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Application of Polymeric Ionic Liquid Solid-Phase Microextraction Sorbent Coatings and Ionic Liquid Stationary Phases for Liquid and Multidimensional Gas Chromatographic Techniques

by

Ali Najafi

Submitted to the Graduate Faculty as partial fulfillment of the requirements for the

Master of Science Degree in

Chemistry

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December 2015
An Abstract of

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Ionic Liquids (ILs) have been studied as an interesting class of compounds in chromatographic separation and sample preparation science. ILs are commonly introduced as ionic salts comprised of unsymmetrical organic cations paired with organic or inorganic anions that possess melting points at or below 100 °C. Polymeric ionic liquids (PILs) are synthetic polymers synthesized from IL monomers containing polymerizable functional groups. These materials exhibit numerous beneficial properties, including high thermal stability, wide viscosity range, negligible vapor pressure, and multiple solvation interactions with various analytes, which makes them influential compounds in separation science. This thesis describes the application of PILs and ILs in solid-phase microextraction (SPME) as sorbent coatings as well as stationary phases in gas chromatography and multidimensional gas chromatography (MDGC).
SPME has been adopted as a simple and cost-effective pre-concentration technique within the field of sample preparation. In an attempt to enhance analytical performance of target analytes, including selectivity, sensitivity, and limits of detection (LODs) in the analysis of complex matrixes, ILs and PILs have been widely exploited as SPME sorbent coatings. Over a decade, ILs and PILs have proven to be excellent candidates for SPME sorbent coatings. Overall, structural tailoring of ILs and PILs results in suitable physicochemical properties which give scientists an opportunity to generate tunable selectivity mechanisms towards various target analytes.

Comprehensive two-dimensional gas chromatography (GC×GC), developed by Liu and Phillips, is a powerful technique used to separate analytes in complex samples. In this technique, a sample is vaporized and subjected to a combination of two chemically different GC stationary phases with different selectivities to obtain higher peak capacity through unique interactions with the sample. Hence, GC×GC offers higher separation power compared to one-dimensional gas chromatography (1D-GC). A typical column sequence involves polysiloxane followed by polyethylene glycol-based stationary phases to allow separation of the analytes based on vapor pressure and polarity, respectively. Currently, most separations of complex matrices are done by these traditional phases. However, their solvation capabilities are redundant. During the last decade, ILs have been acknowledged as promising alternative stationary phases in 1D-GC and GC×GC. ILs can be designed to possess ideal physicochemical properties for GC stationary phases. These properties include broad liquid range, high thermal stability, low background bleed, and multiple solvation interactions. When compared to traditional phases, commercial IL-based GC columns allow unique chromatographic separation of mid-polar to polar analytes.
in samples. However, they exhibit poor retention of non-polar analytes such as aliphatic hydrocarbons. Hence, designing IL-based stationary phases capable of retaining non-polar analytes is highly demanded, as it would expand IL phase versatility to include complex petrochemical separations.

Chapter 1 explains a brief introduction to the fundamental of SPME and the application of ILs and PILs as SPME sorbent coatings.

Chapter 2 focuses on the development of cross-linked PILs as SPME sorbent coatings for high performance liquid chromatography (HPLC). Since the majority of the investigations related to the application of ILs and PILs as SPME sorbent coatings have been focused upon a method coupled with gas chromatography (GC) analysis. For the first time, these materials were fabricated as highly selective and robust sorbent coatings for liquid chromatographic (LC) applications.

Chapter 3 introduces the fundamentals of the MDGC technique and reviews recent applications of IL stationary phases in the field of 1D-GC and MDGC.

The last chapter of this thesis describes tuning the selectivity of IL-based stationary phases in order to enhance separation of aliphatic hydrocarbons from kerosene samples using GC×GC. The structurally tuned trihexyl(tetradecyl)phosphonium tetrachloroferrate ([P₆₆₆₁₄][FeCl₄]) IL stationary phase, exhibited improved separation of aliphatic hydrocarbons by GC × GC compared to the examined commercial columns.
Every challenging work needs self-efforts as well as guidance of elders, especially those who were very close to our heart. This dissertation is dedicated to my family, my lovely parents and sister, M. Mehdi Najafi, Malaktaj Mohammad-khani and Niloufar Najafi for their unfailing love, encouragements and pays of day and night make me able to get such success and honor. And to my love, Sarah Farahani, for her unending love, kindness and support.
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Chapter 1

Ionic liquids in solid-phase microextraction

1.1 Introduction to solid-phase microextraction

Solid-phase microextraction (SPME) is a non-exhaustive microextraction technique that was introduced in the early 1990s by Pawliszyn and co-workers.¹ In comparison to conventional extraction methods, SPME has gained widespread popularity due to its simplicity and high sensitivity by combining sampling and sample preparation into a single step. These characteristics make it to be simpler, and cost-effective, without requiring organic solvents.²

SPME relies on the equilibrium partitioning (absorption) or adsorption of analytes in a sample to a solid sorbent material. The SPME fiber is composed of a solid sorbent material that is coated or immobilized on a support.³ In general, SPME involves two main steps: extraction (sampling) and desorption. The extraction step is defined by immersing the SPME fiber into a sample matrix, wherein partitioning between the analytes and the sorbent coating occurs until equilibrium is reached after a certain period of time. After the extraction (sampling) step, desorption of the extracted analytes is accomplished by thermal desorption or by back-extraction solvent desorption. Thermal desorption can be achieved
by introducing the fiber coating to a gas chromatography (GC) inlet at high temperatures for mostly volatile and/or semi-volatile analytes. The back-extraction solvent desorption approach is performed to desorb semi-volatile and/or non-volatile analytes for analysis via high performance liquid chromatography (HPLC).^4

Generally, two common modes of extraction are involved with the SPME method, namely, (Figure 1-1B) headspace and (Figure 1-1A) direct immersion.^4^5 As shown in Figure 1-1B in the headspace mode, the SPME fiber is exposed to the headspace portion of a sample vial. Semi-volatile and/or volatile analytes can partition to the headspace region resulting to reach equilibration between the sample and the headspace as well as the headspace and the sorbent coating. Direct immersion (Figure 1-1A) is more common for the extraction of semi-volatile and/or low volatile analytes which tend to partition more to the sample matrix. In this mode, a highly robust fiber coating is required since the fiber is in direct contact with the matrix under extreme extraction/desorption conditions.^6^-^7

The nature of the sorbent coating can have a significant impact on selectivity and sensitivity of various analytes in SPME. Currently, commercially available SPME sorbent coatings are vastly applied for the analysis of various complex matrixes. These coatings are typically prepared and designed based on their differences in polarity. Unfortunately, they cannot offer tunable selectivity since complex matrixes are comprised of many different groups of analytes with similar physicochemical properties. Therefore, novel SPME sorbent materials that can improve overall analytical selectivity and sensitivity of the method can be highly useful for the detection of analytes at trace analytical levels.
1.2 Utilizing of ionic liquids as SPME sorbent coatings

Ionic liquids (ILs) are a unique class of ionic salts that have melting points at/or below 100 °C. ILs are typically composed of an organic cation paired with an organic or inorganic anion. Figure 1-2 illustrates common cation and anion structures that exist in many common ILs. Different physicochemical properties, including high thermal stability, negligible vapor pressure and variable viscosity can be imparted and varied by tuning the IL structure.\(^8\) The thermal stability of the sorbent coating plays an important role in SPME, specifically for GC applications since the SPME fiber is exposed to the high temperature GC injector. If the sorbent coating is not sufficiently thermally stable, the fiber lifetime as well as extraction performance can be significantly decreased. However, structural modification of the IL can enhance thermal stability.\(^9\) For example, modification of the cation structure through the introduction of aliphatic hydrocarbon side chains to the nitrogen of the imidazolium ring can increase thermal stability.\(^10\) Additionally, bulky and delocalized anions such as \([\text{NTf}_2]^-\) and \([\text{PF}_6]^-\) often exhibit higher thermal stability over smaller and lower polarizability anions, such as halides.\(^11\) In the case of viscosity, ILs exhibiting resistance to viscosity changes at higher temperatures can be highly beneficial.
for GC applications in order to avoid flowing off the fiber into the GC inlet. ILs with a high viscosity can also be produced with an even distribution of sorbent coating throughout the support. ILs containing halide (e.g., [Cl]−, [Br]−) anions tend to show higher viscosities compared to those comprised of larger and asymmetrical anions. This is due to enhanced electrostatic as well as hydrogen-bonding interactions. 12

The cation and the anion moieties of the IL structures can be functionalized to exhibit varying selectivity towards different analyte classes. 13 For example, introducing the benzyl functional group on the cation moiety of the IL can increase the selectivity towards aromatic compounds due to enhanced π-π interactions. 14 Also, hydrogen bond acidic analytes can undergo favorable interactions with hydrogen bond basic anions. 15 Therefore, the application of ILs as tunable SPME sorbent coatings can be highly beneficial to enhance selectivity for target analytes.

Liu and co-workers were the first to apply an IL as a sorbent coating in SPME. 16 The headspace extraction mode was performed for the extraction of benzene, toluene, ethylbenzene and xylenes (BTEX) in paints using the [C8MIM][PF6] IL. This IL showed better analytical performance including limits of detection (LODs) for BTEX compounds compared to the commercial polydimethylsiloxane (PDMS) fiber. However, due to propensity for this IL to lose viscosity upon contact with the high temperature GC inlet, the applicability of this IL was limited for only one extraction/desorption cycle. Several subsequent studies were reported to address the stability of IL-based sorbent coatings. 17-18 Nafion membrane was used as a stabilizer layer to enhance the stability of an IL-based coating up to 50 extraction/desorption cycles. This was achieved by electrostatic
interactions as well as the ability to accommodate a higher amount of the IL loading on the fiber support. Methoxysilyl functionalization on the nitrogen in the imidazolium ring of the 1-methyl-3-(3-trimethoxysilylpropyl) imidazolium bis[(trifluoromethyl)sulfonyl]imide ([MTPIM][NTf2]) IL allowed chemical linkage to the silanol (-OH) activated surface of the fused silica support. This chemical linkage improved the fiber lifetime up to 16 cycles and provided better analytical performance than commercial fibers including polydimethysiloxane/divinylbenzene (PDMS/DVB) and PDMS/Carboxen fibers.

Figure 1-2: Common cations and anions used to produce ILs

1.3 Application of polymeric ionic liquids as SPME sorbent coating

Polymeric ionic liquids (PILs) are an interesting class of compounds that can be used as sorbent coatings in SPME. PILs are synthetic polymers synthesized from IL monomers. PILs are typically synthesized by functionalizing a polymerizable functional group on the cationic moiety of the IL via free radical polymerization in the presence of a thermal initiator. PILs have several advantages that can make them more effective SPME
sorbent coatings than ILs. PILs exhibit higher thermal stability as well as a resistance to viscosity reduction at higher temperatures. These beneficial features can improve fiber lifetime, robustness and applicability of PILs while retaining the selectivity remains the inherent to ILs. The Anderson group first applied PILs as sorbent coatings in SPME. Three structurally different PILs containing various anion and cation moieties were prepared as the PIL-based sorbent coatings and applied for the extraction of different fatty acid methyl esters (FAMES). These fibers showed superior lifetimes, up to 150 extraction/desorption cycles, due to their excellent thermal stability as well as mechanical stability. Consequently, it was demonstrated that different PIL structures can provide selectivity mechanisms toward different analyte classes. In most cases, selectivity was examined by altering either the cation or anion moiety of IL monomers. Two PILs containing a benzyl moiety were prepared to enhance favorable π-π interactions of the PIL-based sorbent coatings for the extraction of polycyclic aromatic hydrocarbons (PAHs). Additionally, PILs containing hydrogen-bond basic anions, such as halides, exhibited superior extraction performance for polar hydrogen bond acidic analytes. It was shown that CO₂ extraction via chemical reaction rather than effective intermolecular interactions can be achieved. The poly ([ViC₁₆IM][taurinate]) PIL was prepared to extract CO₂ based on a reversible thermodynamically-favored process, wherein CO₂ reacts with the taurinate anion to form carbamate on the fiber followed by the release of CO₂ into a GC injector at a high temperature. In an attempt to demonstrate the applicability of PIL-based sorbent coatings possessing different functionalities, various PIL fibers were prepared for the analysis of genotoxic impurities (GTIs) in water. The [Cl]⁻-based anion PIL fiber exhibited higher extraction performance for anilines while a glucaminium-based PIL with
alkyl and benzyl substituents paired with \([\text{NTf}_2^-]\) anion showed higher sensitivities for alkyl halides and aromatics, respectively. The poly \([\text{VC}_6\text{IM}][\text{NTf}_2]\) PIL SPME sorbent coating was fabricated to investigate the purity of chiral compounds using a chiral GC stationary phase to separate and quantify each enantiomer.\(^{26}\) All of these aforementioned examples were concerned with a physical dip coating strategy to fabricate the PIL-based fibers. However, the physical dip coating route can be limited in the direct immersion extraction mode in complex matrixes. A chemical bonding route was developed as one of the common sorbent loading strategies to overcome this drawback. This route was employed to link 1-vinyl-3-hexadecyylimidazolium \([\text{PF}_6^-]\) to a substrate derivatized with \(\gamma\)-methacryloxypropyltrimethoxysilane via copolymerization.\(^{27}\) The bonded PIL sorbent coating offered higher extraction performance of pyrethoids in vegetables compared to a commercial PDMS fiber. Surface radical chain-transfer polymerization was used to covalently bond and polymerize 1-vinyl-3-octylimidazolium \([\text{VC}_8\text{IM}]^+\) paired with two different anions, including \([\text{PF}_6^-]\) and polymerizable pstyrenesulfonate anions, to modified stainless steel for the analysis of BTEX, anilines, phenols, PAHs and phthalate esters (PAEs) in water samples.\(^{28-29}\)

