Crosslinked Structurally-tuned Polymeric Ionic Liquids as Stationary Phases for the Analysis of Hydrocarbons in Kerosene and Diesel Fuels by Comprehensive Two-dimensional Gas Chromatography

Cheng Zhang,^a Rodney A. Park,^b and Jared L. Anderson^{a,*}

^a Department of Chemistry, Iowa State University, Ames, Iowa, 50011, USA

^b Department of Chemistry and Biochemistry, The University of Toledo, Toledo, OH 43606, USA

Abstract

Structurally tuned ionic liquids (ILs) have been previously applied as the second dimension column in comprehensive two-dimensional gas chromatography (GC×GC) and have demonstrated high selectivity in the separation of **individual** aliphatic hydrocarbons from **other aliphatic hydrocarbons**. However, the maximum operating temperatures of these stationary phases limit the separation of analytes with high boiling points. In order to address this issue, a series of polymeric ionic liquid (PIL)-based stationary phases were prepared in this study using imidazolium-based IL monomers via in-column free radical polymerization. The IL monomers were functionalized with long alkyl chain substituents to provide the needed selectivity for the separation of aliphatic hydrocarbons. Columns were prepared with different film thicknesses to identify the best performing stationary phase for the separation of kerosene. The bis[(trifluoromethyl)sulfonyl]imide ([NTf₂]⁻)-based PIL stationary phase with larger film thickness (0.28 μm) exhibited higher selectivity for aliphatic hydrocarbons and showed a maximum allowable operating temperature of 300 °C. PIL-based stationary phases containing varied amount of IL -based crosslinker were prepared to study the effect of the crosslinker on the selectivity and thermal stability of the resulting stationary phase. The optimal resolution of aliphatic hydrocarbons was achieved when 50% (w/w) of crosslinker was incorporated into the PIL-based stationary phase. The resulting stationary phase exhibited good selectivity for **different groups of** aliphatic hydrocarbons even after being conditioned at 325 °C, ~~a significantly higher operating temperature than can be achieved using commercial PEG stationary phases~~. Finally, the crosslinked PIL-based stationary phase was compared with SUPELCOWAX 10 and DB-17 columns for the separation of

aliphatic hydrocarbons in diesel fuel. Better resolution of aliphatic hydrocarbons was obtained when employing the crosslinked PIL-based stationary phase as the second dimension column.

Keywords: ionic liquid; polymeric ionic liquid; comprehensive two-dimensional gas chromatography; petrochemical separation; stationary phase

*Corresponding Author:

Jared L. Anderson

Department of Chemistry

Iowa State University

Ames, Iowa, 50011, USA

+1 (515) 294-8356

E-mail address: andersoj@iastate.edu

1. Introduction

The trace level separation and analysis of complex mixtures such as petroleum products, fragrances, and organic pollutants can be very challenging. These samples typically contain hundreds to thousands of components which possess a wide range of properties often present at varied concentration levels [1]. Comprehensive two-dimensional gas chromatography (GC×GC) is a powerful and versatile tool for the separation, identification, and quantification of volatile and semi-volatile analytes in complex samples [2-8]. By employing two gas chromatographic separations in a continuous and sequential fashion, the peak capacity of the separation system can be significantly increased. In order to achieve a significant improvement in the resolving power, the two employed stationary phases should possess distinct solvation properties. Polysiloxane and polyethylene glycol (PEG)-derived stationary phases are commonly employed in GC × GC separations. By applying these stationary phases in nonpolar × polar or polar × nonpolar column sets, a broad spectrum of analytes, including hydrocarbons [9,10], fatty acid methyl esters [11,12], flavors and fragrance [13,14] have been successfully separated. However, the main limitation of polyethylene glycol-derived stationary phases is their limited operation at high temperature, which can significantly limit the applications of GC×GC for high temperature analysis.

Ionic liquids (ILs) are class of organic salts with low melting points (usually defined as below 100 °C) and have been applied as stationary phases in gas chromatography [15-17]. These compounds exhibit unique characteristics such as high thermal stability, negligible vapor pressures, wide liquid ranges, and tunable selectivity. A number of IL stationary phases have been commercialized and their thermal stabilities reported [18]. For example, SLB-IL 59 and SLB-IL 60 stationary phases have a maximum allowable operating temperature (MAOT) of 300 °C, which is significantly higher than the polar PEG columns. The increased thermal stability of IL-based stationary phases has expanded the analysis of complex samples with high boiling points, such as coal tar [19] and heavy petroleum fractions [20,21]. However, the resolving power offered by commercial IL-based columns is still limited. For example, aliphatic hydrocarbons can not be resolved on commercial IL-based stationary phases in GC×GC separations [22].

Our group has reported that dicationic ILs containing long free alkyl side chain

substituents and lengthy linkage chains between the two cations exhibit high selectivity in the separation of different groups of aliphatic hydrocarbons when used as second dimension stationary phases in GC×GC [23]. The thermal stability of the dicationic IL-based stationary phases was slightly lower than the PEG column, which may not be sufficient for high temperature GC×GC separations. One approach to improve the thermal stability is to explore polymeric analogs of ILs that possess the necessary structural features to provide high separation selectivity for target analytes. Compared to monocationic or dicationic ILs with similar structural features, PIL-based stationary phases offer similar solvation properties but often exhibit higher thermal stability [24]. The thermal stability of the stationary phases can be further enhanced by creating crosslinked PIL stationary phases.

In this study, a total of 15 PIL-based stationary phases were prepared using imidazolium-based IL monomers via in-column free radical polymerization. To overcome the aforementioned challenges while retaining the unique solvation characteristics of the ILs, all PIL-based stationary phases were functionalized with long alkyl chain substituents to provide the selectivity required for the separation of individual aliphatic hydrocarbons from other aliphatic hydrocarbons in kerosene. The effect of the IL anion, film thickness of the stationary phase, and the chain length/amount of the IL-based crosslinker were evaluated and carefully optimized to prepare a highly selective stationary phase for the separation of aliphatic hydrocarbons under high separation temperatures. The inner surface of the capillary wall was modified with vinyltrimethoxysilane (VTMS) to produce a highly immobilized stationary phase. The best performing crosslinked PIL-based stationary phase was used for the GC×GC separation of diesel samples. Compared to the commercial PEG and DB-17 columns, crosslinked PIL-based stationary phases exhibited better separation performance in terms of selectivity and thermal stability.

