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

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Ionic liquids are a class of solvents with low melting points that consist of organic cations associated with inorganic or organic anions. (Figure 1) These compounds exhibit ideal properties for a stationary phase in gas chromatography such as very low vapour pressure and high thermal stability [1]

The application of new dicationic liquids as stationary phases improved the efficiency as well as the thermal stability of the phases. [2] These unique combinations of cations and anions can provide a variety of different and unique selectivity's when used as capillary GC stationary phases.

This work focuses on the SLB-IL60 ionic liquid phase which has selectivity similar to a polyethylene glycol (PEG) or Wax phase as was previously discussed by Zeng, et.al. [3], Cagliero, et. al [4] Ragonese, et. al [5] and Poole [6]. By injecting a series of non-polar and polar analytes, a number of the ionic liquid columns were evaluated. The new phase based on the phosphonium ionic liquids was applied to several challenging applications usually analysed on a WAX phase. The unique selectivity and high thermal stability of the new phase allowed the development of unique and improved GC separations for these applications.

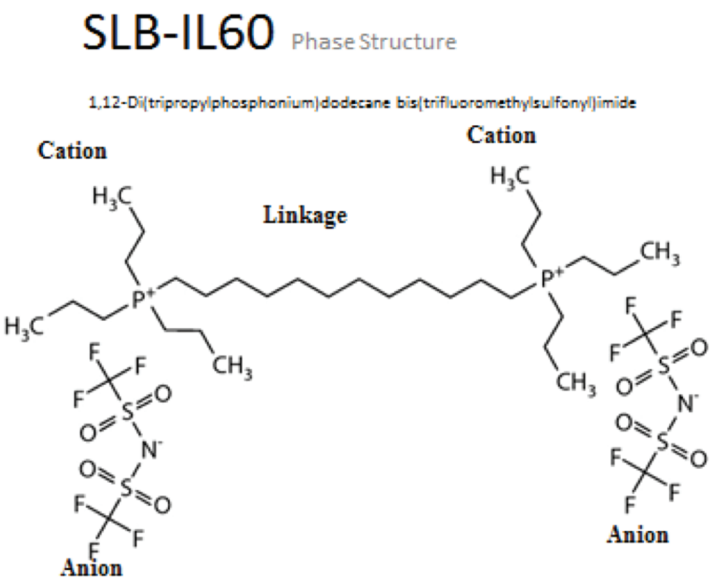

Figure 1: Structure of the SLB-IL60 - 1,12-di(tripropylphosphonium)dodecane bis(trifluoromethylsulfonyl)imide

Results and Discussion

Polarity Classification of Ionic Liquid GC Phases

In order to obtain a single parameter for comparing the relative polarity of the ionic liquid phases to classical and conventional GC phases a polarity scale was suggested by Professor Luigi Mondello of the University of Messina, Italy. This scale is visually represented in Figure 2. Each column is characterised with a series of five probes plus several n-alkane markers to determine the retention index for each probe. The first five McReynolds Probes were used as the marker compounds as these are the traditional probes that have been used to benchmark polarity of GC phases for many years. The compounds are: benzene,