### 1.4 Cross-linked PIL sorbent coatings in SPME

Cross-linked PIL sorbent coatings have also been developed to address potential drawbacks of physical dip coating of pure PILs for the analysis in harsh conditions without sacrificing unique selectivity of pure ILs and PILs. Polar cross-linked PILs were fabricated for the analysis of various organic compounds in water samples using both headspace and direct-immersion modes of extraction.\(^{30}\) On-fiber ultra-violet (UV)-initiated photo
polymerization was developed as a high throughput sorbent loading strategy to fabricate the cross-linked PIL fibers. IL monomer, namely 1-vinyl-3-hexylimidazolium chloride ([VC₆IM][Cl]), was copolymerized with two structurally different IL cross-linkers, including 1,8-di(3-vinylimidazolium) octane dibromide ([((VIM)₂C₈][Br]₂) or 1,12-di(3-vinylimidazolium) dodecane dibromide ([((VIM)₂C₁₂][Br]₂) in the presence of a UV initiator to prepare polar cross-linked sorbent coatings. Method throughput was significantly improved since this route eliminates the need for dispersive organic solvents. Fiber robustness was also enhanced to allow the analysis by the direct-immersion mode in water samples due to the chemical linkage between the sorbent coating and the etched and derivatized fused silica support. In a follow-up study, the benzyl functionalized dicationic IL cross-linker was applied for the analysis of poly chlorinated biphenyls (PCBs) in milk and water samples.¹⁴ The role of IL cross-linker functionalization was examined by obtaining higher sensitivity for PCBs compared to a non-functionalized IL cross-linker as well as a PDMS coating. Polymeric ionic liquid bucky gels were also fabricated based upon on-fiber co-polymerization by thermal free-radical polymerization.³¹ The PIL bucky gel was then applied for the extraction of PAHs in water samples. These sorbent coatings were prepared by the on-fiber copolymerization of 1-vinyl-3-butylimidazolium bis[(trifluoromethyl)sulfonylimide ([VC₄IM][NTf₂]) with a IL cross-linker, namely, 1,12-di (3-vinylimidazolium) di bis[(trifluoromethyl)sulfonylimide (((VIM)₂C₁₂][NTf₂]₂) in the presence of 2,2′-azobis (2-methylpropionitrile) AIBN. Superior extraction performance towards PAHs was observed due to the combination of PIL with multi-wall carbon nanotubes (MWCNTs) to enhance the π-π interactions. Compared to the neat PIL-based sorbent coating, the PIL bucky gel sorbent coatings demonstrated higher extraction
efficiency for the extraction of PAHs. Recently, four cross-linked polymeric ionic liquids were evaluated in automated direct immersion SPME for the analysis of various water pollutants. These cross-linked PILs were prepared based on a benzyl moiety in both IL monomer and cross-linker and compared to non-functionalized IL monomer and cross-linker counterparts. The best extraction performance of the selected analytes was observed for the crosslinked PILs containing the benzyl functional group in the IL monomer and/or IL cross-linker.

1.5 Summary

In this chapter, the theory and operation of the SPME technique were briefly introduced. The relevance of unique physicochemical properties of ILs, PILs, and cross-linked PILs as sorbent coatings in SPME was presented. Subsequently, various fabrication strategies and applications of these materials in SPME were discussed since their introduction to the SPME community. Although the majority of the described investigations were mainly focused on the application of the ILs and the PILs via GC analysis, the application of these materials has not been explored for HPLC applications. The next chapter of this thesis focuses upon the applicability of the cross-linked PILs for HPLC applications. In an attempt to expand the versatility and applicability of these interesting materials to a wider scope of analytical disciplines, three structurally different cross-linked PILs were prepared and applied as highly robust and selective sorbent coatings for SPME-HPLC applications.
Chapter 2

Highly robust and selective cross-linked polymeric ionic liquid-based solid-phase microextraction sorbent coatings for high performance liquid chromatography

Ali Najafi, Jonathan Genson, and Jared L. Anderson

Abstract

Three structurally different cross-linked polymeric ionic liquid (PIL)-based sorbent coatings with different cation and anion moieties were prepared on nickle-titanium (nitinol) supports and employed for direct-immersion SPME followed by offline organic solvent desorption/analysis using high performance liquid chromatography (HPLC). Various extraction conditions including the nature of the desorption solvent, desorption time, extraction time, and pH were optimized for each PIL-based sorbent coating as well as three commercially available sorbent coatings. The evaluation of extraction efficiency for the PIL-based sorbent coating, as well as commercial sorbent coatings, was performed by comparing the overall chromatographic peak areas under optimized extraction/desorption conditions. The role of the cation and anion moiety of the PIL-based sorbent coatings were evaluated for the extraction of model analytes. The analytical performance for all sorbent
coatings was examined under the optimized conditions. Linear ranges and limits of detection (LODs) of model analytes were obtained and compared for each sorbent coating. The LODs of all PIL-based sorbent coatings and commercial fibers for the extraction of model analytes ranged from low parts-per-billion (ppb) to mid parts-per-trillion (ppt) levels using SPME/HPLC-UV method. A normalized calibration slope based on the film thickness of the sorbent coating was used as a comparative tool to evaluate the effect of the nature of sorbent coatings on their analytical performance. A PIL-based sorbent coating with a higher film thickness (~ 55 µm) was prepared to understand the effect of the film thickness on selectivity and sensitivity of the PIL-based sorbent coating. Method validation was accomplished by applying direct immersion extraction of model analytes at two concentration levels from two different water matrixes. Scanning electron micrographs were obtained for all PIL-based sorbent coatings after approximately 100 extraction/desorption cycles, wherein the approximate film thickness for each fiber was estimated and a rough surface morphology was observed for all cross-linked PIL fibers.

2.1 Introduction

Solid-phase microextraction (SPME) has become a very popular method of analyte pre-concentration within the field of sample preparation.\textsuperscript{33} SPME is an equilibrium-based extraction technique governed by the distribution of analytes to a sorbent layer through either a partitioning or adsorption mechanism.\textsuperscript{34-35} In SPME, a thin sorbent layer is coated or immobilized on a solid support and exposed to a sample solution either by headspace or direct-immersion mode. Analytes are then desorbed from the sorbent coating either
thermally for gas chromatographic (GC) methods or by solvent desorption using different organic desorption solvents for liquid chromatographic (LC) methods. Due to the integration of sampling and sample preparation into a single step, SPME has been adopted as a simple, cost effective, and high throughput extraction method. Although many investigations have focused on SPME-GC applications, much attention recently has been devoted on the analysis of semi-volatile, non-volatile, and thermally labile compounds, which are more amenable to HPLC analysis. Currently, SPME-LC methods have been extensively applied for various contaminants, pesticides, metabolomics, pharmacokinetic profiling, and food components. However, the applicability of the SPME-LC methods may be limited due to the lacking variety of commercially available sorbent coatings, which can improve analyte selectivity as well as analytical performance when sampling from complex matrices. The main drawback associated with current commercially available HPLC sorbent coatings is that they tend to swell in various organic solvents. This can cause stripping and peeling of the sorbent from the support when the fiber is retracted into the needle which results in poor analytical performance as well as reduction in fiber lifetime. Therefore, the development of highly robust and selective SPME sorbent coatings for LC analysis is crucial in order to expand SPME applications.

Various sorbent coating materials including molecular imprinted polymers (MIPs), sol-gel technology, carbon nanomaterials, and metal-organic frameworks (MOFs) have been prepared and applied for SPME-LC methods. More recently, multiple monolithic SPME fibers were designed and applied for monitoring estrogenic mimic and trace nitrophenols using HPLC analysis. Polyhedral oligomeric silsesquioxane (POSS)
was used as a cross-linker for the fabrication of a cross-linked methyl methacrylate-POSS hybrid polymeric coating.\textsuperscript{52} In addition, POSS was introduced as a non-ionic cross-linker to produce a cross-linked polymeric ionic liquid-POSS sorbent coating for the extraction of perfluorinated compounds in direct-immersion mode.\textsuperscript{53} Among the aforementioned sorbent coating materials, our group has also investigated a particular class of compounds as SPME sorbent coatings that are known as polymeric ionic liquids (PILs).\textsuperscript{19,54-55}

PILs are synthetic polymers containing ionic liquids (ILs) as the polymerizable monomer. PILs can be designed to possess ideal physicochemical properties as SPME sorbent coatings. These properties include thermal stability, negligible vapor pressure, and resistance in viscosity change.\textsuperscript{25} Moreover, PILs can be structurally customized to exhibit higher selectivity and sensitivity toward different class of analytes. Cross-linked PIL-based sorbent coatings were introduced to expand the application of PILs under harsh extraction conditions.\textsuperscript{14, 30} The IL monomer can be copolymerized with an IL cross-linker in the presence of an initiator to form a highly rigid and robust cross-linked polymeric network. The cross-linked PIL-based sorbent coatings can be applied for the direct-immersion extraction of polar analytes from complex water matrixes.\textsuperscript{30} The overall selectivity of the sorbent coating can be tuned by structural tailoring of the IL monomer and/or cross-linker.

Recently, our group developed a route to chemically immobilize cross-linked PILs on nickel-titanium (nitinol) metal alloys, which significantly enhances the sorbent coating durability and lifetime.\textsuperscript{56} The crosslinked PIL-based nitinol SPME fibers were subjected to various harsh extraction conditions to evaluate their robustness and precision for the extraction of model analytes. The PIL-based sorbent coating displayed superior analytical performance after exposure to common reversed-phase HPLC solvents between each
extraction cycle, which indicates a great potential to apply this highly robust SPME system for HPLC applications.

In an attempt to expand the applicability of the cross-linked PIL-based nitinol SPME fiber system towards HPLC applications, three structurally different cross-linked PIL-based SMPE sorbent coatings were examined in the extraction of wide range of analytes, including endocrine disrupting chemicals (bisphenol-A), anticonvulsants (carbamazepine), antilipemics (gemifibrozil), antimicrobial disinfectant, (irgasan), common water pollutants (2-nitrophenol, 3-terbutylphenol, α,α,α,6-tetrafluoro-m-toluidine), food flavors (benzaldehyde, ethyl benzoate), and polycyclic aromatic hydrocarbons (naphthalene) by the direct-immersion mode followed by off-line solvent desorption using HPLC analysis. The role of the IL monomer and/or cross-linker functionalization on selectivity and sensitivity in the extraction of different analyte classes was examined. The role of cation functionalization was examined to exploit \( \pi-\pi \) interactions through the benzyl moiety within the PIL. In addition, the hydrogen-bond basic bromide anion was used to understand the role of anion towards hydrogen-bond acidic analytes. Various extraction conditions including the nature of the desorption solvent, desorption time, extraction time, and pH were optimized for each PIL sorbent coating as well as three commercial SMPE fibers including polydimethylsiloxane (PDMS), polyacrylate (PA), and polydimethylsiloxane/divinylbenzene (PDMS/DVB). Calibration studies were performed using all cross-linked PIL-based and commercial fibers. Subsequently, the sensitivity of all analytes with respect to each fiber coating was normalized based on the film thickness of the sorbent coating and used to examine the selectivity of each fiber. In an attempt to understand the effect of the sorbent coating
thickness, the analytical performance was evaluated using different thicknesses of the PIL-based sorbent coating. Recovery and reproducibility studies were accomplished for two cross-linked PIL-based fibers in order to validate the accuracy and precision of the developed method.

2.2 Experimental

2.2.1 Reagents and materials

The reagents acrylonitrile, 1-bromohexadecane, 1, 12-dibromododecane, 2-hydroxy-2-methylpropiophenone (DAROCUR 1173), imidazole, 4-vinylbenzyl chloride, 1-vinylimidazole, vinyl trimethoxysilane (VTMS), and acetic acid were purchased from Sigma-Aldrich (St. Louis, MO, USA). Concentrated hydrogen peroxide 30 % (w/w), hydrochloric acid, sodium hydroxide, HPLC-grade acetonitrile, methanol, and acetone were supplied by Fisher Scientific (Fair Lawn, NJ). Lithium bis[(trifluoromethyl)sulfonyl]imide was acquired from SynQuest Laboratories (Alachua, FL, USA). Ultrapure water (18.2 MΩ.cm⁻¹) was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA). The SPME fiber assemblies were provided by Supelco (Bellefonte, PA, USA). 100 µm PDMS, 60 µm PDMS/DVB, and 85 µm PA fibers were obtained by Supelco (Bellefonte, PA, USA). Elastic nitinol wires with 127 µm external diameter were purchased from Nitinol Devices & Components (Fremont, CA, USA). A RPR-100 UV reactor employing a spinning carousel was obtained from Southern New England Ultraviolet Company (Bradford, CT, USA). Amber glass vials (10 mL) with screw caps and polytetrafluoroethylene (PTFE)/silicon septa were purchased from Supelco. The analytes examined in this study included carbamazepine (Cmz),
benzaldehyde (Bnzal), bisphenol-A (BP-A), 2-nitrophenol (2-NP), \(a,a,a,6\)-tetrafluoro-m-toluidine (6-tfTol), 3-terbutylphenol (3-t-ButP), ethyl benzoate (EB), naphthalene (Nap), gemifibrozil (Gfz), and irgasan (Irg) were supplied by Sigma-Aldrich (St. Louis, MO, USA). The structures of studied analytes are shown in Table 2.1. Individual analytical standards of these pure compounds were prepared by dissolving each analyte in acetonitrile at a concentration of 10 mg mL\(^{-1}\). Standard stock solutions were prepared by combining the individual analytical standards at various concentrations and further dilution with acetonitrile. These solutions were stored at 4 °C and used in the daily preparation of an aqueous standard working solution. The working solution was prepared with an analyte concentration ranging from 0.5 to 500 ng mL\(^{-1}\) by spiking a specific volume of the standard stock solution into a 10 mL amber sampling vial.