2. Experimental procedures

2.1. Materials

1-vinylimidazole (99%), 1-bromohexadecane (97%), 1,4 dibromobutane (99%), 1,8 dibromooctane (98%), 1,12-dibromododecane (98%), 2,2'-azobis (2-methylpropionitrile) (98%) (AIBN), vinyltrimethoxysilane (98%) (VTMS), and iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) (97%) were purchased from

Sigma-Aldrich (St. Louis, MO, USA). Lithium bis[(trifluoromethyl)sulfonyl]imide was purchased from SynQuest Labs (Alachua, FL, USA). Methylene chloride, methanol, isopropanol, ethyl acetate, and hexane (HPLC grade) were purchased from Fisher Scientific (Fair Lawn, NJ, USA). Untreated fused silica capillary (0.25-mm I.D.) and SUPELCOWAX 10 column (30 m $\times$ 200 μ m, d_f = 0.20 μ m) were purchased from Supelco (Bellefonte, PA, USA). CP-Wax 52 CB(30 m $\times$ 200 μ m, d_f = 0.20 μ m), DB-WAX (30 m $\times$ 200 μ m, d_f = 0.20 μ m), HP-INNOWax (30 m $\times$ 200 μ m, d_f = 0.20 μ m), and DB-17 (20 m $\times$ 180 μ m, d_f = 0.18 μ m) columns were purchased from Agilent (Santa Clara, CA, USA). Kerosene and diesel fuels were purchased from a local distributor.

2.2. Chromatographic instrumentation

All gas chromatography measurements used to characterize the IL-based columns were performed on an Agilent 6850 gas chromatograph employing a flame ionization detector (GC-FID). Two-dimensional separations were performed on a GC $\times$ GC-FID system using an Agilent 6890 GC-FID equipped with a two-stage cryogenic loop modulator. A full description and illustration of the home built system has been previously reported [22].

2.3 Synthesis of ionic liquid monomer and cross-linkers

Chemical structures of the IL monomers and IL-based cross-linkers used in this work are shown in Figure 1. Synthesis of the IL monomer and cross-linkers was performed according to previously reported procedures [25-27]. Briefly, 0.05 mol of 1-vinylimidazole and 0.075 mol of 1-bromohexadecane were mixed in 15 mL of isopropanol at 70 °C for 24 h. The product was then dissolved in 10 mL of water and washed purified with three 10 mL aliquots of ethyl acetate. The water layer containing the IL monomer was recovered and dried under vacuum at 80 °C for 24 h to yield [VHDIM] [Br]. The halide counteranion was then exchanged to [NTf₂] or [FeCl₃Br] by metathesis reaction using one equivalent of lithium bis[(trifluoromethyl)sulfonyl]imide or FeCl₃•6H₂O. The mixture was then stirred overnight at room temperature and washed with water to yield [VHDIM] [NTf₂] and [VHDIM] [FeCl₃Br]. The IL-based crosslinker was synthesized by reacting 0.1 mol of 1-vinylimidazole with 0.05 mol of 1,4 dibromobutane in 15 mL of isopropanol at 70 °C for 24 h. The dicationic IL was then dissolved in 10 mL of water and washed

purified with three 10 mL aliquots of ethyl acetate, and dried under vacuum at 80 °C for 24 h. Crosslinkers with octyl or dodecyl linkage chains separating the two cations were synthesized using a similar approach [27]. The halide counteranion was then exchanged to [NTf₂] or [FeCl₃Br] by metathesis reaction using one molar equivalent of lithium bis[(trifluoromethyl)sulfonyl]imide or FeCl₃•6H₂O to yield [(VIM)₂C₄] 2[NTf₂], [(VIM)₂C₈] 2[NTf₂], [(VIM)₂C₁₂] 2[NTf₂], and[(VIM)₂C₁₂] 2[FeCl₃Br]. The NMR spectra for all IL monomers and IL-based crosslinkers are shown in Figure S1-S6 (Supplementary Information).

2.4. GC column preparation

Surface modification of the capillary was performed using two methods prior to coating. In the first method, the capillary was filled with VTMS. Both ends of the capillary were then sealed and the capillary placed in a GC oven at 85 °C for 2 h to chemically bond the organosilane to the silanol groups on the inner capillary surface. The capillary was then purged with nitrogen and conditioned at 150°C for 10 min. In the second method, the capillary was filled with VTMS vapor at 150°C for 30 min. The capillary was then purged with nitrogen and conditioned at 150°C for 10 min.

Prior to coating the IL-based columns, all IL monomers and crosslinkers were placed under vacuum at 75 °C overnight to remove any traces of solvent. A 0.25% (w/v) or 0.45% (w/v) coating solution was prepared by dissolving the mixture of IL monomer, IL cross-linker and AIBN (3.5% w/w) in dry methylene chloride. Five-meter segments of capillary column were coated by the static method at 40°C. After coating, the two ends of the GC capillary were sealed and the capillary was placed in a GC oven and heated from 40 °C to 80 °C at 2 °C min⁻¹. The capillary was then held isothermally at 80 °C for 5 h to ensure complete polymerization. The prepared columns were conditioned from 30 °C to 100 °C at 2 °C min⁻¹ and held isothermally at 100 °C for 3 h. Hydrogen was used as a carrier gas at a constant flow of 1 mL min⁻¹. Column efficiency was determined using naphthalene at 100 °C. All coated columns possessed efficiencies of at least 1875 plates per meter. The composition, efficiency, and retention factor of naphthalene for all PIL-based columns prepared and evaluated in this study are shown in Table 1.

2.5. Chromatographic analysis by GC×GC-FID

When evaluating the selectivity of the PIL-based columns by GC×GC-FID analysis, the primary column consisted of a Rtx-5 capillary column (30 m × 250 μ m, d_f = 0.25 μ m, Restek, Bellefonte, PA, USA) connected to a second dimension PIL-coated capillary column (1.2 m × 250 μ m, d_f = 0.15 or 0.28 μ m). In all experiments, 0.5 μ L of the kerosene or diesel sample was injected using a 300:1 split ratio at 250 °C. The GC oven for the separation of kerosene was programmed from 40 °C to 120 °C at 2 °C min⁻¹, followed by a secondary ramp from 120 °C to 200 °C at 20 °C min⁻¹. The temperature program for the separation of diesel was set from 50 °C to 240 °C at 5 °C min⁻¹ and held for 5 min. Hydrogen was employed as a carrier gas at a constant flow of 1.2 mL min⁻¹. The modulation period was 7 s for all separations. All separations were performed in duplicate.