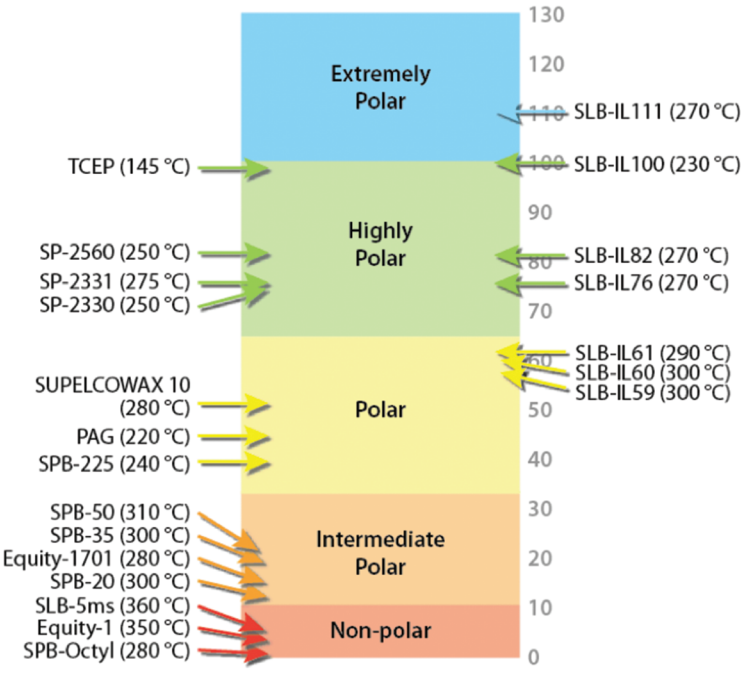

Figure 2: Visual Polarity Comparison of Ionic Liquid and Conventional GC Phases

n-butanol, 2-pentanone, nitropropane, and 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 McReynold's Constants are summed to obtain Polarity (P) values, which are then normalised to SLB-IL100 (set at P=100) to obtain Polarity Number (P.N.) values.

To investigate the selectivity of the various ionic liquid GC phases, a test mix composed of aliphatic, aromatic and polar compounds was analysed at one isothermal temperature. Figure 3 compares the chromatograms. The analyses showed the more polar the stationary phase is the greater retention of polar compounds and less retention of the nonpolar aliphatic compounds. Tridecane (C13) demonstrates the typical shorter retention of an aliphatic hydrocarbon as the column polarity increases. The columns are listed in order of least polar (SLB-IL59) to most polar (SLB-IL111). The least polar phases, (SLB-IL59, 60 and 61) are based on dicationic phosphonium cations. SLB-IL76 has a trigonal phosphonium cation. The three most polar ionic liquid phases (SLB-IL82, 100 and 111) are all dicationic imidazolium cations.

SLB-IL60 is an ionic liquid phase with a polarity that is similar to that of a polyethylene glycol (PEG) phase. SLB-IL60 is able to undergo the same analyte-phase interactions as polyethylene glycol (PEG) columns, but at different relative amounts. Based on its unique phase structure, the SLB-IL60 column is also able to undergo additional interactions that PEG columns cannot. With PEG columns, possible interactions appear to be dispersive, hydrogen bonding, and acid-base interactions. With the SLB-IL60 column, possible interactions appear to be dispersive, dipole-dipole, dipole-induced dipole, pi-pi, hydrogen bonding, and acid-base interactions. Due to these additional interaction mechanisms, the SLB-IL60 column will retain some polar and polarisable analytes relatively longer, and some non-polar analytes relatively less. This results in unique and alternate selectivity compared to PEG columns.

Figure 4 compares the selectivity of the SLB-IL60 to that of Supelcowax 10 performed by evaluating a series of normal alkanes (C15,16,17,18 and 20) along with 2-octanone, 1-octanol, 2,6-dimethylaniline and 2,6-dimethylphenol. The elution pattern is similar on both columns as 2-octanone elutes prior to C15 and 1-octanol elutes