### 2.2.2 Instrumentation

High-performance liquid chromatographic analysis was carried out using a LC-20A liquid chromatograph (Shimadzu, Japan) with two LC-20AT pumps, a SPD-20 UV/VIS detector, and a DGU 20A3 degasser. All chromatographic analysis were performed using a C\(_{18}\) column (250 mm × 4.6 mm i.d., 5 μm- particle size) from Restek (Bellefonte, PA, USA) with a guard column (Kromasil™ C\(_{18}\) 5-μm particle-size) from Supelco (Bellefonte, PA, USA). Data acquisition and data processing were accomplished with Shimadzu LC solution software. All separations were performed utilizing acetonitrile and water with the addition of 0.1 % (v/v) acetic acid and a flow rate of 1.0 mL min\(^{-1}\). For the separation of the studied analytes, the separation gradient began at 50 % acetonitrile and was gradually increased to 90 % in 25 min. UV detection at 254 nm was employed for all 10 compounds.
Table 2.1. Chemical structures of all model analytes

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Structure</th>
<th>Analyte</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbamazepine (Cmz)</td>
<td><img src="image" alt="Carbamazepine Structure" /></td>
<td>3-terbutylphenol (3-terButP)</td>
<td><img src="image" alt="3-terbutylphenol Structure" /></td>
</tr>
<tr>
<td>Benzaldehyde (Bzal)</td>
<td><img src="image" alt="Benzaldehyde Structure" /></td>
<td>Ethyl benzoate (EB)</td>
<td><img src="image" alt="Ethyl benzoate Structure" /></td>
</tr>
<tr>
<td>Bisphenol-A (BP-A)</td>
<td><img src="image" alt="Bisphenol-A Structure" /></td>
<td>Naphthalene (Nap)</td>
<td><img src="image" alt="Naphthalene Structure" /></td>
</tr>
<tr>
<td>2-nitrophenol (2-NP)</td>
<td><img src="image" alt="2-nitrophenol Structure" /></td>
<td>Gemfibrozil (Grz)</td>
<td><img src="image" alt="Gemfibrozil Structure" /></td>
</tr>
<tr>
<td>α,α,α-6-tetrafluoro-m-toluidine (6-tfTol)</td>
<td><img src="image" alt="α,α,α-6-tetrafluoro-m-toluidine Structure" /></td>
<td>Irgasan (Irg)</td>
<td><img src="image" alt="Irgasan Structure" /></td>
</tr>
</tbody>
</table>
evaluated in this study. Figure 2-1 shows a liquid chromatogram obtained for separation of the studied analytes.

Scanning electron microscopy micrographs were obtained using a JEOL JSM-7500F field emission scanning electron microscope (SEM).

![Liquid chromatogram](image)

Figure 2-1. Liquid chromatogram for separation of 10 model analytes. (1) carbamazepine, (2) benzaldehyde, (3) bisphenol-A, (4) 2-nitrophenol, (5) α,α,α-6-tetrafluoro-m-toluidine (6) 3-terbutylphenol, (7) ethyl benzoate, (8) naphthalene, (9) gemifibrozil, (10) irgasan

2.2.3 Ionic liquid synthesis and fabrication of SPME fibers

The IL monomers, namely, 1-vinyl-3-hexadecylimidazolium bromide ([VC\textsubscript{16}IM][Br]), 1-vinyl-3-hexadecylimidazolium bis[(trifluoromethyl)sulfonyl]imide ([VC\textsubscript{16}IM][NTf\textsubscript{2}]), 1-vinylbenzyl-3-hexadecylimidazolium bis[(trifluoromethyl)sulfonyl]imide ([VBC\textsubscript{16}IM][NTf\textsubscript{2}]); and IL cross-linkers, namely, 1,12-di(3-vinylimidazolium)dodecane dibromide ([(VIM)\textsubscript{2}C\textsubscript{12}][Br]\textsubscript{2}), 1,12-di(3-vinylimidazolium)dodecane bis[(trifluoromethyl)sulfonyl]imide ([(VIM)\textsubscript{2}C\textsubscript{12}][NTf\textsubscript{2}]\textsubscript{2})
and, 1,12-di(3-vinylbenzylimidazolium)dodecane bis[(trifluoromethyl)sulfonyl]imide ([(VBIM)₂C₁₂][NTf₂]₂) were synthesized following the previously reported procedure.¹⁴,¹⁹,₅⁷ An on-fiber UV-initiated polymerization approach was applied to prepare the cross-linked PIL-based SPME sorbent coatings onto nickel-titanium (nitinol) metal alloys according to a recently published method.³⁰,⁵⁶ Prior to coating the IL monomers/cross-linkers, surface modifications were accomplished on the unmodified nitinol wire to prevent sloughing of the coating. First, the surface of the nitinol wire was functionalized with an active hydroxyl functional group (Ti-OH) by immersing it in boiling hydrogen peroxide solution 30 % (w/v) for 2 h at 72 °C. Afterwards, the activated substrate was reacted with VTMS for 2 h at 85 °C in order to form a chemical linkage between the organosilane and the surface of the substrate. A 1 cm length of modified nitinol wire was then attached to the commercial SPME fiber assembly (Supelco) and dip coated with a mixture of IL monomer, IL cross-linker (50 % by weight of monomer) and 3 % (w/w) of the photo initiator DARCOUR 1173. The dip coated fiber was then placed into a UV polymerization chamber and exposed to 360 nm UV light for 0.5 h to prepare the [NTf₂]⁻-based PIL sorbent coating as well as 254 nm UV light for 2 h to prepare the [Br]⁻-based PIL sorbent coating.

2.2.4 SPME procedure

After on-fiber UV polymerization of the sorbent coatings, the fibers were first conditioned by immersing into 50 μL of methanol (conditioning solvent) for 30 min. A 20 μL portion of the conditioning solvent was then injected into HPLC to monitor the chromatographic background. Fibers may need additional conditioning steps before starting the extraction/desorption cycle if the background is not sufficiently clean. After
conditioning step, all extractions were performed in direct-immersion mode followed by off-line solvent desorption of the extracted analytes from the sorbent coating prior to HPLC-UV analysis. The SPME fiber was directly immersed into a 10 mL amber vial containing a working solution of analytes under an 800 rpm agitation rate at ambient temperature. After the sampling step, off-line desorption was performed by placing the fiber into a sealed end 10-100 µL pipet tip (Fisher Scientific) containing 50 µL desorption solvent. A heat gun was used to seal the end of the pipet tip. A volume of 20 µL of desorption solvent was then injected for the HPLC-UV analysis. Additional desorption steps were performed prior to the next extraction/desorption cycle to remove possible carryover effects.

Recovery studies were accomplished in two different water matrixes, namely tap water obtained from laboratory and river water obtained from the Maumee River in Maumee, OH (USA). River water samples were filtered through a 3 mL syringe with 0.45 µL filter units (Fisher Scientific). The relative recovery was determined by adding a known concentration of the analyte to a sample solution followed by obtaining the experimental concentration relative to the actual concentration.

2.3 Result and discussions

2.3.1 Optimization of desorption conditions

Optimization of adequate desorption conditions is an integral component to SPME-LC method development. It can often be time consuming since the process involves the optimization of desorption solvent, desorption time, solvent volume, and evaluation of any
carryover effects. In many cases, it may be difficult to achieve complete desorption of analytes from the SPME sorbent in SPME-LC methods due to the slow kinetics of desorption process. Therefore, it is important to design carefully desorption optimization experiments.

In this study, desorption process was carried out using the off-line desorption mode in which the extracted analytes were desorbed in the minimum amount of desorption solvent prior to the HPLC analysis. In the off-line desorption mode, optimum solvent volume chosen based on sensitivity of the method. The amount of 50 µL as desorption volume was chosen to fully immerse the sorbent coating into the sealed end pipet tip as well as sufficiently small to ensure a high sensitivity of analytes for the developed method. The maximum desorption efficiency of the analytes can be achieved by optimization of desorption time and composition of desorption solvent. The nature of the desorption solvent for Fiber 1, Fiber 2, and Fiber 3 (see Table 2.2 for chemical composition) on desorption efficiency of the studied analytes was evaluated by selecting three common reversed-phase organic solvents including methanol, acetonitrile, and a mixture of methanol/water 80:20 % (v/v). Figure 2-2 shows the effect of the desorption solvent using the three PIL-based fiber coatings. In nearly all cases, methanol provided the highest desorption efficiency compared to the other desorption solvents, except for Irg and 3-t-ButP. Fiber 1 and Fiber 2 containing [NTf₂]⁻ anions showed significantly better desorption efficiencies for Bnzd in methanol than the other solvents. However, Fiber 3 containing the [Br]⁻ anion showed a slightly better desorption efficiency of Bnzd in methanol than acetonitrile and methanol/water mixture. This may be due to the stronger hydrogen-bonding interactions of this hydrogen bond acidic analyte with Fiber 3 containing the
hydrogen bond basic [Br]⁻ anion rather than desorption solvent. Fiber 3 showed significantly better desorption efficiency of Irg in methanol. However, slightly lower and comparable desorption efficiency of Irg was observed in methanol compared to the other solvents for Fiber 1 and 2, respectively. This may be due to different solvation characteristics of the [Br]⁻-based sorbent coating in methanol compared to the [Ntf₂]⁻-based sorbent coating, which can enhance the desorption efficiency of Irg in methanol by Fiber 3. For 3-t-ButP, Fiber 1 and 3 exhibited slightly better desorption efficiency in methanol compared to the other solvents. However, better desorption efficiency of this analyte was observed using the mixture of methanol/water for Fiber 2. The effect of the desorption solvent for the commercial fibers is shown in Figure 2-3. For PA and PDMS fibers (Figure 2-3B, Figure 2-3C), acetonitrile provided a slightly better desorption efficiency than methanol for most analytes. However, methanol showed a higher desorption efficiency for PDMS/DVB fiber (Figure 2-3A). Therefore, methanol was selected as desorption solvent for all PIL-based and PDMS/DVB fibers while acetonitrile was chosen as a desorption solvent for PA and PDMS fibers in all subsequent studies.

Desorption time is an important factor which can impact desorption efficiency. Figure 2-4 illustrates the desorption time profiles for Fiber 1, Fiber 2, and Fiber 3. All extractions were performed in 30 min by using the direct immersion mode. Desorption profiles were obtained by exposing the coating in methanol for different time intervals raising from 10 min to 60 min. As shown in Figure 2-4A, Fiber 1 provided the highest desorption efficiency after 30 min for most analytes, except for BP-A. In the case of Fiber 2 shown in Figure 2-4B, optimum desorption time was achieved at approximately 40 min. The optimal desorption efficiency for all analytes was reached after 20 min for Fiber 3.
shown in Figure 2-4C. As a result, in the case of Fiber s1 and 3, desorption times of 30 min were chosen as a compromise and Fiber 2, 40 min desorption time was selected for all subsequent studies. The analytical precision of all model analytes ranged from 1.2-14.1 % for all PIL-based sorbent coatings at significantly long desorption time (60 min), which indicated the robustness of the PIL-based sorbent coatings for SPME-LC applications.

The desorption time profiles were also obtained for all commercial fibers (Figure 2-5). Desorption time was varied from 10 min to 40 min and the results indicate that all analytes reach their maximum desorption efficiencies after 30 min. This time was chosen as the optimum desorption time for all commercial fibers.

It is important to emphasize that the optimal desorption time can minimize analyte carry over. In this study, most of the analytes reached their complete desorption at the optimized desorption time. However, for some analytes such as 2-NP and 3-t-ButP, additional washes were required to eliminate carry over completely prior to the next extraction/desorption cycle.
Table 2.2. Chemical composition of all studied cross-linked PIL-based sorbent coatings.

<table>
<thead>
<tr>
<th>Fiber name</th>
<th>IL monomer</th>
<th>IL Cross-linker&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Approximate film thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fiber 1</td>
<td><img src="image1" alt="Monomer Structure" /></td>
<td><img src="image2" alt="Cross-linker Structure" /></td>
<td>14</td>
</tr>
<tr>
<td>Fiber 2</td>
<td><img src="image3" alt="Monomer Structure" /></td>
<td><img src="image4" alt="Cross-linker Structure" /></td>
<td>13</td>
</tr>
<tr>
<td>Fiber 3</td>
<td><img src="image5" alt="Monomer Structure" /></td>
<td><img src="image6" alt="Cross-linker Structure" /></td>
<td>14</td>
</tr>
</tbody>
</table>

<sup>a</sup> Amount fixed at 50% (w/w) with respect to the IL monomer.

<sup>b</sup> Calculated based on the average film thickness (see section 2.3.7)
Figure 2-2. Extraction peak areas of model analytes in different desorption solvents (☐) methanol, ( [] ) acetonitrile, ( []) methanol/water 80/20 % (v/v) for A) Fiber 1, B) Fiber 2, C) Fiber 3.
Figure 2-3.
Extraction peak areas of the model analytes in different desorption solvents (□) methanol, (■) acetonitrile, (■) methanol/water (80/20 % (v/v)) for A) PDMS/DVB fiber, B) PA fiber, C) PDMS fiber.
Figure 2-4. Desorption time profiles obtained for A) Fiber 1, B) Fiber 2, and C) Fiber 3. Concentration of the analytes were (♦) Cmz 200 ng mL⁻¹; (■) Bnzal 400 ng mL⁻¹; (Δ) BP-A 400 ng mL⁻¹; (○) 2-NP 10 ng mL⁻¹; (●) 6-tfTol 400 ng mL⁻¹; (◇) 3-t-butP 200 ng mL⁻¹; (□) EB 200 ng mL⁻¹; (♦) Nap 100 ng mL⁻¹; (▲) Gfz 25 ng mL⁻¹; (■) Irg 10 ng mL⁻¹.
**Figure 2.5.** Desorption time profiles obtained for A) PDMS/DVB fiber, B) PA fiber, and C) PDMS fiber. Concentration of the analytes were (●) Cmz 200 ng mL⁻¹; (■) Bnzal 400 ng mL⁻¹; (Δ) BP-A 400 ng mL⁻¹; (○) 2-NP 10 ng mL⁻¹; (●) 6-tfTol 400 ng mL⁻¹; (◊) 3-t-butP 200 ng mL⁻¹; (□) ethylbenzoate 200 ng mL⁻¹; (×) Nap 100 ng mL⁻¹; (▲) Gfz 25 ng mL⁻¹; (==) Irg 10 ng mL⁻¹.
2.3.2 Effects of extraction time

Extraction time is a fundamental parameter that has a great influence on the analyte extraction efficiency. The optimum extraction time can be governed by reaching equilibrium where the maximum sorption of analytes is achieved. The sorption-time profiles of model analytes for each PIL-based and commercial fibers were studied by applying different extraction time periods ranging from 15 min to 60 min. Extractions were performed under an agitation rate of 800 rpm followed by offline solvent desorption under optimized desorption conditions. The results are shown in Figure 2-6 and Figure 2-7, respectively. In the case of all PIL-based fiber coatings, equilibration was achieved in approximately 45 min for the majority of analytes. However, BP-A and 3-t-ButP are an exception as equilibration was not reached even after 60 min. For 6-tfTol, equilibration was reached after 45 min for Fiber 1 (Figure 2-6A) and in the case of Fiber 2 and Fiber 3 (Figure 2-6B and 2-6C), equilibration was achieved at an extraction time longer than 60 min. It is worth mentioning that analytes can demonstrate different partition behaviors to the various sorbent coatings that can result in different equilibration times. Since most of the analytes achieved equilibration at 45 min, this optimum extraction time was selected for all subsequent studies.

