures 1 and 2

Columns:

SP-2331, 30 m x 0.25 mm I.D. x 0.20  $\mu\text{m}$  (24257)

SLB-IL100, 30 m x 0.25 mm I.D. x 0.20  $\mu\text{m}$  (28884-U)

Oven: 60 °C (1 min.), 8 °C/min. to 230 °C

Inj.: 250 °C

MSD interface: 220 °C

Carrier Gas: helium, 1.5 mL/min constant flow

Injection: 1  $\mu\text{L}$ , splitless (splitter open at 1 min.)

Liner: 4 mm I.D. single taper

Sample: PCB congener mix, 2.5 ppm @ in n-hexane

### PCB Congener IDs

#0: Biphenyl

#1: 2-monochlorobiphenyl

#3: 4-monochlorobiphenyl

#10: 2,6-dichlorobiphenyl

#15: 4,4'-dichlorobiphenyl

#30: 2,4,6-trichlorobiphenyl

#37: 3,4,4'-trichlorobiphenyl

#54: 2,2',6,6'-tetrachlorobiphenyl

#77: 3,3',4,4'-tetrachlorobiphenyl

#104: 2,2',4,6,6'-pentachlorobiphenyl

#126: 3,3',4,4',5-pentachlorobiphenyl

#155: 2,2',4,4',6,6'-hexachlorobiphenyl

#169: 3,3',4,4',5,5'-hexachlorobiphenyl

#188: 2,2',3,4',5,6,6'-heptachlorobiphenyl

#189: 2,3,3',4,4',5,5'-heptachlorobiphenyl

#202: 2,2',3,3',5,5',6,6'-octachlorobiphenyl

#194: 2,2',3,3',4,4',5,5'-octachlorobiphenyl

#208: 2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl

#206: 2,2',3,3',4,4',5,5',6-nonachlorobiphenyl

#209: Decachlorobiphenyl

### **Conclusions**

Three geminal dicationic ionic liquid stationary phases have been evaluated. The cation group has the greatest influence on the selectivity of the ionic liquid phases in this study while the spacer linkage appears to only minimally affect the selectivity. A 1,9-di(3-vinyl-imidazolium) nonane bis((trifluoromethyl) sulfonyl imidate (IL3) Ionic liquid phase has a polarity similar to TCEP. Ionic Liquid 3 has an approximate maximum temperature of at least 240 °C which is a significant improvement over the 140 °C maximum temperature of TCEP.

### **Acknowledgements**

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