The thermal stability of the PIL-based stationary phases was evaluated by programming the GC oven after GC×GC separations from 40 °C to a specific temperature (i.e., 250, 275, 300, and 325 °C) at a ramp of 10 °C min⁻¹ and then held at that temperature for 30 min. After the thermal conditioning step, the GC×GC separation was performed and the resolution of selected analytes from kerosene was compared with those obtained prior to high temperature conditioning. The MAOT was determined to be the highest separation temperature achieved before a significant decrease in resolution was observed.

3. Results and discussion

3.1. Thermal stability of dicationic ILs for GC×GC separation

It was recently reported that dicationic ILs containing long free alkyl side chain substituents and long linkage chains between the two cations exhibit high selectivity for the separation of different groups of aliphatic hydrocarbons in kerosene when used as second dimension stationary phases in GC×GC [23]. This feature is important for the separation of nonpolar analytes within complex samples. However, the MAOT of the stationary phase also needs to be considered because the IL-based stationary phases should possess high thermal stability to permit high temperature separation. In order to test the robustness of the dicationic IL-based stationary phase, a quantitative measurement was carried out by calculating the resolution of selected pairs of analytes within the GC×GC contour plot. As shown in Figure 2, three pairs of

analytes were selected for comparison and their relative resolution was calculated based on their retention times and peak widths on the second dimension column. The thermal stability of the column was tested by evaluating the resolving power of these three pairs of analytes from kerosene after high temperature conditioning at elevated even temperatures. This approach is capable of detecting any viscosity and/or morphology change of the stationary phases at elevated temperature that may result in a change to the efficiency and resolving power of the stationary phases. The best performing IL from a previous study [23], [(C₁₀im)₂C₁₀] [NTf₂, FeCl₃Br] (see Figure 1), was tested using this approach. As shown in Table 2, a significant decrease in resolution was obtained when this IL was conditioned at 250 °C. The stationary phase was thermally stable in the temperature range between 250 °C to 275 °C, as the resolution values of the analytes did not change appreciably when the column was conditioned up to 275 °C. After the stationary phase was conditioned to 300 °C, the stationary phase exhibited very poor column efficiency and the resolution between analytes 3 and 4 could not be measured (see Table 2). The MAOT of the dicationic IL-based stationary phase was determined to be approximately 275 °C, which is insufficient for high temperature GC×GC separations.

3.2. Non-crosslinked linear PILs as stationary phases for GC×GC separations

PILs have been demonstrated as alternative materials to improve the thermal stability of monocationic and dicationic IL-based stationary phases. Monocationic IL monomers and IL-based crosslinkers can be polymerized within the column to form PIL-based stationary phases, which have been shown to exhibit MAOTs higher than 300 °C [24]. The structures for all IL monomers applied in this study are shown in Figure 1. Both IL monomers possess hexadecyl side chain substituents to enhance their selectivity towards nonpolar analytes. IL monomers containing NTf₂⁻ or FeCl₃Br⁻ counteranions were synthesized to examine their effects on the selectivity and thermal stability of the resulting PILs. Due to the fact that the film thickness of the stationary phase can play an important role in GC×GC separations, stationary phases with film thicknesses of 0.15 μm and 0.28 μm were prepared using the neat [VHDIM] [NTf₂] IL monomer. As shown in Figures 3A and 3B, a wider distribution of the analytes within the separation window was observed when employing the PIL-based stationary phase with a 0.28 μm film thickness as the second dimension column. In order to better evaluate the selectivity of the second dimension column, the resolution between

selected pairs of analytes within the kerosene sample was calculated and is shown in Table 1. The column with 0.28 μm film thickness (column 2) exhibited significantly higher resolving power for the selected analytes compared to the column with 0.15 μm film thickness (column 1). By comparing PILs possessing different anions, it can be observed that the PIL containing the FeCl_3Br^- anion (column 3) exhibited higher resolution than the NTf_2^- -based PIL stationary phase (column 1). This is in good agreement with previously reported results for dicationic ILs (non-polymerized) possessing similar structural features [23].

In order to further test the thermal stability of the non-crosslinked linear PIL-based column, the better performing PIL (column 2) was examined by evaluating the resolving power towards selected pairs of analytes within kerosene ~~after being conditioned at high oven temperatures~~ ~~at elevated oven temperatures~~. As indicated in Table 2, no significant loss of resolution was observed after the column was conditioned to 250 $^\circ\text{C}$. However, after conditioning at 325 $^\circ\text{C}$, an approximate 50% loss of resolution for the selected pairs of analytes was observed compared to the resolution of the column conditioned at 250 $^\circ\text{C}$. Although the linear PIL stationary phase exhibited significantly higher selectivity than the non-polymerized dicationic ILs ~~at higher temperature~~ ~~after being conditioned at high temperature~~, the thermal stability was still not sufficient for high temperature separations. In order to produce more robust stationary phases that are able to endure higher temperatures, crosslinked PIL-based stationary phases were subsequently examined.

3.3. Effect of IL-based crosslinker linkage chain on GC $\times$ GC separation

In order to better understand the effects of different crosslinkers on the efficiency, selectivity, and thermal stability of the PIL-based stationary phases, PILs with varying amounts of dicationic IL-based crosslinker (i.e., 25 and 50% w/w), and crosslinkers possessing different lengths of linkage chains between the two cations (i.e., $[(\text{VIM})_2\text{C}_4] 2[\text{NTf}_2]$, $[(\text{VIM})_2\text{C}_8] 2[\text{NTf}_2]$ and $[(\text{VIM})_2\text{C}_{12}] 2[\text{NTf}_2]$) were compared. The structures of all studied crosslinkers are shown in Figure 1. The column composition and efficiencies are shown in Table 1 and the accompanying contour plots demonstrating the separations of kerosene using these stationary phases are shown in Figure 4.