In the case of the commercial fibers, the results clearly demonstrated that equilibration was not reached for most analytes even after 60 min. This is due to the much higher film thickness for commercial fibers which generally requires a longer extraction time for analytes to partition or adsorb to the sorbent coating. An extraction time of 45 min
was chosen as a compromise for all commercial fibers to avoid extensive extraction procedures as well as sufficient extraction efficiencies for analytical performance studies.

**Figure 2-6.** Direct immersion sorption time profiles obtained for A) Fiber 1, B) Fiber 2, and C) Fiber 3. Concentration of analytes were (♦) Cmz 200 ng mL\(^{-1}\); (■) Bnzal 400 ng mL\(^{-1}\); (△) BP-A 400 ng mL\(^{-1}\); (○) 2-NP 10 ng mL\(^{-1}\); (●) 6-tfTol 400 ng mL\(^{-1}\); (◇) 3-t-butP 200 ng mL\(^{-1}\); (□) EB 200 ng mL\(^{-1}\); (×) Nap 100 ng mL\(^{-1}\); (▲) Gfz 25 ng mL\(^{-1}\); (≡) Irg 10 ng mL\(^{-1}\).
Figure 2-7. Direct immersion sorption time profiles obtained for A) PDMS/DVB fiber, B) PA fiber, and C) PDMS fiber. Concentration of the analytes were (●) Cmz 200 ng mL\(^{-1}\); (■) Bnzal 400 ng mL\(^{-1}\); (∆) BP-A 400 ng mL\(^{-1}\); (○) 2-NP 10 ng mL\(^{-1}\); (●) 6-tfTol 400 ng mL\(^{-1}\); (◇) 3-t-butP 200 ng mL\(^{-1}\); (□) ethylbenzoate 200 ng mL\(^{-1}\); (×) Nap 100 ng mL\(^{-1}\); (▲) Gfz 25 ng mL\(^{-1}\); (≡) Irg 10 ng mL\(^{-1}\).
2.3.3 Effects of pH

It is well-known that the extraction of acidic and basic compounds depends significantly upon the pH of the extraction system. The extraction efficiency of acidic and basic compounds can be improved at low and high pH values, respectively due to largely presence of these compounds in their neutral forms. Therefore, sensitivity of the ionizable analytes in their neutral forms can be improved significantly by adjusting the pH of the sample. The effect of pH on the extraction efficiency of studied analytes was examined by directly immersing the sorbent coatings into the sample solution at pH 2, 4, and 7. All extractions were performed for each sorbent coating under the optimum extraction time as well as the optimized desorption conditions. For the three PIL fibers shown in Figure 2-8, the extraction efficiency for the majority of the analytes including Cmz, Bnzal, EB, Nap, and Irg were largely unchanged when the pH was low. For BP-A and 6-tfTol, the extraction efficiency improved slightly at lower pH values due to possible electrostatic interactions between the analytes and PIL-sorbent coatings. The two phenols, 2-NP and 3-t-ButP, exhibited pH sensitive behavior, when the pH of the sample solution was lowered, the amount of 2-NP extracted was decreased while the amount of 3-t-ButP extracted significantly improved. For Fibers 1 and 3 (Figures 2-8A and 2-8C), the 10 ng/mL of 2-NP was not detected at pH 2; however, for Fiber 2 (Figure 2-8B), the amount of 2-NP was still detectable at the 10 ng/mL level. In the case of Fiber 1 and 3, the extraction efficiency of Gfz increased at pH 4, since this analyte possesses a pKₐ of 4.42 at 25 °C. However, the extraction efficiency of Gfz was slightly higher at pH 2 compared to pH 4 for Fiber 2. This may be due to the mainly presence of Gfz in the neutral form, which
results in the better extraction efficiency of this analyte at low pH values. Based on the combined results obtained for the PIL-based fibers, a compromised pH of 7 was chosen for Fiber 1 and Fiber 3 in which all analytes can be detected, even though higher extraction efficiency was achieved for phenolic compounds at low pH values. In the case of Fiber 2, pH 2 was chosen for Fiber 2, where a higher extraction efficiency was obtained for higher numbers of analytes.

As shown in Figure 2-9A, the extraction efficiency of the PDMS/DVB fiber for the majority of analytes was not significantly altered by varying the pH, except for 3-t-ButP and Gfz. These analytes exhibited a better extraction efficiency at low pH since their neutral forms were dominant in the acidic condition. Interestingly, Gfz was not detected at pH 4 and pH 7 using the PA (Figure 2-9B) and PDMS (Figure 2-9C) fibers. However, the extraction efficiency of Gfz was significantly enhanced at pH 2. Since pH 2 demonstrated an optimal extraction efficiency for the model analytes using all commercial fibers, this pH level was selected for the calibration study of these fibers.

2.3.4 Evaluation of extraction efficiency for PIL-based fibers and commercial SPME fibers

The extraction efficiency of the SPME sorbent coating can be evaluated by comparing the overall extraction peak areas of model analytes. Figure 2-10 represents the chromatographic peak areas of the studied analytes obtained at optimized extraction/desorption conditions for all PIL-based fiber coatings. The role of the anion moiety for Fiber 3 was examined due to the higher extraction peak areas obtained for
Figure 2-8. Extraction peak area of model analytes at (□) pH = 2, (■) pH = 4, (■■) pH = 7 aqueous solution. Extraction data obtained using A) Fiber 1, B) Fiber 2, C) Fiber 3.
Figure 2-9. Extraction peak area of model analytes at (□) pH = 2, (◼) pH = 4, (■) pH = 7 aqueous solution. Extraction data obtained using A) PDMS/DVB, B) PA fiber, C) PDMS fiber.
phenolic compounds including, 2-NP and 3-t-ButP. This may be due to the presence of the hydrogen bond basic bromide anion comprised in this coating which is known to enhance selectivity toward hydrogen-bond acidic analytes.\textsuperscript{15} On the other hand, the role of the cation moiety understood in which Fiber 1 containing the vinyl benzyl moiety exhibited better extraction for aromatic compounds, such as Nap and Cmz, due to enhanced π-π interactions.\textsuperscript{14, 25, 31} In regards to extraction precision (n=3), all PIL fibers exhibited a percentage relative standard deviation (RSD) ranging from 2.3-13.1 %, 1.8-10.9 %, and 1.7-8.1 %, for Fiber 1, Fiber 2, and Fiber 3, respectively.

The extraction efficiency of the commercial SPME fibers toward model analytes was evaluated by comparing the overall chromatographic peak areas at optimized conditions. As shown in Figure 2-11, the PDMS/DVB fiber demonstrated the best extraction efficiency for most analytes. The polar PA fiber exhibited better extraction efficiency than the PDMS fiber, specifically for highly polar analytes such as BP-A. The PDMS fiber showed poor extraction efficiency for most polar analytes. For example, BP-A was not detected by the PDMS fiber. Also, the PDMS and PA fibers were not able to extract 2-NP at the 10 ng/mL level. On the contrary, this analyte was extracted at the same concentration level by the PDMS/DVB fiber under optimized extraction/desorption conditions. Since both the PA and PDMS/DVB fibers showed significantly better extraction efficiencies than the PDMS fiber, these commercial SPME sorbent coatings were selected for a comparative study with the PIL-based SPME sorbent coatings.
Figure 2-10. Comparison of the extraction efficiency for the PIL-based fibers including (□) Fiber 1, (■) Fiber 2, and (■■) Fiber 3. Extraction peak areas were obtained under optimized extraction/desorption conditions.
Figure 2-11. Comparison of the extraction efficiency for commercial SPME fibers including (□) PDMS/DVB, (■) PA fiber, and (■) PDMS fiber. Extraction peak areas were obtained under the optimized extraction/desorption conditions.
2.3.5 Analytical performance of all sorbent coatings in the extraction of the model analytes

After carefully optimizing each extraction/desorption parameter for each individual sorbent coating, all sorbent coatings were subjected to the calibration study. All extractions were performed according to the optimized extraction/desorption conditions discussed in the previous sections. The figures of merit including sensitivities (calibration slopes), linear ranges, correlation coefficients (R), and limits of detection (LODs) obtained for all PIL-based fibers as well as commercial fibers including PA and PDMS/DVB fibers are listed in Table 2.3 and Table 2.4, respectively. Calibration data was acquired using a minimum of seven calibration levels ranging from 0.5 to 500 ng mL\(^{-1}\). As shown in Table 2.3, Fiber 1 exhibited a better sensitivity (represented by the slope of the calibration curve) for aromatic compounds including Nap and Cmz. As mentioned previously, this may be related to \(\pi-\pi\) interactions between the fiber coating and analytes. On the other hand, relatively better sensitivity for polar analytes, such as BP-A, was observed for Fiber 3 containing the hydrogen basic bromide anion. The effect of pH on sensitivity for analytes including 2-NP, 3-t-ButP, and Gfz was clearly observed since the calibration data was obtained at pH 2 for Fiber 2 compared to the other PIL fibers. Fiber 2 showed a better sensitivity for 3-t-ButP and Gfz compared to Fiber 1 and Fiber 3. Lower sensitivity was observed for 2-NP compared to the other PIL fibers due to lower amount of this analyte extracted at pH 2. The LODs were calculated by decreasing the analyte concentration until a signal to noise ratio of 3:1 was observed. The overall LODs for all model analytes were in the range of 2.5-20 ng mL\(^{-1}\), 2-20 ng mL\(^{-1}\), and 2.5-20 ng mL\(^{-1}\) for Fiber 1, Fiber 2, and
Fiber 3, respectively. The correlation coefficient varied between 0.991 and 0.999 for all PIL-fibers.

As shown in Table 2.4, the PDMS/DVB fiber exhibited up to 1 order of magnitude better sensitivity for most analytes (except BP-A) compared to the PA fiber. Wider linear ranges and lower LODs were obtained for the PDMS/DVB fiber compared to the PA fiber. The linear ranges were spanned from 0.5 to 500 ng mL\(^{-1}\) for the PDMS/DVB fiber and 2.5-500 ng mL\(^{-1}\) for the PA fiber. The overall LODs for all analytes were in the range of 0.2-2.5 ng mL\(^{-1}\) for the PDMS/DVB fiber and 1-25 ng mL\(^{-1}\) for the PA fiber with correlation coefficients between 0.996 and 0.999 for both fibers.

In comparison with the PA fiber, the PIL-based fibers demonstrated wider linear ranges and lower LODs of model analytes, except for Bnzal and Irg. The PIL-based fibers also exhibited comparable linear ranges (low to high ppb levels) and LODs (trace ppb levels) for some of the model analytes including, 2-NP, Nap, Gfz, and Irg compared to the PDMS/DVB fiber, despite their lower film thicknesses compared to commercial fibers. However, additional normalization of the calibration slope with respect to the film thickness for each sorbent coating was required in order to compare selectivity, and sensitivity of the commercial fibers to the PIL-based fibers.
<table>
<thead>
<tr>
<th>Analytes</th>
<th>Fiber 1</th>
<th>Fiber 2</th>
<th>Fiber 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Slope ± SD&lt;sup&gt;a&lt;/sup&gt;</td>
<td>LOD&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Slope ± SD</td>
</tr>
<tr>
<td>Cmz</td>
<td>14.1 ± 0.52</td>
<td>40-500</td>
<td>0.991</td>
</tr>
<tr>
<td>Bnzal</td>
<td>7.74 ± 0.86</td>
<td>40-500</td>
<td>0.991</td>
</tr>
<tr>
<td>BP-A</td>
<td>14.0 ± 1.15</td>
<td>20-500</td>
<td>0.991</td>
</tr>
<tr>
<td>2-NP</td>
<td>93.4 ± 6.96</td>
<td>5-500</td>
<td>0.997</td>
</tr>
<tr>
<td>6-tTol</td>
<td>14.2 ± 1.76</td>
<td>40-500</td>
<td>0.990</td>
</tr>
<tr>
<td>3-t-ButP</td>
<td>9.06 ± 0.67</td>
<td>40-500</td>
<td>0.996</td>
</tr>
<tr>
<td>EB</td>
<td>12.6 ± 1.43</td>
<td>40-500</td>
<td>0.991</td>
</tr>
<tr>
<td>Nap</td>
<td>168 ± 14.7</td>
<td>5-500</td>
<td>0.998</td>
</tr>
<tr>
<td>Gfz</td>
<td>5.43 ± 0.36</td>
<td>20-500</td>
<td>0.995</td>
</tr>
<tr>
<td>Irg</td>
<td>170 ± 11.9</td>
<td>5-500</td>
<td>0.999</td>
</tr>
</tbody>
</table>