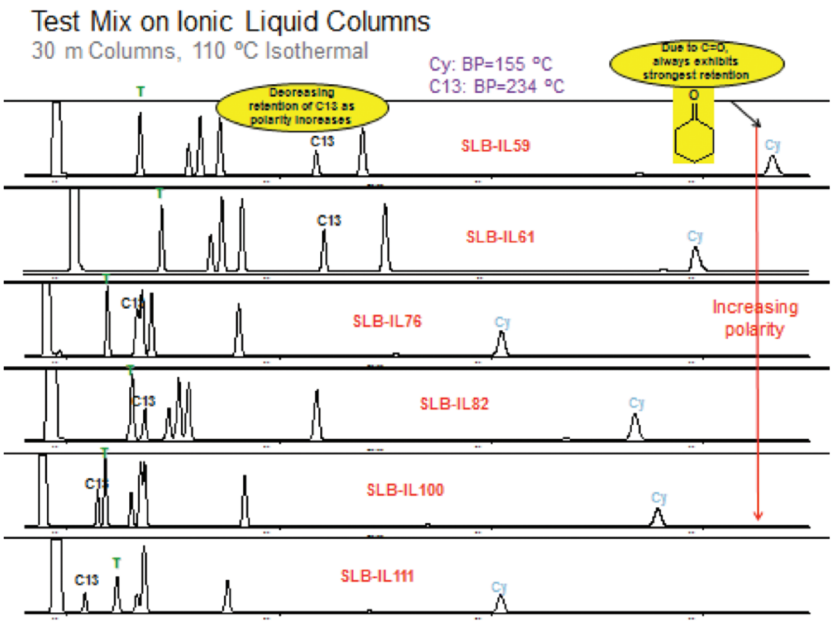

Figure 3: Comparison of the Ionic liquid Column Selectivity, 30m x 0.25mm ID x 0.25µm df, Oven: 110°C, Inj, 250°C, Det. FID 250°C, Carrier Gas: Helium, 25cm/ sec at 110°C, Injection: 1µl, 100:1 Split, Sample Components: toluene, ethylbenzene, p-xylene, isopropylbenzene, cyclohexanone, 1,2,4-trimethylbenzene, 1,2,4,5,- tetramethylbenzene, n-tridecane (C13).

Complimentary Selectivity to Wax

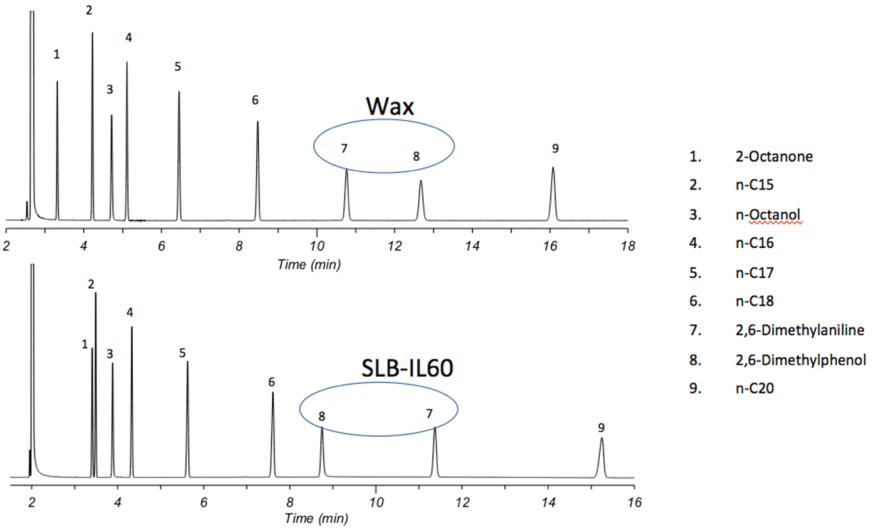

Figure 4: Selectivity Comparison of SLB-IL60 and Supelcowax-10
SLB-IL60 column: SLB-IL60, 30 m x 0.25 mm I.D., 0.20 µm (29505-U)
Supelcowax 10: 30 m x 0.25 mm I.D., 0.25 µm
oven: SLB-IL60- 130°C isothermal
Supelcowax 10- 155°C isothermal
inj. temp.: 250°C
carrier gas: helium, 25cm/sec set at the isothermal temperature
detector: FID, 250°C
injection: 1 µL, split 100:1

between the C15 and C16 alkanes. A difference in selectivity is demonstrated as 2,6-dimethylphenol elutes prior to 2,6-dimethylaniline on the SLB-IL60 column.