With regard to the PIL-based stationary phases containing different crosslinkers, a few trends can be observed by comparing columns 5, 6, and 7 in Table 1. Column 7

containing the crosslinker with a dodecyl linkage chain exhibited higher column efficiency than column **5** and **6**, which possessed crosslinkers with shorter linkage chains (octyl and butyl chain). One possible explanation may be that the crosslinker with a shorter linkage chain produces a more rigid polymer matrix, resulting in slower mass transfer between the analytes and stationary phase. In order to test this assumption, the rigidity of the PIL stationary phase was varied by decreasing the amount of the [(VIM)₂C₄] 2[NTf₂] crosslinker from 50% (w/w) to 25% (w/w). A slightly higher column efficiency was obtained for column **4** (efficiency = 1974 plates/m) compared to column **5** (efficiency = 1875 plates/m). Moreover, a wider distribution of the analytes and narrower peak widths were observed for column **4**, as shown in Figure 4A. By comparing the contour plots for columns **5**, **6**, and **7** in Figure 4, it is evident that the stationary phases comprised of the [(VIM)₂C₁₂] 2[NTf₂] crosslinker (Figure 4D) exhibited the best separation of kerosene. This is in good agreement with previous work using structurally tuned ILs for GC×GC separations and further demonstrates that longer linkage chain between the two imidazolium cations is an important structural feature for the separation of aliphatic hydrocarbons [23]. This result also indicates that the necessary structural features for separation of aliphatic hydrocarbons can be imparted into IL-based crosslinkers to produce crosslinked PIL-based stationary phases and that the selectivity is preserved.

The resolution for selected analytes using the crosslinked PILs as second dimension columns is shown in Table 1. The highest resolution for selected analytes was obtained using column **7** as the second dimension column, which contains 50% (w/w) of the [(VIM)₂C₁₂] 2[NTf₂] crosslinker. The result was compared with column **2**, comprised of a non-crosslinked PIL stationary phase prepared by the polymerization of the neat [VHDIM][NTf₂] IL monomer. A significant increase in resolution was obtained when the stationary phase was partially crosslinked using the IL-based crosslinker. The retention times of the analytes on the two contour plots were very similar, as shown in Figure 3B and 4D. However, the peak widths produced by column **7** are much smaller, yielding higher resolution compared to column **2** (see Table 1).

3.4. GC×GC separation of kerosene using PIL-based stationary phases with varied amount of crosslinkers

It has been previously reported that PIL-based stationary phases containing low to

moderate amount of crosslinker exhibited modest column efficiency and are stable up to 285 °C [24]. By increasing the ratio of the crosslinker, the thermal stability of the PIL-based stationary phases can be increased to 380 °C, but the efficiency may be sacrificed. In order to evaluate the effect of the amount of crosslinker on the selectivity and thermal stability of the stationary phases, PIL-based stationary phases with varied amount of the [(VIM)₂C₁₂] 2[NTf₂] crosslinker (i.e., 25, 50, 75, and 100% w/w and neat crosslinker) were prepared and compared. The GC×GC separation of kerosene using these column sets are shown in Figures 4 and 5. For comparison purposes, the resolution for selected analytes in kerosene was also calculated and is shown in Table 1. It can be observed that the selectivity for low boiling analytes can be increased by adding small amounts of crosslinker to the PIL-based stationary phases. This is highlighted in the example of column **8** which exhibited better resolution for analytes 1 and 2 compared to column **2**. The same trend can be observed when the amount of crosslinker was increased from 25% (w/w) to 50% (w/w). Column **7** exhibited the highest resolution for all three pairs of analytes. However, when 75% (w/w) of the crosslinker was incorporated into the stationary phase, a significant drop in the overall resolving power was observed (see Table 1). As shown in Figure 5B, an increased amount of the crosslinker can apparently increase the rigidity of the PIL-based stationary phase and subsequently increase the peak width within the second dimension column. This trend was also observed for column **10** which contains 100% (w/w) of crosslinker (see Figure 5C). The retention times for all analytes separated by column **10** decreased significantly and broader peaks were observed. In order to further examine the performance of the highly crosslinked PIL-based stationary phase, a stationary phase consisting of neat polymerized [(VIM)₂C₁₂] 2[NTf₂] crosslinker (column **11**) was prepared. Although acceptable column efficiency (1897 plates/m) was obtained, very poor GC×GC separation of kerosene was observed for the highly crosslinked PIL-based stationary phase (see Figure S7).

As mentioned earlier, the FeCl₃Br⁻-based PIL stationary phase (column **3**) exhibited good selectivity for different groups of aliphatic hydrocarbons in the GC×GC separation of kerosene. In order to further improve the separation performance of the FeCl₃Br⁻-based PIL stationary phase at high oven temperatures, a column containing the [VHDIM][FeCl₃Br] IL monomer and 50% (w/w) of [(VIM)₂C₁₂]2[FeCl₃Br] crosslinked stationary phase was prepared. It can be observed

in Table 2 that the partially crosslinked FeCl_3Br^- -based PIL (column **12**) provided better resolution for selected analytes compared to the non-crosslinked linear FeCl_3Br^- -based PIL (column **3**). It was also observed that although the FeCl_3Br^- -based stationary phase possesses smaller film thickness (0.15 μm) than the NTf_2^- -based stationary phase (0.28 μm), it exhibited very similar resolution for the selected analytes compared to column **7** (see Table 1).

The three best performing crosslinked PIL stationary phases, namely, columns **7**, **8** and **12** were selected for evaluation of their thermal stabilities ~~at elevated oven~~ ~~temperatures~~. The two NTf_2^- -based stationary phases (column **7** and **8**) exhibited a small but steady decrease in resolution after being conditioned at 250, 275, and 300 $^\circ\text{C}$, respectively, as shown Table 2. After being conditioned at 325 $^\circ\text{C}$, the PIL-based stationary phase containing 25% (w/w) of crosslinker exhibited a significant decrease in resolution. However, better thermal stability was obtained for the PIL-based stationary phase with 50% (w/w) of crosslinker. Even after being conditioned at 325 $^\circ\text{C}$, column **7** still exhibited good retention and selectivity for the target analytes. However, as shown in Table 2, the FeCl_3Br^- -based stationary phase (column **12**) did not exhibit good thermal stability and very poor resolution was observed after the column was conditioned at 275 $^\circ\text{C}$. In spite of its high selectivity for aliphatic hydrocarbons, the low MAOT of the FeCl_3Br^- -based PIL stationary phases makes it undesirable for high temperature separations.