<sup>a</sup> SD: error of the slope for n = 7.
<sup>b</sup> Calculated by decreasing the analyte concentration until a 3:1 S/N was achieved.
<table>
<thead>
<tr>
<th>Analytes</th>
<th>Linear range (ng mL⁻¹)</th>
<th>Slope ± SDᵃ</th>
<th>LODᵇ (ng mL⁻¹)</th>
<th>R</th>
<th>Linear range (ng mL⁻¹)</th>
<th>Slope ± SD</th>
<th>R</th>
<th>LOD (ng mL⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cmz</td>
<td>50-500</td>
<td>8.73 ± 0.33</td>
<td>25</td>
<td>0.998</td>
<td>5-500</td>
<td>89.421 ± 1.95</td>
<td>0.999</td>
<td>2.5</td>
</tr>
<tr>
<td>Bnzal</td>
<td>25-500</td>
<td>22.1 ± 0.29</td>
<td>10</td>
<td>0.999</td>
<td>5-500</td>
<td>322.4 ± 4.92</td>
<td>0.999</td>
<td>2.5</td>
</tr>
<tr>
<td>BP-A</td>
<td>25-500</td>
<td>56.9 ± 1.04</td>
<td>10</td>
<td>0.999</td>
<td>25-500</td>
<td>14.06 ± 0.18</td>
<td>0.999</td>
<td>10</td>
</tr>
<tr>
<td>2-NP</td>
<td>25-500</td>
<td>17.7 ± 0.31</td>
<td>20</td>
<td>0.999</td>
<td>2.5-200</td>
<td>161 ± 2.16</td>
<td>0.999</td>
<td>1</td>
</tr>
<tr>
<td>6-tfTol</td>
<td>25-500</td>
<td>38.6 ± 0.97</td>
<td>10</td>
<td>0.999</td>
<td>5-500</td>
<td>134 ± 4.75</td>
<td>0.997</td>
<td>2.5</td>
</tr>
<tr>
<td>3-t-ButP</td>
<td>25-500</td>
<td>20.3 ± 0.44</td>
<td>10</td>
<td>0.999</td>
<td>25-500</td>
<td>40.5 ± 1.24</td>
<td>0.998</td>
<td>2.5</td>
</tr>
<tr>
<td>Ethenzoate</td>
<td>25-500</td>
<td>27.3 ± 1.02</td>
<td>10</td>
<td>0.997</td>
<td>5-500</td>
<td>267 ± 1.50</td>
<td>0.999</td>
<td>2.5</td>
</tr>
<tr>
<td>Nap</td>
<td>5-500</td>
<td>194 ± 5.83</td>
<td>2.5</td>
<td>0.998</td>
<td>0.5-500</td>
<td>1103 ± 18.21</td>
<td>0.999</td>
<td>0.2</td>
</tr>
<tr>
<td>Gfz</td>
<td>25-500</td>
<td>30.5 ± 0.88</td>
<td>20</td>
<td>0.998</td>
<td>5-500</td>
<td>85.28 ± 2.73</td>
<td>0.997</td>
<td>2.5</td>
</tr>
<tr>
<td>Irg</td>
<td>2.5-500</td>
<td>585 ± 13.3</td>
<td>1</td>
<td>0.998</td>
<td>2.5-500</td>
<td>518 ± 16.6</td>
<td>0.996</td>
<td>1</td>
</tr>
</tbody>
</table>

ᵃ SD: error of the slope for n = 7.
ᵇ Calculated by decreasing the analyte concentration until a 3:1 S/N was achieved.
2.3.6 Sensitivity and selectivity comparison of the PIL-based fibers to the commercial fibers using normalized calibration slope

It is well-known that the extraction efficiency of analytes in SPME is associated with several factors including the nature of sorbent coating, sorbent volume which can be estimated based upon the film thickness, and the sorbent coating’s surface area.\textsuperscript{34}

It can be assumed that all sorbent coatings presented in this study contain the similar surface areas due to the identical fiber length (1 cm). However, the film thickness of the PDMS/DVB fiber (60 µm) and the PA fiber (85 µm) are significantly higher than the PIL-based fibers (~14 µm). Hence, in order to understand the effect of the sorbent coating on selectivity and sensitivity of analytes, these factors were normalized with respect to the film thickness for each sorbent coating.\textsuperscript{25} The sensitivity of the studied analytes for each sorbent coating was normalized by dividing the slope of the calibration curve by the film thickness. It is worth mentioning that the effect of the sorbent coating on sensitivity of analytes can be also quantified using the external calibration curve for calculating analyte-fiber partition coefficient in order to obtain absolute sensitivity based upon the overall recovered analyte throughout the extraction. Figure 2-12 represents film thickness normalization of the calibration slope for the model analytes using all fibers. After normalization, all PIL-based sorbent coatings demonstrated significantly higher sensitivities for all studied analytes when compared to the PA fiber. In the case of the PDMS/DVB fiber, higher normalized calibration slopes were obtained for analytes containing aromatic rings including Cmz, Bnzal, 6-tfTol, Etbenzoate, and Nap than the PIL.
fibers. This may be due to the presence of the divinylbenzene moieties that make up the cross-linker which enhance π-π interactions toward aromatic compounds. Fiber 1, which is comprised of a vinylbenzyl moiety, showed comparable normalized slope with the PDMS/DVB fiber. Interestingly, for more polar analytes such as 2-NP, 3-t-ButP, Gfz, and Irg, the PIL fibers exhibit higher extraction affinity than the PDMS/DVB fiber. This may be due to the cation and anion moieties of the PIL fibers, which can favorably interact with polar analytes through electrostatic and hydrogen-bonding interactions.\textsuperscript{25} In general, it can be concluded that structural tailoring of the PIL-based fibers provides a wide range of selectivity toward both polar and non-polar compounds. The latter also demonstrates the versatility of the PIL-based SPME fibers for the extraction of different analyte classes.

**Figure 2-12.** Comparison of film thickness normalization of the calibration slope for all sorbent coatings in the extraction of the model analytes. (□) Fiber 1, (❖) Fiber 2, (■) Fiber 3, (●) PA fiber, (□) PDMS/DVB fiber.
2.3.7 Effect of the PIL-based fiber film thickness on analytical performance

After all extractions, the PIL fibers were sacrificed for the visual analysis via SEM in order to estimate their film thickness. The cross-section and surface morphology of all PIL sorbent coatings are illustrated in Figure 2-13. As reported in Table 2.2, the average film thickness of the PIL fibers, namely Fiber 1, Fiber 2, and Fiber 3 were estimated to be 14 µm, 13 µm, and 14 µm, respectively. After approximately 100 extraction/desorption cycles, a rough surface morphology was observed for all cross-linked PIL fibers due to the presence of the IL cross-linker. As mentioned previously, the overall extraction efficiency is related to the film thickness of the sorbent coating. In an attempt to understand the role of the film thickness on the sensitivity of the studied model analytes, Fiber 1 with a higher film thickness (with an average film of ~ 55 µm) was prepared and subjected to the developed method. The analytical performance for Fiber 1 possessing a film thickness of ~ 55 µm was examined using the developed method under similar extraction/desorption conditions, which were optimized for Fiber 1 possessing a smaller film thickness. The calibration curve was obtained by varying the analyte concentration ranging from 5-500 ng mL\(^{-1}\) with the minimum seven calibration levels. As shown in Table 2.5, the thicker sorbent coating exhibited approximately a 1.4 to 6 higher calibration slope when compared to the 14 µm fiber. However, for mostly polar analytes, namely 2-NP, BP-A, and 3-t-ButP, the slopes for the thicker sorbent coating were similar and/or lower than the slope for the thinner fiber. Since the calibration study was not performed under optimized extraction/desorption conditions, a longer extraction time was required for the thicker fiber in order to reach equilibration of the more polar analytes, which have a higher matrix.
Figure 2-13. Scanning electron micrographs of the cross-linked PIL-based fibers after 100 direct immersion extractions followed by offline organic solvent desorption. (A) Fiber 1 (~14 µm), (B) Fiber 2 (~13 µm), (C) Fiber 3 (~14 µm), (D) Fiber 1 possessing higher thickness (~55 µm), (E) Surface morphology of Fiber 1. Numbers in parenthesis represent the approximate average film thickness for each fiber.
affinity in the aqueous solution. In general, wider linear ranges and better LODs of model analytes were achieved using the thicker fiber. The linear ranges of the model analytes ranged from 5-500 ng mL\(^{-1}\) and the LODs of the analytes ranged from 1-20 ng mL\(^{-1}\). The correlation coefficients varied between 0.995 and 0.999. It can be concluded that by increasing the film thickness of the sorbent coating, better sensitivity can be achieved, although longer sampling times are needed for most polar analytes.

**Table 2.5.** Analytical performance of Fiber 1 possessing a higher film thickness (~ 55 µm) for the extraction of model analytes

<table>
<thead>
<tr>
<th>Analytes</th>
<th>Slope ± SD</th>
<th>Linear ranges (ng mL(^{-1}))</th>
<th>R</th>
<th>LOD (ng mL(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbamazepine</td>
<td>17.62 ± 0.78</td>
<td>20-500</td>
<td>0.987</td>
<td>20</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>46.39 ± 1.05</td>
<td>10-500</td>
<td>0.998</td>
<td>5</td>
</tr>
<tr>
<td>Bisphenol A</td>
<td>14.37 ± 0.41</td>
<td>10-500</td>
<td>0.997</td>
<td>5</td>
</tr>
<tr>
<td>2-nitrophenol</td>
<td>83.65 ± 3.42</td>
<td>5-500</td>
<td>0.994</td>
<td>5</td>
</tr>
<tr>
<td>Toluidine</td>
<td>48.57 ± 2.10</td>
<td>5-500</td>
<td>0.994</td>
<td>5</td>
</tr>
<tr>
<td>3-terbutylphenol</td>
<td>9.46 ± 1.00</td>
<td>10-500</td>
<td>0.963</td>
<td>5</td>
</tr>
<tr>
<td>Ethylbenzoate</td>
<td>49.46 ± 2.16</td>
<td>5-500</td>
<td>0.993</td>
<td>5</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>397.14 ± 15.91</td>
<td>5-500</td>
<td>0.993</td>
<td>2</td>
</tr>
<tr>
<td>Gemfibrozil</td>
<td>8.91 ± 0.37</td>
<td>20-500</td>
<td>0.996</td>
<td>20</td>
</tr>
<tr>
<td>Irgasan</td>
<td>412.98 ± 12.24</td>
<td>5-500</td>
<td>0.996</td>
<td>1</td>
</tr>
</tbody>
</table>

\(^{a}\) SD: error of the slope for n = 7.

\(^{b}\) Calculated by decreasing the analyte concentration until a 3:1 S/N was achieved.
2.3.8 Method validation and accuracy using PIL-based SPME fibers

To demonstrate the applicability of the PIL-based fibers as well as validation of the developed method, recovery studies were performed using two real water samples, including river and tap water. Based on the calibration data, two spiked concentration levels, namely 40 ng mL\(^{-1}\) and 200 ng mL\(^{-1}\) were selected in order to obtain a relative recovery percentage of the studied analytes in the real water samples. Fiber 1 and Fiber 2 were selected as representative SPME fibers since these fibers showed acceptable analytical performance for the studied analytes. As shown in Table 2.6, the relative recovery of Fiber 1 ranged from 41.9 ± 5.54 % to 127 ± 11.8 % at 40 ng mL\(^{-1}\) and 52.9 ± 9.7 % to 119 ± 10.41 % at 200 ng mL\(^{-1}\) for the river water sample, while the recovery of Fiber 1 ranged from 37.5 ± 5.44 % to 125 ± 14.7 % at 40 ng mL\(^{-1}\) and 34.1 ± 3.73% to 110 ± 14.5 % at 200 ng mL\(^{-1}\) for the tap water sample.

In the case of Fiber 2, recovery ranged from 76.7 ± 11.4 % to 103 ± 6.37 % at 40 ng mL\(^{-1}\) and 77.2 ± 8.67 % to 122 ± 13.4 % at 200 ng mL\(^{-1}\) for the river water sample, while the recovery ranged from 67.2 ± 0.52 % to 98.2 ± 13.2 % at 40 ng mL\(^{-1}\) and 61.2 ± 5.65 % to 105 ± 10.6 % at 200 ng mL\(^{-1}\) for the tap water sample. In general, Fiber 2 demonstrated a better relative recovery at both spiked concentration levels in both water samples compared to Fiber 1. For example, Fiber 1 showed a poorer recovery of 2-NP, 37.5 ± 5.44 % and 41.9 ± 5.54 % at 40 ng mL\(^{-1}\) for both tap and river water, respectively. However, the recovery of 2-NP was significantly improved using Fiber 2, (67.2 ± 0.52 % and 84.2 ± 0.61 % at 40 ng mL\(^{-1}\)) in both tap and river water samples. The recovery results for 2-NP using the PIL-based fiber were encouraging since the recoveries of phenolic
compounds from water samples using direct-immersion SPME coupled with the HPLC is challenging. The overall RSD for Fiber 1 in both water samples ranged from 3.34-14.7 % at 40 ng mL⁻¹ and 3.73-16.44 % at 200 ng mL⁻¹. In the case of Fiber 2, the overall RSD in both water samples ranged from 0.52-17.9 % at 40 ng mL⁻¹ and 1.62-13.6 % at 200 ng mL⁻¹. These recoveries and precision results are acceptable for the direct-immersion extraction and organic solvent desorption as well as the high complexity of the real water samples. The recovery results further indicate that the cross-linked PIL nitinol-based SPME fibers are capable of being employed for SPME-LC applications, which is involved with several extraction/desorption cycles as well as various sampling conditions.
Table 2.6. Relative recovery (%) and precision results of Fiber 1 and Fiber 2 for the extraction of model analytes from real water samples.