FAME analyses also demonstrate the similarity and differences in the selectivity of the SLB-IL60 columns and traditional PEG columns. Traditional PEG phases typically elutes FAME isomers by degree of unsaturation within a carbon chain length with minimal overlap of the even carbon chain lengths. Figure 5 compares the elution pattern of a PUFA 3 fish oil sample on the SLB-IL60 and an Omegawax 250 capillary column. A similar elution pattern is demonstrated for the C18 carbon number series. As the carbon chain lengths increase along with the degree of unsaturation in

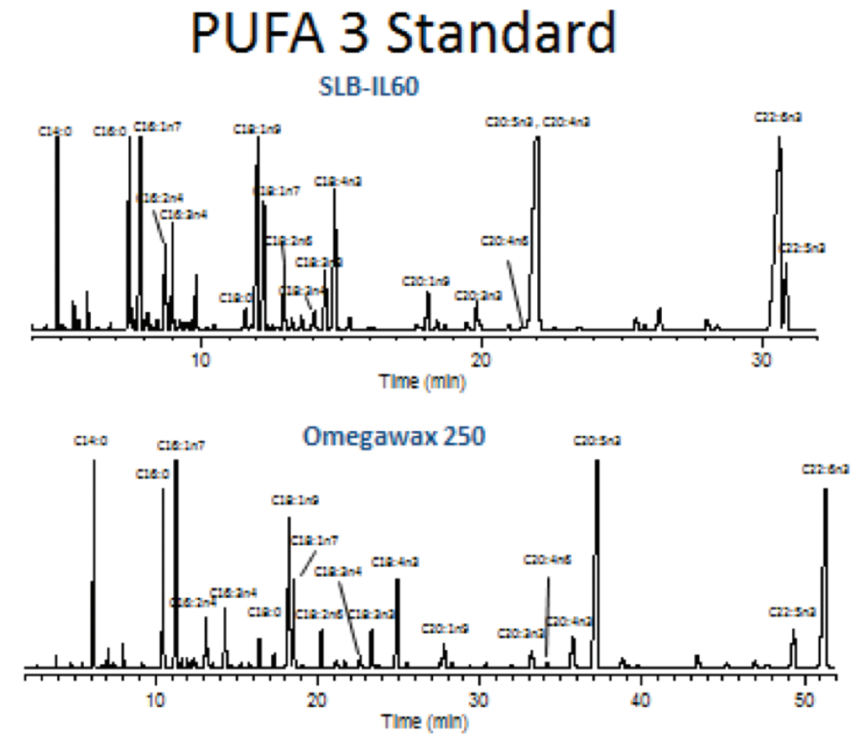

Figure 5: FAME Selectivity Comparison of SLB-IL60 and Omegawax 250
Conditions
Omegawax 250: 30 m x 0.25 mm I.D., 0.25 µm
SLB-IL60 column: SLB-IL60, 30 m x 0.25 mm I.D., 0.20 µm (29505-U)
oven: SLB-IL60- 180°C isothermal
Omegawax 250- 190°C isothermal
inj. temp.: 250°C
carrier gas: helium, 1 mL/min
detector: FID, 250°C
injection: 1 µL, split 100:1

the FAME compounds some unique shifting in the elution pattterns are demonstrated. Specifically, the SLB-IL60 column elutes the C22:6n3 FAME prior to the C22:5n3 FAME while the Omegawax 250 provides the typical PEG elution pattern of these two compounds.

Another application that demonstrates differences in selectivity of the SLB-IL60 and a traditonal PEG column is the analysis of cis and trans fatty acid methyl esters (FAMEs). Traditional PEG phases typically elute the cis isomers as a group prior to the trans isomers group with little to no separation of the geometric isomers of the same degree of unsaturation (monoene, diene, triene, etc>). Figure 6 demonstrates the separation of C18:1 and C18:2 cis and trans FAMEs on both the SLB-IL60 and the traditional PEG column.

Traditional polyethylene glycol phases (PEG) are known to provide cis & trans isomer separation with the cis isomer eluting prior to the trans isomer. The SLB-IL60 ionic liquid column (with a PEG like polarity) offers a unique selectivity for cis and trans isomer separations as the trans isomer elutes prior to the cis isomers. The elution of the trans isomer prior to the cis isomer is similar to the selectivity of the more highly polar cyanosilicone phases containing greater than 90% cyanopropyl substitution in the polymer backbone.