3.5. Immobilized PIL-based stationary phases using vinyltrimethoxysilane (VTMS) treated columns

Modification of the silica surface using vinyl alkoxysilane is a well-known strategy in polymer science [28,29]. After modification, the surface can be polymerized using monomers and crosslinkers to form a crosslinked network, which can significantly increase the mechanical strength and thermal stability of the polymer matrix [30]. Two modification procedures that have been previously reported include liquid phase reaction and vapor phase reaction [29]. Liquid phase reaction utilizes an alkoxysilane solution for modification and is typically easier to operate. This approach has been used previously by our group to immobilize crosslinked PILs as the outer sorbent coating on a fused silica support for solid phase microextraction analysis [27], thereby hindering the sloughing of the PIL sorbent at high temperatures. It has also been reported that passing alkoxysilane vapor through the silica substrate

allows better control of reaction conditions and can lead to a more reproducible monolayer modification [31]. In order to identify the best approach for surface modification, PIL-based stationary phases were prepared on capillary treated using liquid phase reaction and vapor phase reaction. Following VTMS surface modification, two PIL-based stationary phases that exhibited the highest resolving power for kerosene, namely, neat [VHDIM] [NTf₂] and [VHDIM] [NTf₂] with 50% (w/w) of the [(VIM)₂C₁₂] 2[NTf₂] crosslinker, were coated on these capillary columns. As shown in Table 1, moderate to very high column efficiencies were obtained for the neat [VHDIM] [NTf₂] stationary phase (column **13**) and crosslinked stationary phase (column **14**) prepared using the liquid phase treated capillary. However, in the case of column **15** prepared by the VTMS vapor treated column, somewhat lower column efficiency was obtained. One possible explanation may be due to the higher reactivity of the VTMS vapor at higher temperature [29].

Columns **13**, **14**, and **15** were ~~subjected to~~ employed for the GC×GC separation of kerosene and the results are shown in Figure 6 and Table 1. A few interesting trends can be observed by comparing the PIL-based stationary phases prepared on the untreated capillary (column **1**) and VTMS treated capillary (column **13**). Due to the crosslinked network apparently formed by grafting of the PIL stationary phase onto the silica capillary, column **13** exhibited higher resolution for selected analytes than column **1**. This is in good agreement with the results obtained in Section 3.4 since the partially crosslinked PIL (column **4**) exhibited higher resolution compared to the non-crosslinked PIL (column **1**). However, when comparing the observed resolution between column **7** and column **14**, a decrease in resolution was observed after the crosslinked PIL stationary phase was immobilized onto the capillary. As the degree of crosslinking was increased by grafting the PIL stationary phase to the capillary surface, the resolving power towards selected pairs of analytes of the best performing PIL-based stationary phase was decreased. When the amount of crosslinker was increased from 50 % (w/w) to 75 % (w/w), column **9** exhibited a decreased resolution for the selected analyte pairs compared to column **7** (see Table 1). As shown in Figure 6, the VTMS vapor treated column (column **15**) exhibited poor resolving power for kerosene in the GC×GC separation and very broad peaks were observed. The resolution for selected analytes on column **15** (Figure 6C) was much lower than column **14** (Figure 6B), indicating that the liquid phase reaction is a better approach for surface modification.

The thermal stability of column **13** was tested as it exhibited the best selectivity for **different groups of** aliphatic hydrocarbons in kerosene. Compared to column **2**, which has the same stationary phase composition and is coated on untreated capillary column, column **13** exhibited almost no loss of resolution after being conditioned at 275 °C. After conditioning to 325 °C, the column still exhibited good retention and selectivity for the target analytes. The results indicate that the MAOT of the neat [VHDIM][NTf₂] stationary phase can be significantly enhanced by exploiting a VTMS treated capillary column. However, comparing the resolving power of column **13** and column **7** (the best performing PIL-based stationary phase in Section 3.4), column **7** produced superior selectivity for aliphatic hydrocarbons.

3.6. Selectivity and thermal stability comparison for PIL-based and commercial PEG stationary phases

Due to its polar nature, PEG stationary phases have been widely applied as second dimension columns for the separation of hydrocarbons in GC×GC [9,10]. However, it is also well-known that PEG columns have lower MAOTs (250-260 °C) and exhibit high column bleed and surface activity at higher temperatures resulting in shifting of the retention time. In order to better evaluate the analytical performance of the crosslinked PIL stationary phases, four commercial PEG-based columns, namely, SUPELCOWAX 10, DB-WAX, CP-Wax 52 CB, and HP-INNOWax were evaluated as reference stationary phases for the separation of aliphatic hydrocarbons at high temperature. The GC×GC separations of kerosene using the four commercial PEG-based columns are shown in Figure 7. A similar distribution of the analytes within the separation window can be observed for all columns indicative of their similar composition. The resolving power for selected analytes is shown in Table 2. To conduct a fair comparison, the resolution of select analytes from column **7** after conditioning at 275 °C was determined, as this temperature is higher than the MAOTs of most commercial PEG phases. Column **7** provided higher resolution compared to the PEG columns, especially for analytes with lower boiling points (i.e., analytes 1 and 2, 3 and 4). In order to **evaluate the selectivity of the crosslinked PIL-based stationary after high temperature conditioning**~~compare the thermal stability of the crosslinked PIL-based stationary~~, column **7** and the four commercial PEG-based columns were subsequently conditioned at 275 °C, 300 °C, and 325 °C. As shown in Table 2, the resolution for all PEG stationary phases were slightly decreased when the

column was conditioned from 275 to 325 °C, which is a higher temperature than the suggested MAOT of these columns. Column 7 exhibited higher resolution compared to all PEG phases and its performance was not significantly affected after conditioning at 325 °C. ~~The MAOT of column 7 is approximately 45 °C higher than that of the most widely employed PEG-based stationary phases.~~

3.7. GC×GC separation of diesel fuel using selected crosslinked PIL-based stationary phase

In order to further examine the resolving power of the crosslinked PIL-based stationary phase towards aliphatic hydrocarbons, it is necessary to test the column using a more complex sample possessing high boiling constituents. Diesel fuel was selected as a model analyte in this study due to its high complexity and the fact that its group-type separation using GC×GC has been well described [32-35]. The GC×GC separation of diesel fuel employing the Rtx-5- column 7 column set is shown in Figure 8A. Two distinct groups of analytes can be observed within the contour plot. Within the expanded chromatogram for this column set in Figure 8D, saturated hydrocarbons elute in a long and wide band at the bottom of the contour plot, occupying approximately 40% of the second dimension separation window. The aromatic compounds exhibit a wider range of retention times on the second dimension column and occupy nearly the remainder of the separation window. Two of the most widely used stationary phases in petroleum analysis, namely, SUPELCOWAX 10 and DB-17 (containing 50% phenyl) were evaluated for comparison purposes. The distribution of the analytes within the GC×GC contour plots are in good agreement with previously reported results employing similar stationary phases as the second dimension column [32,33]. It can be observed in Figure 8B and 8E that the SUPELCOWAX 10 column exhibits similar resolving power for aromatic compounds compared to column 7, as the aromatic compounds also occupy the top half of the GC×GC chromatogram. However, the aliphatic hydrocarbons elute in a much narrower band (approximately 25% of the second dimension separation window). A very similar separation of saturated hydrocarbons was observed for the DB-17 column compared to SUPELCOWAX 10 (see Figure 8C and 8F). However, as shown in Figure 8F, only 60% of the separation space was utilized by the Rtx-5 × DB-17 column set. Moreover, a slight merge of the saturated hydrocarbon and aromatic regions in the GC×GC contour plot was observed. The crosslinked PIL-based

stationary phase exhibited unique selectivity in the separation of individual aliphatic hydrocarbons from other aliphatic hydrocarbons within diesel fuel compared to the SUPELCOWAX 10 and DB-17 columns.