<table>
<thead>
<tr>
<th>Analytes</th>
<th>Fiber 1</th>
<th>Fiber 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>River water ng mL(^{-1})</td>
<td>% RSD(^{a}) a ng mL(^{-1})</td>
</tr>
<tr>
<td>Cmz</td>
<td>127</td>
<td>11.8</td>
</tr>
<tr>
<td>Bnzal</td>
<td>81.8</td>
<td>8.9</td>
</tr>
<tr>
<td>BP-A</td>
<td>95.4</td>
<td>3.34</td>
</tr>
<tr>
<td>2-NP</td>
<td>41.9</td>
<td>5.54</td>
</tr>
<tr>
<td>6-tfTol</td>
<td>96.8</td>
<td>10.3</td>
</tr>
<tr>
<td>3-t-ButP</td>
<td>104</td>
<td>3.86</td>
</tr>
<tr>
<td>EB</td>
<td>53.9</td>
<td>7.14</td>
</tr>
<tr>
<td>Nap</td>
<td>96.2</td>
<td>2.94</td>
</tr>
<tr>
<td>Gfz</td>
<td>63.4</td>
<td>5.43</td>
</tr>
<tr>
<td>Irg</td>
<td>67.1</td>
<td>12.1</td>
</tr>
</tbody>
</table>

\(^{a}\)Precision data obtained for n = 3.
2.4 Conclusions

This study demonstrates the applicability and versatility of PIL-based sorbent coatings for various SPME-LC applications. Structural tailoring of the PIL-based fibers offers a tunable selectivity mechanism towards various analyte classes. The [Br]⁻ based fiber exhibited overall selectivity towards more polar analytes which may due to the hydrogen bond basicity of the [Br]⁻ anion. The PIL-based fiber composed of benzyl moiety may enhance the selectivity of aromatic compounds due to π-π interactions. Higher sensitivity and lower LODs of the PIL-based fibers compared to the commercial fibers for the extraction of polar analytes introduce an alternative SPME-LC sorbent coating to the SPME community for exploring a wider scope of analytical applications. Acceptable precision under extensive extraction/desorption conditions, including the nature of the desorption solvent, desorption time, extraction time, and pH further proved the applicability of the PIL fibers as robust and selective sorbents for LC applications. Also, it indicates that selectivity and sensitivity can be easily manipulated by varying the sampling conditions for various PIL fibers. Better analytical performance in terms of sensitivity, linear ranges, and LODs obtained for most of the analytes by increasing the film thickness of the PIL sorbent coating. The latter encourages our group to prepare PIL-based sorbent coatings possessing higher film thicknesses for future studies when detection at trace levels is required for more challenging cases. Recovery study results from two complex water matrixes also indicate the suitability of the PIL fibers to quantify various analyte classes using the developed method.
Chapter 3

Ionic liquids in gas chromatography and multidimensional gas chromatography

3.1 Principles of multidimensional gas chromatography (MDGC)

Gas chromatography (GC) is a separation technique used in the separation and identification of volatile and semi-volatile compounds in the gas phase. Over four decades ago, multidimensional gas chromatography (MDGC) was introduced to the chromatographic community. MDGC offers higher peak capacity than conventional one-dimensional gas chromatography (1D-GC), allowing for the resolution of sample constituents with similar polarities or volatilities. 61 In this technique, analytes are vaporized and subjected to a series of GC columns with chemically different stationary phases coupled through an interface. In MDGC, analyte separation is maintained on each column, leading to an increase in the separation power compared to the 1D-GC. 62 Two modes of MDGC are commonly employed, namely, heart-cutting and comprehensive. In heart-cutting MDGC, only a select few fractions of effluent from the first column are transferred to the second column for further separation. 63 While this technique is useful for targeted
analysis, it can be very time consuming if comprehensive sample analysis is the major goal. Liu and Phillips developed a powerful way to overcome limitations stemming from heart-cutting by using a modulator to transfer the entire first column effluent to the second column in a technique known as comprehensive two-dimensional gas chromatography (GC×GC). Figure 3-1 depicts a GC×GC system equipped with thermal modulation capable of accomplishing comprehensive analyte separation. As shown in Figure 3-1, effluent from the first column is focused in the modulation loop using a jet of cold nitrogen and rapidly pulsed into the second column using a jet of heated nitrogen. This cycle is repeated throughout the duration of the chromatographic run. As a result, every component of a sample mixture can interact with both GC stationary phases. Additionally, the maximum number of analytes that can be separated in a given GC×GC column set (peak capacity) is greatly enhanced compared to 1D-GC. The peak capacity in GC×GC is often improved by pairing columns with unique separation mechanisms. Most separations in GC×GC have been accomplished by employing non-polar polysiloxane-based family followed by polar polyethylene glycol-based stationary phases to allow separation of analytes based on their vapor pressure and polarity, respectively. Although these traditional stationary phases have been successfully used to separate a variety of complex samples,

![Figure 3-1: Schematic of a GC×GC system equipped with thermal loop modulation](image)
their solvation capabilities are not sufficiently diverse to utilize the entire retention space in GC×GC.⁶⁶

3.2 Application of ionic liquids as stationary phases in GC

During the last two decades, ILs have been investigated for various applications in separation science.⁵⁴ ILs are non-molecular organic solvents possessing melting points at or below 100 °C. They are comprised of organic cations and either organic or inorganic anions that may be structurally tuned to meet the requirements for a variety of applications.⁵⁴ Specifically, ILs are emerging as useful GC stationary phases due to their unique physico-chemical properties which includes exhibiting a broad liquid range, high viscosity, and high thermal stability. In addition, ILs have been shown to possess unique solvation capabilities and selectivities on the distinct solute/solvent interactions.⁸ Armstrong and co-workers were the first to show that imidazolium-based ILs can be engineered to separate both polar and non-polar analytes.⁶⁸ For instance, by altering the anionic portion of the imidazolium IL from chloride [Cl]⁻ to hexafluorophosphate [PF₆]⁻, a significant difference in selectivity was observed for polar analytes compared to the non-polar compounds. Further investigation of different classes of ILs, including monocationic imidazolium, pyridinium, and pyrrolidinium revealed that the hydrogen donor ability of the IL stationary phases was dominated by the IL cation. On the other hand, the anionic portion was found to assume the role of hydrogen acceptor anion from proton donor analytes such as alcohols and carboxylic acids.⁶⁹ Subsequently, dicationic,⁷⁰ tricationic,⁷¹ and phosphonium⁷²-based cations were exploited to improve high thermal stability and liquid range of ILs compared to traditional monocationic stationary phases. Recently, in an
attempt to broaden the applicability of IL stationary phases, task-specific ionic liquids (TSILs) were introduced by functionalizing the IL cation with various substituents.\textsuperscript{73} For example, the incorporation of aromatic moieties in the IL cation enhanced the selectivity for aromatic compounds, such as polycyclic aromatic hydrocarbons (PAHs). This is due to the enhanced \( \pi-\pi \) type interactions between analytes and the aromatic groups of the IL cation.\textsuperscript{74} Introduction of polar functional groups, such as hydroxyl moieties, can result in increased selectivity for hydrogen accepting analytes.\textsuperscript{75} As a result, tuning the IL-based GC stationary phase structure may enhance selectivity required for separation of very complex sample constituents with similar polarities.

3.3 Use of ILs in MDGC (GC\( \times \)GC)

Different column selectivity, which can be represented by an independent separation mechanism, is the important requirement to obtain higher peak capacity in MDGC techniques.\textsuperscript{76} Many traditional non-ionic GC stationary phases are characterized as either polar or non-polar phases. These columns show a lack of diversity in terms of solvation capabilities, which can limit their ability to resolve complex samples by GC\( \times \)GC. Due to this drawback, IL-based columns have emerged as alternative GC\( \times \)GC stationary phases. Employing IL-based columns can enable unique solvation capabilities and selectivities, in addition to higher thermal stabilities relative to traditional phases. ILs have been implemented as contemporary phases paired with traditional non-ionic phases in various GC\( \times \)GC separations.\textsuperscript{77} Since most GC\( \times \)GC separations can be regulated based on analyte volatility in the first dimension followed by contribution of different interactions in the second dimension, it is common to use IL columns as the second dimension to
evaluate their performance in terms of retention mechanisms. Currently, a large number of commercially available IL columns, such as the Supelco Low Bleed (SLB) family, contain various imidazolium or phosphonium-based dications which are usually paired with mostly bis[(trifluoromethyl)sulfonyl]imide ([NTf₂]) or trifluoromethanesulfonate ([TfO⁻]) anions.⁶⁹,⁷¹ As their names indicate, these commercial SLB-IL columns exhibit high separation efficiency and possess maximum allowable operating temperatures (MAOT) up to 300 °C. Commercial IL stationary phases have been employed in the separation of number of analytes such as fatty acid methyl esters,⁷⁸ flavor and fragrance compounds,⁷⁹ aromatic hydrocarbons,⁸⁰ alkylphosphonates,⁸¹ alkyl halides,⁸² and other polar analytes (oxygen-, nitrogen- and sulfur-containing compounds). These studies indicate that IL columns demonstrate much higher retention and selectivity toward mostly polar analytes compared to non-polar analytes due to the dipole-dipole interaction, hydrogen-bonding interaction as well as additional electrostatic interactions between ions.⁸³ However, in both the non-polar × polar and polar × non-polar column sets, it was observed that non-polar analytes were not significantly retained by the SLB-IL columns. Therefore, tuning IL stationary phases with non-polar substituents can enable better retention of non-polar analytes in complex samples.

3.4 Characterization of ILs using the Abraham Solvation Model

The Abraham solvation model is a linear free energy relationship model that describes the specific interaction capability of the stationary phases with respect to solute probes.⁸⁴ This model has previously been used to characterize both traditional and IL-based columns.⁵⁴ This model, shown in equation 3-1, The variables including
chromatographic retention factor \((k)\) and solute descriptors for each probe molecule are measured and subjected to multiple linear regression analysis (MLRA) to obtain the system constants \(e, s, a, l,\) and \(b\).

\[
\log k = c + eE + sS + aA + bB + lL \quad \text{(Equation 3-1)}
\]

The solute descriptors, namely, excess molar refraction \((E)\), solute dipolarity/polarizability \((S)\), solute hydrogen bond acidity and basicity \((A, B)\), solute cavity formation \((L)\) are used to define solute interactions with solvent. The solute descriptors for various probe molecules can be found from literature. \(^{84}\) The system constants describe the specific interaction capability of the stationary phase. These interactions are defined as the ability of the liquid stationary phase to interact with analytes by electron lone pair interactions \((e)\), dipole-type and dispersive interactions \((s \text{ and } l, \text{ respectively})\), and the hydrogen bond basicity and acidity of the stationary phase \((a \text{ and } b, \text{ respectively})\). Poole and co-workers have demonstrated that many traditional non-ionic stationary phases have provided reasonably similar system constants. \(^{85}\) However, values obtained for ILs are highly unique and depend solely on the nature of the cation and/or anion. Therefore, assessment by the solvation parameter model is a crucial guide for IL structural tuning to achieve desirable stationary phase system constants for a specific sample.

3.5 Summary

In this chapter, a brief introduction to the principles of MDGC was presented. The importance and evolution of IL-based GC stationary phases in chromatographic separation science specifically, conventional 1D-GC techniques as well as MDGC techniques, was discussed. The Abraham solvation model was also introduced as a tool to describe various
solvation capabilities of stationary phases with various ranges of probe molecules. This model also provides a systematic pathway to structurally tune IL-based stationary phases by characterizing specific solute-solvent (stationary phase) interactions. In the next chapter, a series of ILs are evaluated as stationary phases in comprehensive two-dimensional gas chromatography (GC×GC) for the separation of aliphatic hydrocarbons from kerosene. IL-based stationary phases were designed to demonstrate the role of dispersion interactions on the chromatographic retention of non-polar analytes by GC×GC. The analytical performance of the best IL candidate provided improved separation of aliphatic hydrocarbons by GC×GC compared to commercially available columns, including OV-1701, SUPLECOWAX10, SLB-IL60, SLB-IL100, and SLB-IL111.
Chapter 4

Tuning the selectivity of ionic liquid stationary phases for enhanced separation of non-polar analytes in kerosene using multidimensional gas chromatography

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Abstract

In this paper, a series of ionic liquids (ILs) are evaluated as stationary phases in comprehensive two-dimensional gas chromatography (GC×GC) for the separation of aliphatic hydrocarbons from kerosene. IL-based stationary phases were carefully designed to evaluate the role of cavity formation/dispersive interaction on the chromatographic retention of non-polar analytes by GC×GC. The maximum allowable operation

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temperature (MAOT) of the IL-based columns was compared to that of commercial IL-based columns. Evaluation of the solvation characteristics of GC columns guided the selection of the best performing IL-based stationary phases for the resolution of aliphatic hydrocarbons, namely, trihexyl(tetradecyl)phosphonium tetrachloroferrate ([P66614][FeCl4]) and trihexyl(tetradecyl)phosphonium tris(pentafluoroethyl)trifluorophosphate ([P66614][FAP]) ILs. The best performing [P66614][FeCl4] IL-based column exhibited a MAOT of 320 °C, higher than the commercial SUPELCOWAX 10 (MAOT of 280 °C) and commercial IL-based columns (MAOT up to 300 °C). The analytical performance of the structurally tuned [P66614][FeCl4] IL stationary phase improved the separation of aliphatic hydrocarbons by GC×GC compared to the commercial columns examined (e.g., OV-1701, SUPELCOWAX 10, SLB-IL60, SLB-IL100, and SLB-IL111).