Thermal Stability

Higher temperature GC columns are desirable, as they may allow decreased analysis times, elevated bake-out to remove large non-target compounds, and analysis of higher boiling compounds. However, higher oven temperatures also tend to accelerate the amount of column bleed. When working with a flame ionisation detector (FID), excessive bleed is undesirable as it lowers the signal-to-noise, resulting in a loss of sensitivity. Column manufacturers routinely list the maximum temperature a column can safely be used at before the level of column bleed renders the column unusable.

To illustrate the lower FID bleed characteristic of the SLB-IL60 column, it was compared directly to five popular commercially available PEG columns, each from a different manufacturer. All columns were 30 m x 0.25 mm I.D., 0.25 µm dimensions, except the SLB-IL60 column, which has a 0.20 µm film thickness. The slightly lower film thickness for the SLB-IL60 column contributes to a slightly lower bleed than the 0.25 µm films for the PEG columns but it is not the major factor for the lower bleed.

Table 1 shows the maximum temperature limits for all columns tested.

*Table 1. Maximum Temperature Limits**

Column	Isothermal	Programmed
PEG 1	280°C	280°C
PEG 2	260°C	270°C
PEG 3	250°C	260°C
PEG 4	250°C	260°C
PEG 5	280°C	300°C
SLB-IL60	300°C	300°C

** Obtained from paperwork included with commercial columns.*

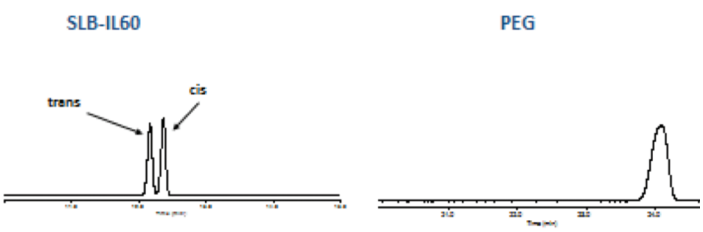

Figure 6a: C18:1n9 cis & trans FAMEs @ 180°C

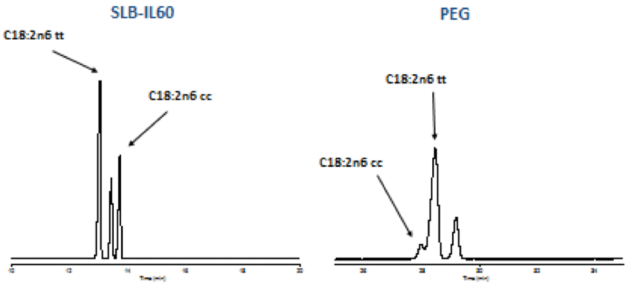

Figure 6b: C18:2n6 cis & trans FAMEs @ 180°C

FID Bleed Comparison

Following column installation of new columns, conditioning, and the analysis of two test mixes to demonstrate the column and system were working properly, a temperature programmed bleed run was performed. The final temperature used for each column was based on its programmed temperature limit. An overlay of all six chromatograms is displayed in Figure 7. As shown, only the PEG 4 column exhibited a lower FID bleed level than the SLB-IL60, but did so at a final oven temperature that was 40°C lower. The PEG 5 column exhibited the highest FID bleed, which is surprising considering it has a 300°C limit for progammed use.

Conclusions

Ionic liquid GC columns provide advantages in terms of selectivity, maximum temperature and thermal stability to conventional columns of similar polarity. SLB-IL60 offers a slightly different selectivity compared to PEG phases and a higher maximum temperature and lower FID bleed than PEG/WAX phases.