4. Conclusions

A total of fifteen PIL-based stationary phases were examined as second dimension columns in this study for the separation of aliphatic hydrocarbons within kerosene using GC×GC. The IL monomers were functionalized with long alkyl chain substituents to provide the selectivity required for the resolution of different groups of aliphatic hydrocarbons. The thermal stability of the PIL-based stationary phase was further enhanced by employing IL -based crosslinkers. The PIL-based stationary phase containing 50% (w/w) of crosslinker with a dodecyl linkage chain exhibited the highest resolving power in the separation of aliphatic hydrocarbons. This best performing crosslinked PIL-based stationary phase was compared with four commercial PEG-based columns for the separation of aliphatic hydrocarbons after high temperature conditioning. The crosslinked PIL-based stationary phase exhibited higher resolution for selected analytes and better thermal stability compared to PEG phases. Finally, the crosslinked PIL-based stationary phase was compared with SUPELCOWAX 10 and DB-17 columns for the resolution of aliphatic hydrocarbons in diesel fuel. Better separation of hydrocarbon compounds was obtained when using crosslinked PIL-based stationary phase as the second dimension column. This result proved that the solvation properties and thermal stability of PIL-based stationary phases can be tuned by varying the structure and composition of the IL monomer and crosslinker. This study demonstrates for the first time that structurally tuned IL monomers and crosslinkers can be designed and incorporated into crosslinked PIL-based stationary phases that exhibit high thermal stability and that the unique selectivity of the stationary phase is preserved.

Acknowledgements

The authors acknowledge funding from Chemical Measurement and Imaging Program at the National Science Foundation (Grant number CHE-1413199).

References

- [1] F. Santos, M. Galceran, The application of gas chromatography to environmental analysis, *Trends Anal. Chem.* 21 (2002) 672-685.
- [2] J. Dallüge, J. Beens, U.A.T. Brinkman, Comprehensive two-dimensional gas chromatography: a powerful and versatile analytical tool, *J. Chromatogr. A* 1000 (2003) 69-108.
- [3] P.J. Marriott, R. Shellie, Principles and applications of comprehensive two-dimensional gas chromatography, *Trends Anal. Chem.* 21 (2002) 573-583.
- [4] M. Adahchour, J. Beens, R.J.J. Vreuls, U.A.T. Brinkman, Recent developments in comprehensive two-dimensional gas chromatography (GCxGC): I. Introduction and instrumental set-up, *Trends Anal. Chem.* 25 (2006) 438-454.
- [5] J.V. Seeley, S.K. Seeley, Multidimensional gas chromatography: fundamental advances and new applications, *Anal. Chem.* 85 (2012) 557-578.
- [6] M. Adahchour, J. Beens, U.A.T. Brinkman, Recent developments in the application of comprehensive two-dimensional gas chromatography, *J. Chromatogr. A* 1186 (2008) 67-108.
- [7] P.J. Marriott, S.-T. Chin, B. Maikhunthod, H.-G. Schmarr, S. Bieri, Multidimensional gas chromatography, *Trends Anal. Chem.* 34 (2012) 1-21.
- [8] L. Mondello, P.Q. Tranchida, P. Dugo, G. Dugo, Comprehensive two-dimensional gas chromatography-mass spectrometry: A review, *Mass Spectrom. Rev.* 27 (2008) 101-124.
- [9] C. Vendeuvre, F. Bertoncini, L. Duval, J.-L. Duplan, D. Thiébaud, M.-C. Hennion, Comparison of conventional gas chromatography and comprehensive two-dimensional gas chromatography for the detailed analysis of petrochemical samples, *J. Chromatogr. A* 1056 (2004) 155-162.
- [10] C.A. Bruckner, B.J. Prazen, R.E. Synovec, Comprehensive two-dimensional high-speed gas chromatography with chemometric analysis, *Anal. Chem.* 70 (1998) 2796-2804.
- [11] L. Mondello, A. Casilli, P.Q. Tranchida, P. Dugo, G. Dugo, Detailed analysis and

group-type separation of natural fats and oils using comprehensive two-dimensional gas chromatography, *J. Chromatogr. A* 1019 (2003) 187-196.

[12] H.-J. de Geus, I. Aidos, J. de Boer, J.B. Luten, A.T. Udo, Characterisation of fatty acids in biological oil samples using comprehensive multidimensional gas chromatography, *J. Chromatogr. A* 910 (2001) 95-103.

[13] L. Mondello, A. Casilli, P.Q. Tranchida, G. Dugo, P. Dugo, Comprehensive two-dimensional gas chromatography in combination with rapid scanning quadrupole mass spectrometry in perfume analysis, *J. Chromatogr. A* 1067 (2005) 235-243.

[14] R. Shellie, P.J. Marriott, A. Chaintreau, Quantitation of suspected allergens in fragrances (Part I): evaluation of comprehensive two-dimensional gas chromatography for quality control, *Flavour Frag. J* 19 (2004) 91-98.

[15] C.F. Poole, S.K. Poole, Ionic liquid stationary phases for gas chromatography, *J. Sep. Sci.* 34 (2011) 888-900.

[16] C. Yao, J.L. Anderson, Retention characteristics of organic compounds on molten salt and ionic liquid-based gas chromatography stationary phases, *J. Chromatogr. A* 1216 (2009) 1658-1712.

[17] T.D. Ho, C. Zhang, L.W. Hantao, J.L. Anderson, Ionic liquids in analytical chemistry: fundamentals, advances, and perspectives, *Anal. Chem.* 86 (2013) 262-285.

[18] C.F. Poole, N. Lenca, Gas chromatography on wall-coated open-tubular columns with ionic liquid stationary phases, *J. Chromatogr. A* 1357 (2014) 87-109.