4.1 Introduction

Multidimensional gas chromatography (MDGC) is an extremely valuable tool for the separation, detection, and identification of volatile and semi-volatile constituents in many complex samples. As in any MDGC technique, two or more gas chromatographic separations are employed in a sequential fashion. The paramount requirement to effectively enhance peak capacity in the composite system is to employ a combination of GC stationary phases possessing different selectivities. Until recently, most chromatographic separations employed the contemporary poly(siloxane)- and poly(ethylene glycol)-based stationary phases. Their combination and use in MDGC offered separations with higher peak capacities compared to conventional gas
chromatography (1D-GC). However, the solvation capabilities offered by commercial stationary phases is limited and can often times be redundant.66

Ionic liquids (ILs) are organic salts that possess melting points at or below 100 °C. They are typically comprised of an organic cation paired with an inorganic or organic counter anion. Unlike contemporary stationary phases, ILs are capable of undergoing a multitude of different solvation interactions that can provide unique chromatographic selectivities.8, 79, 85 In addition, ILs can be structurally tailored to possess high viscosities and thermal stabilities permitting the production of GC columns that exhibit high separation efficiency and broader maximum allowable operating temperatures (MAOT).69, 89 Today’s commercial IL stationary phases reportedly consist of various cations paired with the bis[(trifluoromethyl)sulfonyl]imide ([NTf₂]⁺) anion and possess MAOTs up to 300 °C.90

Commercial IL stationary phases have been employed in the separation of mid- to high-polarity analytes, such as fatty acid methyl esters,78, 91 flavor and fragrance compounds,79, 92 aromatic hydrocarbons,80 alkylphosphonates,81 alkyl halides,82 and other polar analytes (oxygen-, nitrogen- and sulfur-containing compounds) by 1D-GC and comprehensive two-dimensional gas chromatography (GC×GC).82, 93-94 However, in both the non-polar × polar and polar × non-polar column sets, it was observed that non-polar analytes, such as aliphatic hydrocarbons and monoterpene hydrocarbons, were not significantly retained by the IL-based columns, namely, SLB-IL59, SLB-IL61, SLB-IL100, and SLB-IL111.80-82, 91-94 These results seem to indicate that less polar IL stationary phases may be interesting alternatives for the separation of non-polar analytes in complex samples. Recently, commercial IL-based columns, namely, SLB-IL59, SLB-IL76, SLB-
IL82, and SLB-IL100 were characterized as being very polar and highly cohesive with similar solvation capabilities. Thus, rational structural design of IL stationary phases may impart the required solvation capabilities needed to separate non-polar analytes in complex samples. Also, IL-based columns should possess high MAOTs to allow highly efficient separation of high boiling point analytes. These features are of utmost importance on the separation of non-polar analytes with a broad range of vapor pressures, such as those found in the fields of petroleomics, fuel analysis, and flavor and fragrance analysis.

Recently, our group has shown that the solvation capabilities of IL-based stationary phases can be tailored through careful structural design of the IL. It was observed that imparting longer alkyl substituents into the cationic moiety had a significant effect on the cohesive forces of the IL and could also be regulated by the anionic component. In an effort to overcome the shortcomings of commercial IL stationary phases, new IL stationary phases capable of expanding the range of analytes that can be efficiently separated by GC×GC employing IL-based columns have been developed. In this study, two groups of IL stationary phases are carefully examined in the separation of aliphatic hydrocarbons from kerosene. The first group consists of more cohesive imidazolium-based IL stationary phases, while the second group consists of less cohesive phosphonium-based IL stationary phases capable of non-specific dispersive interactions. From these experiments, the role of dispersive interactions on the chromatographic retention of non-polar analytes was evaluated. The assessment of the solvation characteristics of GC columns guided the selection of the best performing IL-based stationary phases for the resolution of aliphatic hydrocarbons. The analytical performance and MAOT of the IL-based columns derived in this study were compared to that of commercial columns (i.e., OV-1701, SUPELCOWAX...
10, SLB-IL60, SLB-IL100, and SLB-IL111). This study demonstrates that oriented structural design of IL-based stationary phases can provide greater selectivities for classes of analytes that current IL-based columns separate poorly. These new IL-based stationary phases provide improved separation of non-polar analytes in complex samples as well as the ability to perform separations at high temperatures. This is very important in the fields of petroleomics, fuel analysis, and flavor and fragrance analysis where highly selective and low bleed stationary phases are essential.

4.2 Materials and methods

4.2.1 Chemicals and materials

Kerosene was purchased from a local distributor. The reagents 1-methylimidazole, 1-chlorobutane, iron (III) chloride hexahydrate (FeCl₃•6H₂O), and a C₈-C₂₀ n-alkanes standard mixture were purchased from Sigma-Aldrich (St. Louis, MO, USA). The OV-1701 silicone oil (poly(cyanopropylphenyl(dimethyl)siloxane) with 14% cyanopropylphenylsiloxane monomer incorporation) and a 30 m × 200 µm SUPELCOWAX 10 (PEG) column (df = 0.20 µm) were purchased from Supelco (Bellefonte, PA, USA). The 15 m × 100 µm SLB-IL60 [1,12-di(tripropylphosphonium)dodecane] [NTf₂] (df = 0.08 µm), 20 m × 180 µm SLB-IL100 [poly(1,9-di(3-vinylimidazolium)nonane] [NTf₂] (df = 0.14 µm), and 30 m × 250 µm SLB-IL111 [1,5-di(2,3-dimethylimidazolium)pentane] [NTf₂]) (df = 0.20 µm) columns were provided as a gift by Supelco. The trihexyl(tetradecyl)phosphonium chloride ([P₆₆₆₁₄][Cl]) IL was purchased from Strem Chemicals (Newburyport, MA, USA) and the trihexyl(tetradecyl)phosphonium tris(pentafluoroethyl)trifluorophosphate ([P₆₆₆₁₄][FAP])
IL was provided as a gift by Merck KGaA (Darmstadt, Germany). Forty-six probe molecules were selected for the characterization of the IL stationary phases using the solvation parameter model (see Appendix A).

4.2.2 Instrumentation

All gas chromatography measurements used to characterize the stationary phases and determine the MAOT (i.e., bleed profile) of the IL-based columns were performed on an Agilent 6890 GC-FID. Two-dimensional separations were performed on a GC×GC-FID prototype assembled on an Agilent 6890 GC-FID equipped with a two-stage cryogenic loop modulator. A full description and illustration of the GC×GC prototype are included in the Supporting Information.

4.2.3 Ionic liquid synthesis and preparation of IL-based GC columns.

The detailed synthesis procedures of the 1-butyl-3-methylimidazolium tetrachloroferrate ([C₄MIM][FeCl₄]), [C₄MIM][NTf₂], [P₆₆₆₁₄][FeCl₄], and [P₆₆₆₁₄][NTf₂] are included as Appendix A. Prior to coating the IL-based columns, all ILs were placed under vacuum at 60 °C overnight to remove residual water. A 0.25% (w/v) coating solution was prepared by dissolving the neat IL in dry methylene chloride. During preparation of the IL coating solutions, no wetting agents were employed as they may alter the selectivity of the stationary phase. Five-meter untreated capillary columns were coated by the static method at 40 °C. The solvation parameter model was used to characterize the IL-based columns. Detailed descriptions of the column preparation and characterization are included as Appendix A.
GC×GC-FID analysis. While evaluating the selectivities of the IL-based columns, the primary column consisted of a Rtx-5 capillary column (poly(diphenyldimethylsiloxane) with 5% diphenylsiloxane monomer incorporation) (df = 0.25 µm) (Restek, Bellefonte, PA, USA) connected to the secondary capillary column coated with an IL-based stationary phase. A total of eight IL stationary phases, listed in Table A.7, were used to investigate the Rtx-5 × IL column set. The following five IL-based columns were examined: [C4MIM][NTf2], [C4MIM][FeCl4], [P66614][NTf2], [P66614][FAP] and [P66614][FeCl4]. For comparison, three commercially available IL-based columns were also evaluated, namely, SLB-IL60, SLB-IL100, and SLB-IL111. In addition, SUPELCOWAX 10 and OV-1701 were used as reference stationary phases for the analysis of aliphatic hydrocarbons.

In all experiments, 1 µL of the kerosene sample was injected using a 300:1 split ratio at 250 °C. The chromatographic oven 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. Hydrogen was employed as carrier gas at a constant flow of 1.2 mL min⁻¹, except for the SLB-IL60 column, which employed 0.6 mL min⁻¹. The modulation period was 7 s for all experiments. All experiments were performed in duplicate.

4.3 Results and discussion

4.3.1 Solvation parameter model.

The solvation parameter model, developed by Abraham and co-workers, is a linear free-energy relationship that describes and estimates the strength of individual solvation interactions of the stationary phase. The model, as described by Equation 4-1,
uses $k$ as the retention factor of each probe molecule and the parameters $E$, $S$, $A$, $B$, $L$ as the solute descriptors. The model measures the contribution of specific intermolecular interactions during the solvation process, namely, the ability of the liquid stationary phase to interact with analytes by electron lone pair interactions ($e$), dipole-type and dispersive interactions ($s$ and $l$, respectively), and the hydrogen bond basicity and acidity of the stationary phase ($a$ and $b$, respectively).\(^{84}\)

$$\log k = c + eE + sS + aA + bB + lL \quad (4-1)$$

The system constants are estimated by multiple linear regression analysis of the retention factor for a number of solutes with known solute descriptors. The choice of solute and the corresponding solute descriptors is of fundamental importance in order to provide accurate estimate of the solvation capabilities of the stationary phase. The selected solutes must have a broad coverage of the solute descriptor space and be sufficient in number to allow statistical and chemical validity of the model.\(^{98}\)

### 4.3.2 Characterization of Ionic Liquid Stationary Phases.

A significant advantage of IL-based stationary phases is their ability to have moderate to high thermal stability while also exhibiting a broad multitude of solvation capabilities, characteristic of their unique selectivities. For the past several years, the use of commercial IL-based stationary phases in the analysis of complex samples has revealed comparable and even superior chromatographic performance compared to contemporary polar stationary phases (e.g., OV-1701 and SUPELCOWAX 10 columns). However, these results seem to be limited to the separation of mid- to high-polarity analytes.\(^{78-82, \, 91-94}\) Despite their success, commercial IL-based stationary phases lack the resolving power for
non-polar analytes, particularly cycloalkanes, saturated and unsaturated hydrocarbons (i.e., aliphatic hydrocarbons). This lack of selectivity has dampened enthusiasm among some separation scientists who may downplay the feature of structural tuning (in terms of cation/anion pairing and structural features of each component) when developing ILs to exhibit high selectivity and strong resolving power.

To address the limitations of commercial IL-based stationary phases, kerosene was selected as the model complex sample because it comprises of numerous aliphatic hydrocarbons and its group-type separation by GC×GC is already known and well described in previously reported literature (see Appendix A). Five IL-based stationary phases were carefully designed and evaluated as the 2D column in GC×GC separations by employing the common non-polar × polar setup. In addition, three commercial IL-based stationary phases and two traditional polar stationary phases were evaluated for comparison purposes. A total of ten column sets, as listed in Table A.7, were examined in this study.

This study began by examining the Rtx-5 × IL column sets. As in any MDGC separation, the column set must combine stationary phases with different selectivities (i.e., solvation capabilities). The Rtx-5 stationary phase is characterized by low cohesion, with governing contribution to retention being the favorable cavity formation/dispersion interactions. This stationary phase is also weakly dipolar/polarizable and hydrogen bond basic, as shown in Table A.8. Hence, an appropriate 2D column should possess complementary solvation interactions (i.e., capable of dipole-type interactions, electron lone pair interactions, hydrogen bond basic or hydrogen bond acid).

Typically, the use of more polar secondary columns, such as OV-1701 (MAOT of 250 °C) and SUPELCOWAX 10 (MAOT of 280 °C), generates increased resolution of
non-polar analytes in GC×GC separations. Poly(cyanopropylphenyldimethylsiloxane) stationary phases (e.g., OV-1701) are more cohesive and strongly dipolar/polarizable and hydrogen bond basic, while PEG stationary phases (e.g., SUPELCOWAX 10) are also more hydrogen bond basic and strongly dipolar/polarizable but are generally less cohesive.66 Figure A-6 (A) and Figure 4-1 (A) show the GC×GC-FID chromatograms for the separation of aliphatic hydrocarbons in kerosene employing the Rtx-5 × OV-1701 and Rtx-5 × SUPELCOWAX 10 column sets, respectively. It can be observed that the separation of aliphatic hydrocarbons was significantly enhanced when using SUPELCOWAX 10 compared to OV-1701. Recently, some commercial IL-based columns were characterized as being highly cohesive phases with governing contribution to retention being dipole-type and hydrogen bond basic interactions.66 In Figure 4-1 (B) to (D) is shown the separation of aliphatic hydrocarbons in kerosene by GC×GC-FID employing commercial IL-based 2D columns, namely SLB-IL60 (MAOT of 300 °C), SLB-IL100 (MAOT of 230 °C), and SLB-IL111 (MAOT of 270 °C). It can be observed that aliphatic hydrocarbons are not be resolved by any of the commercial IL-based columns. Hence, the structural design of IL-based stationary phases to provide greater selectivity for classes of analytes that commercial IL-based columns separate poorly is desperately needed.

The [C₄MIM][NTf₂] and [C₄MIM][FeCl₄] ILs were evaluated as 2D stationary phases in GC×GC separations employing the Rtx-5 × IL column sets. Figure 4-2 (A) shows a GC×GC-FID chromatogram of kerosene using the Rtx-5 × [C₄MIM][NTf₂] column set. The [C₄MIM][NTf₂] IL stationary phase (MAOT of 185 °C) is more cohesive and exhibits no hydrogen bond acidic behavior and no electron lone pair interactions, but it is hydrogen
bond basic and can accommodate strong dipole-type interactions (see Table A.8). However, the [C₄MIM][NTf₂] IL stationary phase did not resolve the aliphatic hydrocarbons in kerosene. The [C₄MIM][FeCl₄] IL stationary phase (MAOT of 230 °C) is cohesive, more hydrogen bond basic, and is capable of stronger dipole-type interactions than the [C₄MIM][NTf₂] IL. Figure 4-2 (B) shows a GC×GC-FID chromatogram of kerosene using the Rtx-5 × [C₄MIM][FeCl₄] column set. By visual inspection, it can be observed that this IL stationary phase also did not resolve the non-polar aliphatic hydrocarbons. In the light of these results, it seems that more cohesive IL stationary phases cannot provide the selectivity required for the separation of aliphatic hydrocarbons.