References

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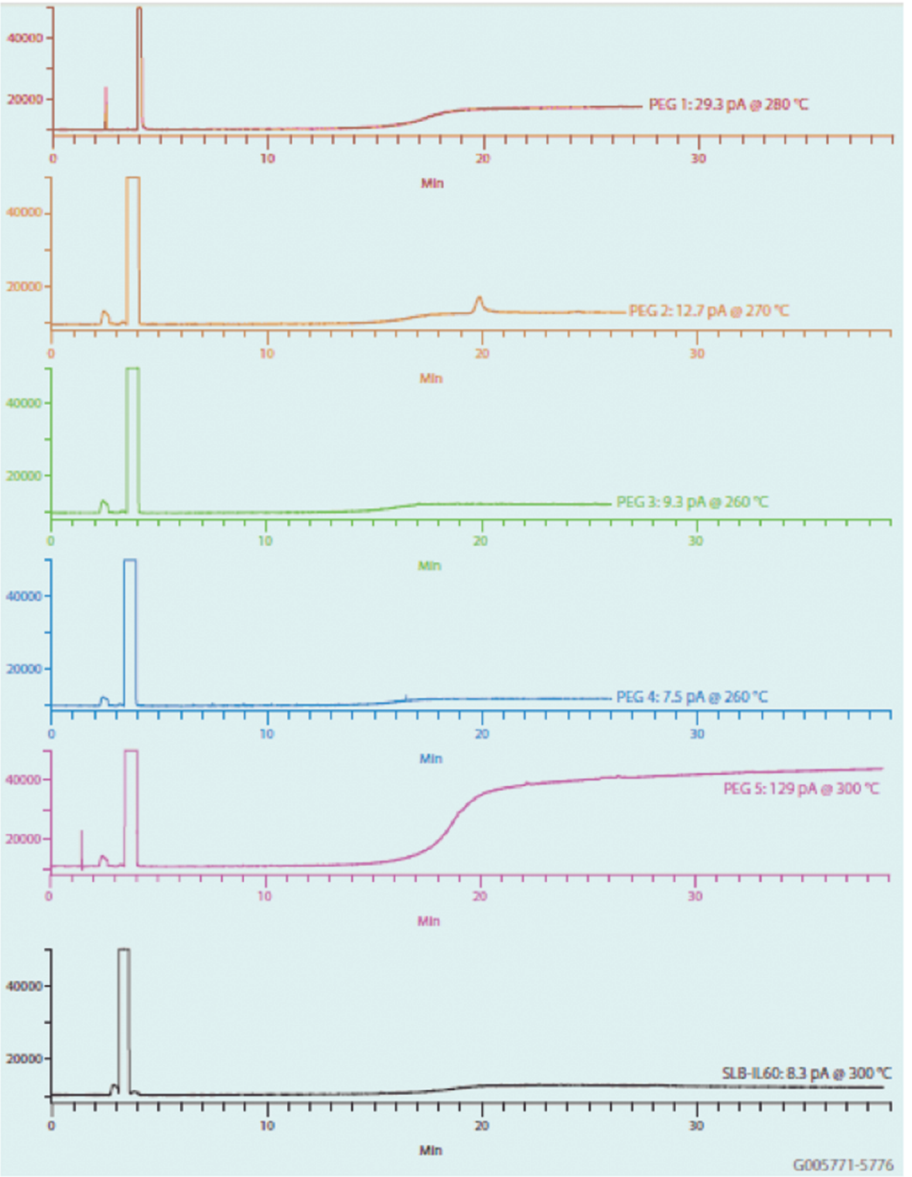

Figure 7: FID Bleed Chromatograms
Conditions
PEG columns: 30 m x 0.25 mm I.D., 0.25 µm
SLB-IL60 column: SLB-IL60, 30 m x 0.25 mm I.D., 0.20 µm (29505-U)
oven: 50°C (2 min), 15°C/min to column programmed temperature limit (10 min)
inj. temp.: 250°C
carrier gas: helium, 1 mL/min
detector: FID, at column programmed temperature limit
injection: 1 µL, splitless
sample: methylene chloride