[19] P. Antle, C. Zeigler, A. Robbat Jr, Retention behavior of alkylated polycyclic aromatic sulfur heterocycles on immobilized ionic liquid stationary phases, *J. Chromatogr. A* 1361 (2014) 255-264.

[20] L. Mahé, T. Dutriez, M. Courtiade, D. Thiébaud, H. Dulot, F. Bertoncini, Global approach for the selection of high temperature comprehensive two-dimensional gas chromatography experimental conditions and quantitative analysis in regards to sulfur-containing compounds in heavy petroleum cuts, *J. Chromatogr. A* 1218 (2011) 534-544.

580 [21] T. Dutriez, J. Borrás, M. Courtiade, D. Thiébaud, H. Dulot, F. Bertoncini, M.-C.
581 Hennion, Challenge in the speciation of nitrogen-containing compounds in heavy
582 petroleum fractions by high temperature comprehensive two-dimensional gas
583 chromatography, *J. Chromatogr. A* 1218 (2011) 3190-3199.

584 [22] L.W. Hantao, A. Najafi, C. Zhang, F. Augusto, J.L. Anderson, Tuning the
585 selectivity of ionic liquid stationary phases for enhanced separation of nonpolar
586 analytes in kerosene using multidimensional gas chromatography, *Anal. Chem.* 86
587 (2014) 3717-3721.

588 [23] C. Zhang, I.C. Ingram, L.W. Hantao, J.L. Anderson, Identifying important
589 structural features of ionic liquid stationary phases for the selective separation of
590 nonpolar analytes by comprehensive two-dimensional gas chromatography, *J.*
591 *Chromatogr. A* 1386 (2015) 89-97.

592 [24] J.L. Anderson, D.W. Armstrong, Immobilized ionic liquids as
593 high-selectivity/high-temperature/high-stability gas chromatography stationary phases,
594 *Anal. Chem.* 77 (2005) 6453-6462.

595 [25] Y. Meng, J.L. Anderson, Tuning the selectivity of polymeric ionic liquid sorbent
596 coatings for the extraction of polycyclic aromatic hydrocarbons using solid-phase
597 microextraction, *J. Chromatogr. A* 1217 (2010) 6143-6152.

598 [26] C. Zhang, J.L. Anderson, Polymeric ionic liquid bucky gels as sorbent coatings
599 for solid-phase microextraction, *J. Chromatogr. A* 1344 (2014) 15-22.

600 [27] T.D. Ho, H. Yu, W.T.S. Cole, J.L. Anderson, Ultraviolet photoinitiated on-fiber
601 copolymerization of ionic liquid sorbent coatings for headspace and direct immersion
602 solid-phase microextraction, *Anal. Chem.* 84 (2012) 9520-9528.

603 [28] T. Browne, M. Chaimberg, Y. Cohen, Graft polymerization of vinyl acetate onto
604 silica, *J. Appl. Polym. Sci.* 44 (1992) 671-677.

605 [29] P.V. Der Voort, E. Vansant, Silylation of the silica surface a review, *J. Liq.*
606 *Chromatogr. Related Technol.* 19 (1996) 2723-2752.

607 [30] V. Nguyen, W. Yoshida, J.D. Jou, Y. Cohen, Kinetics of free-radical graft
608 polymerization of 1-vinyl-2-pyrrolidone onto silica, *J. Polym. Sci., Part A: Polym.*

Chem. 40 (2002) 26-42.

[31] D.G. Kurth, T. Bein, Monomolecular layers and thin films of silane coupling agents by vapor-phase adsorption on oxidized aluminum, *J. Phys. Chem.* 96 (1992) 6707-6712.

[32] F. Adam, F. Bertoncini, V. Coupard, N. Charon, D. Thiébaud, D. Espinat, M.-C. Hennion, Using comprehensive two-dimensional gas chromatography for the analysis of oxygenates in middle distillates: I. Determination of the nature of biodiesels blend in diesel fuel, *J. Chromatogr. A* 1186 (2008) 236-244.

[33] J.V. Seeley, S.K. Seeley, E.K. Libby, J.D. McCurry, Analysis of biodiesel/petroleum diesel blends with comprehensive two-dimensional gas chromatography, *J. Chromatogr. Sci.* 45 (2007) 650-656.

[34] P.A. Bueno, J.V. Seeley, Flow-switching device for comprehensive two-dimensional gas chromatography, *J. Chromatogr. A* 1027 (2004) 3-10.

[35] J.V. Seeley, S.K. Seeley, E.K. Libby, Z.S. Breitbach, D.W. Armstrong, Comprehensive two-dimensional gas chromatography using a high-temperature phosphonium ionic liquid column, *Anal Bioanal Chem* 390 (2008) 323-332.

Figure Captions:

Figure 1. Chemical structures and abbreviations of the dicationic IL, IL monomers, and IL-based crosslinkers examined in this study.

Figure 2. Expanded GC×GC contour plot showing the analytes selected for determining the resolving power of the stationary phase.

Figure 3. GC×GC separations of kerosene employing linear (non-crosslinked) PIL-based stationary phases as second dimension columns: (A) Rtx-5 × column **1**, (B) Rtx-5 × column **2**, and (C) Rtx-5 × column **3**. See Table 1 for a description of each column designation and composition.

Figure 4. GC×GC chromatograms showing the effect of linkage chain length of IL-based crosslinker on the separation of kerosene: (A) Rtx-5 × column **4**, (B) Rtx-5 × column **5**, (C) Rtx-5 × column **6**, and (D) Rtx-5 × column **7**.

Figure 5. GC×GC contour plots of kerosene employing PIL-based stationary phases as the second dimension columns containing with varied amount of crosslinkers: (A) Rtx-5 × column **8**, (B) Rtx-5 × column **9**, (C) Rtx-5 × column **10**, and (D) Rtx-5 × column **12**.

Figure 6. GC×GC chromatograms of kerosene employing PIL-based stationary phases coated on vinyltrimethoxysilane (VTMS) treated columns: (A) Rtx-5 × column **13**, (B) Rtx-5 × column **14**, (C) Rtx-5 × column **15**.

Figure 7. GC×GC separations of kerosene employing various commercial PEG-based stationary phases as second dimension columns: (A) Rtx-5 × CP-Wax 52 CB, (B) Rtx-5 × DB Wax, (C) Rtx-5 × INNOWax, and (D) Rtx-5 × SUPELCOWAX 10.

Figure 8. GC×GC contour plots showing the separation of diesel fuel employing commercial and crosslinked PIL-based stationary phases as second dimension columns: (A) Rtx-5 × column **7**, (B) Rtx-5 ×SUPELCOWAX 10, and (C) Rtx-5 × DB-17. Expanded GC×GC contour plots showing the separation of hydrocarbons in diesel fuel: (D) Rtx-5 × column **7**, (E) Rtx-5 ×SUPELCOWAX 10, and (F) Rtx-5 × DB-17.

Figure 1.

Dicationic IL

IL monomers

IL-based
crosslinkers

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Figure 8.

Table 1: PIL-based stationary phases examined in this study

Column No.	IL monomers and crosslinkers used for preparing PIL-based GC stationary phases	Film thickness	Retention factor (k) ^a	Efficiency (Plates/meter)	Resolution of selected analytes ^b		
					1 and 2	3 and 4	5 and 6
1	Neat [VHDIM] [NTf ₂]	0.15 µm	10.8	2276	1.11	0.65	2.07
2	Neat [VHDIM] [NTf ₂]	0.28 µm	13.2	2811	1.52	0.82	4.55
3	Neat [VHDIM][FeCl ₃ Br]	0.15 µm	11.3	1986	1.21	0.86	3.36
4	[VHDIM] [NTf ₂] + 25% [(VIM) ₂ C ₄] 2[NTf ₂]	0.28 µm	7.6	1974	1.25	0.73	1.88
5	[VHDIM] [NTf ₂] + 50% [(VIM) ₂ C ₄] 2[NTf ₂]	0.28 µm	8.0	1875	- ^c	- ^c	1.71
6	[VHDIM] [NTf ₂] + 50% [(VIM) ₂ C ₈] 2[NTf ₂]	0.28 µm	10.6	2335	1.01	1.25	2.18
7	[VHDIM] [NTf ₂] + 50% [(VIM) ₂ C ₁₂] 2[NTf ₂]	0.28 µm	11.7	2575	2.16	1.75	5.36
8	[VHDIM] [NTf ₂] + 25% [(VIM) ₂ C ₁₂] 2[NTf ₂]	0.28 µm	12.5	2457	1.73	1.20	4.15
9	[VHDIM] [NTf ₂] + 75% [(VIM) ₂ C ₁₂] 2[NTf ₂]	0.28 µm	8.7	1994	1.60	0.74	3.59
10	[VHDIM] [NTf ₂] + 100% [(VIM) ₂ C ₁₂] 2[NTf ₂]	0.28 µm	7.8	2316	0.96	0.48	2.50
11	Neat [(VIM) ₂ C ₁₂] 2[NTf ₂]	0.28 µm	5.5	1897	- ^c	- ^c	- ^c
12	[VHDIM] [FeCl ₃ Br] + 50% [(VIM) ₂ C ₁₂] 2[FeCl ₃ Br]	0.15 µm	11.6	2625	1.54	0.80	4.87
13	Neat [VHDIM] [NTf ₂] on VTMS treated column	0.28 µm	10.2	2148	1.37	0.94	3.82
14	[VHDIM] [NTf ₂] + 50% [(VIM) ₂ C ₁₂] 2[NTf ₂] on VTMS treated column	0.28 µm	10.1	3842	1.44	0.97	3.73
15	[VHDIM] [NTf ₂] + 50% [(VIM) ₂ C ₁₂] 2[NTf ₂] on VTMS gas treated column	0.28 µm	7.8	1948	1.28	0.71	2.63

^a: Measured isothermally for naphthalene at 100 °C, flow rate 1 mL min⁻¹.^b: Selected pairs of analytes are shown within the representative contour plot in Figure 2.^c: Due to the poor separation, the resolution of selected analytes could not be measured.

Table 2: Resolution of selected analytes on tested columns ~~after being conditioned at high oven temperature~~ ~~at elevated oven temperatures~~.

Condition Temperature (°C)	Resolution of analyte pairs					
	1 and 2	3 and 4	5 and 6	1 and 2	3 and 4	5 and 6
	[(C ₁₀ im) ₂ C ₁₀] [NTf ₂ , FeCl ₃ Br]			Neat [VHDIM] [NTf ₂] (Column 2)		
100	0.90	0.48	3.25	1.52	0.82	4.55
250	0.61	0.26	2.57	1.35	0.76	3.13
275	0.55	0.25	2.42	1.44	0.66	3.35
300	0.48	- ^a	1.86	1.60	0.40	1.48
325	- ^a	- ^a	- ^a	0.84	0.45	1.65
	[VHDIM] [NTf ₂] + 25% [(VIM) ₂ C ₁₂] 2[NTf ₂] (Column 8)			[VHDIM] [NTf ₂] + 50% [(VIM) ₂ C ₁₂] 2[NTf ₂] (Column 7)		
100	1.73	1.20	4.15	2.16	1.75	5.36
250	1.47	0.95	3.98	1.69	1.24	4.09
275	1.32	0.81	3.41	1.59	1.33	3.83
300	1.03	0.68	2.92	1.29	1.05	3.29
325	0.71	0.41	1.88	1.02	0.81	2.85
	[VHDIM] [FeCl ₃ Br] + 50% [(VIM) ₂ C ₁₂] 2[FeCl ₃ Br] (Column 12)			Neat [VHDIM] [NTf ₂] on VTMS treated column (Column 13)		
100	1.54	0.80	4.87	1.37	0.94	3.82
250	1.48	0.77	4.06	1.29	0.84	3.82
275	- ^a	0.10	0.92	1.15	0.80	3.50
300	- ^a	- ^a	- ^a	1.07	0.56	2.45
325	- ^a	- ^a	- ^a	0.82	0.63	2.49
	SUPELCOWAX 10			DB-WAX		
100	0.86	0.50	3.46	0.73	0.41	3.57
250	0.82	0.53	3.34	0.64	0.42	3.60
275	0.76	0.50	3.44	0.67	0.29	3.45
300	0.87	0.44	3.21	0.55	0.34	3.23
325	0.87	0.33	2.70	0.56	0.22	2.66
	HP-INNOWax			CP-Wax 52 CB		
100	0.63	0.33	3.63	0.80	0.49	3.09
250	0.56	0.32	3.43	0.73	0.44	3.08
275	0.50	0.31	3.55	0.67	0.45	3.02
300	0.54	0.25	3.39	0.74	0.50	3.01
325	0.50	0.21	2.80	0.76	0.43	2.54

^a: Due to the poor separation, the resolution of selected analytes could not be measured.