4.3.3 Structural tuning of ionic liquid stationary phases

Heavily alkylated phosphonium ILs, such as [P₆₆₆₁₄][NTf₂] and [P₆₆₆₁₄][FAP], have been previously characterized by the solvation parameter model. The data in these studies indicated that imparting long alkyl chains to the cationic moiety generates less cohesive IL stationary phases capable of non-specific dispersive interactions. Figure A-6 (B) illustrates a GC×GC-FID chromatogram of kerosene using the Rtx-5 × [P₆₆₆₁₄][NTf₂] column set. The resulting separation indicates that less cohesive IL stationary phases might possess the selectivity needed to enhance the resolution of aliphatic hydrocarbons. It has been shown previously that solvation capabilities of IL stationary phases are largely determined by the nature of the counter anion. Recently, it was demonstrated that replacing the [NTf₂]⁻ anion by the [FAP]⁻ anion, while maintaining the same cation, reduced significantly the cohesion of the IL stationary phase. To explore the selectivity of the [P₆₆₆₁₄][FAP] IL, the Rtx-5 × [P₆₆₆₁₄][FAP] column set was evaluated. Figure 4-2
(C) shows a GC×GC-FID chromatogram of kerosene exploring this column set. It can be readily observed that enhanced resolution of the aliphatic hydrocarbons was attained with the less cohesive [P_{6614}][FAP] IL stationary phase when compared to the commercial IL-based stationary phases, shown in Figure 4-1. Also, symmetric chromatographic peaks were observed for aliphatic hydrocarbons that indicated no significant column reactivity toward these non-polar compounds (see Table A.9). In addition, the [P_{6614}][FAP] IL (MAOT of 290 °C) can be operated at higher operating temperatures than the OV-1701, SUPELCOWAX 10, SLB-IL100, and SLB-IL111 commercial columns.

4.3.4 Evaluation of multiple solvation capabilities

In an attempt to outperform the SUPELCOWAX 10 PEG stationary phase, an IL stationary phase capable of stronger dipole-type interactions while maintaining low cohesion forces was sought. Inspection of the [C_{4}MIM][NTf_{2}] and [C_{4}MIM][FeCl_{4}] IL system constants indicated that the [FeCl_{4}]^{-} anion may impart the required solvation capabilities, while also providing high thermal stability to the resulting IL. IL-based stationary phases exhibiting high thermal stability are necessary to provide efficient separation of high boiling point analytes while minimizing baseline signal drift due to stationary phase volatilization/degradation during high temperature GC analysis.

The [P_{6614}][FeCl_{4}] IL stationary phase possesses comparable cohesion forces to the [P_{6614}][FAP] IL, but is more hydrogen bond basic and can engage in stronger dipole-type interactions, as shown in Table A.8. Figure 4-2 (D) represents a GC×GC-FID chromatogram of kerosene using the Rtx-5 × [P_{6614}][FeCl_{4}] column set. It can be readily observed that increased resolution of the aliphatic hydrocarbons was achieved as compared
to the commercial IL-based phases and the more cohesive imidazolium ILs, namely, [C₄MIM][NTf₂] and [C₄MIM][FeCl₄]. Figure 4-3 shows a side-by-side comparison of an expanded region of the GC×GC-FID chromatogram of kerosene exploring the Rtx-5 × SUPELCOWAX 10 and Rtx-5 × [P₆₆₁₄][FeCl₄] column sets. Visual inspection of these chromatograms show that the [P₆₆₁₄][FeCl₄] IL exhibits increased resolution of the aliphatic hydrocarbons when used as the 2D stationary phase compared to SUPELCOWAX 10. For validation, comparison of the separation performance metric for the selected analytes, shown in Figure 4-3, indicated that larger values of 2D separation capacity were attained when the structurally tuned [P₆₆₁₄][FeCl₄] IL was examined as the 2D stationary phase (Table A.9). This IL-based column provided greater selectivity, symmetrical peaks, and absence of column reactivity toward non-polar analytes (see Tables B.10 and B.11) that commercial columns separate poorly. In addition, the [P₆₆₁₄][FeCl₄] IL can operate at a MAOT of 320 °C, which is higher than those exhibited by all of the commercial GC columns examined in this study. Also, the analytical performance of the [P₆₆₁₄][FeCl₄] IL-based column was not affected by the continuous exposure to the GC oven’s temperature program used in the analysis of kerosene. Finally, the outstanding thermal stability of this stationary phase is 40 °C higher than that of the SUPELCOWAX 10 stationary phase.
Figure 4-1. GC×GC-FID chromatograms of kerosene employing several Rtx-5 × polar column sets: (A) SUPELCOWAX 10, (B) SLB-IL60, (C) SLB-IL100, and (D) SLB-IL111.
Figure 4-2. GC×GC-FID chromatograms of kerosene employing several Rtx-5 × IL column sets: (A) [C₄MIM][NTf₂] IL, (B) [C₄MIM][FeCl₄] IL, (C) [P₆₆₆₁₄][FAP] IL, and (D) [P₆₆₆₁₄][FeCl₄] IL.
Figure 4-3. Expanded GC×GC-FID chromatograms of kerosene employing (A) Rtx-5 × SUPELCOWAX 10 and (B) Rtx-5 × [P66614][FeCl4] column set. The separation performance metrics for the selected pair of analytes are shown in Tables B.9 and B.10.

4.4 Conclusion

ILs have drawn considerable attention as GC stationary phases because of their tunable physical and chemical properties. However, commercial IL-based GC columns have not explored all of the solvation properties that can be offered by ILs. In this study, cavity formation/dispersive interaction was demonstrated as an important solvation interaction on the chromatographic retention of non-polar analytes in GC×GC separations. Evaluation of the solvation characteristics of GC columns successfully guided the selection of the best performing IL-based stationary phases for the resolution of aliphatic hydrocarbons, namely, the [P66614][FeCl4] and [P66614][FAP] ILs. Careful structural design of the [P66614][FeCl4] IL produced a stationary phase capable of strong dipole-type and dispersive interactions and thereby improved the resolution of aliphatic hydrocarbons from
kerosene compared to the commercial columns examined. The $[\text{P}_{66614}][\text{FeCl}_4]$ IL-based GC column exhibited a MAOT of 320 °C, significantly higher than that of other commercial IL-based and SUPELCOWAX 10 columns. This study demonstrates that oriented structural design of IL-based stationary phases can provide greater selectivities for the classes of analytes that current commercial IL-based stationary phases separate poorly.
Chapter 5

Summary

In the first chapter of this thesis, fundamentals, principles, and the application of ILs, PILs, and cross-linked PILs in SPME were discussed and presented. ILs, PILs, and cross-linked PILs can demonstrate superior selectivity, as well as excellent analytical performance, for the extraction of target analyte classes owing to the unique physicochemical properties required for the SPME sorbent coatings.

Chapter 2 mainly focused upon the applicability of the cross-linked PILs for high performance liquid chromatography (HPLC) applications. A number of cross-linked PILs were developed, and applied, as SPME-HPLC sorbent coatings in the analysis of various model analytes via HPLC analysis. The [Br]− based fiber demonstrated overall selectivity towards more polar analytes which may be due to the hydrogen bond basicity of the [Br]− anion. The PIL-based fiber comprised of benzyl moiety may enhance the selectivity of aromatic compounds due to π-π interactions. The better sensitivity and LODs of the PIL-based fibers were obtained for the extraction of polar analytes when compared to the
commercial fibers. This led to the introduction of new a SPME-LC sorbent coating to the SPME community in order to expand the PIL-based SMPE fiber’s analytical applications.

Chapter 3 describes a brief overview of MDGC as well as recent advancements and applications of IL-based GC stationary phases in conventional 1D-GC and MDGC. ILs may be designed to possess ideal physicochemical properties for GC stationary phases. These properties include broad liquid range, high thermal stability, low background bleed, and multiple solvation interactions. A typical column sequence involves polysiloxane followed by polyethylene glycol-based stationary phases to allow separation of the analytes by GC×GC based upon vapor pressure and polarity, respectively. Currently, most separations of complex matrices are done by these traditional phases. However, their solvation capabilities are oftentimes redundant. IL-based stationary phases that are capable of multiple solvation interactions with analytes can favorably resolve separation complexity in the complex samples.

A series of ILs are evaluated as stationary phases in GC × GC for the separation of aliphatic hydrocarbons from kerosene-often referred to as the unresolved complex mixture in separation science. IL-based stationary phases were carefully designed and characterized by the Abraham solvation parameter model. Evaluation of the solvation characteristics of GC columns guided the selection of the best performing IL-based stationary phases for the resolution of aliphatic hydrocarbons, namely, trihexyl(tetradecyl)phosphonium tetrachloroferrate ([P66614][FeCl4]) and trihexyl(tetradecyl)phosphonium tris(pentafluoroethyl)trifluorophosphate ([P66614][FAP]) ILs. The best performing [P66614][FeCl4] IL-based column exhibited a MAOT of 320 °C, higher than the commercial SUPELCOWAX 10 (MAOT of 280 °C) and commercial IL-
based columns (MAOT up to 300 °C). The structurally tuned [P_{66614}][FeCl_{4}] IL stationary phase exhibited improved separation of aliphatic hydrocarbons by GC × GC when compared to the examined commercial columns.
References:


357–358 (0), 97-102.


2010, 1217 (18), 3144-3149.


Appendix A

Supplemental Figures and Tables Accompanying Chapter 4
Samples.

Kerosene was purchased from a local distributor (Toledo, OH, USA). This sample was selected as the model complex sample because it comprises of numerous aliphatic hydrocarbons, namely, cycloalkanes, saturated and unsaturated hydrocarbons. Also, its group-type separation by GC×GC is already well known and it has been described in previously reported literature.\textsuperscript{A1-A7}

Chemicals and Materials.

Forty-six probe molecules were selected for the characterization of the IL stationary phases using the solvation parameter model. Cyclohexanol and ethylbenzene were purchased from J. T. Baker (Phillipsburg, NJ, USA) and Eastman Kodak Company (Rochester, NJ, USA), respectively. Bromoethane, butyraldehyde, and 2-nitrophenol were purchase from Acros Organics (Morris Plains, NJ, USA). Acetic acid, methyl caproate, naphthalene, and propionic acid were purchased from Supelco. 1-butanol, \textit{N,N}-dimethylformamide, ethyl acetate, 2-propanol, and toluene were purchased from Fluka (Steinheim, Germany). Acetophenone, aniline, benzaldehyde, benzene, benzonitrile, benzyl alcohol, 1-bromohexane, 1-bromooctane, 2-chloroaniline, 1-chlorobutane, 1-chlorohexane, 1-chlorooctane, cyclohexanone, 1-decanol, 1,2-dichlorobenzene, 1,4-dioxane, ethyl phenyl ether, 1-iodobutane, nitrobenzene, 1-nitropropane, 1-octanol, octylaldehyde, 1-pentanol, 2-pentanone, propionitrile, pyridine, and pyrrole were purchased from Sigma-Aldrich.


**Instrumentation.**

Conditioning of all capillary columns was performed using a Hewlett-Packard 5890 GC-FID. All gas chromatography measurements used to characterize the stationary phase and determine the maximum allowable operating temperature (MAOT) (i.e., bleed profile) of the IL-based columns were performed on an Agilent 6890 GC-FID equipped with a split/splitless injector. Two-dimensional separations were performed on a lab-made GC×GC-FID prototype, previously described in the literature,\textsuperscript{A8} assembled on an Agilent 6890 GC-FID equipped with a split/splitless injector and a two-stage cryogenic loop modulator. Modulation was achieved by alternating hot or cold pulses of N\textsubscript{2}(g) to a delay loop (1.0 m untreated capillary column, 250 µm I.D.). An Asco three-way solenoid valve (Florham Park, NJ, USA) was used to toggle the continuous N\textsubscript{2}(g) stream. The N\textsubscript{2}(g) was continuously and periodically directed to the heating system or the cooling system, which was cooled by liquid nitrogen.\textsuperscript{A9} A solid-state relay and a low-cost 8-bit Arduino Uno microcontroller board were employed to control the actuator of the solenoid valve.\textsuperscript{A10} The microcontroller board monitored the GC remote start/stop to synchronize the modulation events,\textsuperscript{A10} similar to the setup described by Seeley.\textsuperscript{A11} Illustrations of the prototype are shown in Figure A-1 and A-2. Agilent ChemStation was used for data acquisition and processing and GC Image 2.04 (Zoex Corporation, Houston, TX, USA) was used for data visualization. Microsoft Visual Basic 6.0 was used to create a graphical interface to control the modulator.

**Ionic Liquid Synthesis.**
The trihexyl(tetradecyl)phosphonium tetrachloroferrate ([P$_{66614}$][FeCl$_4$]) IL was synthesized using a previously reported procedure from the literature.$^{12,13}$ A round bottom flask was charged with equimolar quantities of trihexyl(tetradecyl)phosphonium chloride ([P$_{66614}$][Cl]) and FeCl$_3$$\cdot$6H$_2$O in anhydrous methanol. This reaction mixture was allowed to stir at room temperature for 24 h. After solvent evaporation under reduced pressure, the crude compound was washed with water. The IL was dried under vacuum at 70 °C for 48 h to remove residual water. The trihexyl(tetradecyl)phosphonium bis[(trifluoromethyl)sulfonyl]imide ([P$_{66614}$][NTf$_2$]) IL was synthesized using a previously reported procedure from the literature.$^{14}$

Synthesis of the 1-butyl-3-methylimidazolium tetrachloroferrate ([C$_4$MIM][FeCl$_4$]) IL was performed in two steps using a reported procedure from the literature.$^{15}$ In the first step, the 1-butyl-3-methylimidazolium chloride ([C$_4$MIM][Cl]) IL was synthesized and characterized using $^1$H and $^{13}$C nuclear magnetic resonance spectroscopy (NMR) and electrospray ionization mass spectrometry (ESI-MS).$^{16}$ In the second step, a round bottom flask was charged with equimolar quantities of [C$_4$MIM][Cl] and FeCl$_3$$\cdot$6H$_2$O in methanol. This reaction mixture was stirred at room temperature for 24 h under a nitrogen atmosphere. After solvent evaporation, the crude compound was washed with water and dried at 70 °C under reduced pressure for 48 h. The $^1$H and $^{13}$C NMR spectra are shown in Figure A-3 and A-4. The [C$_4$MIM][NTf$_2$] IL was synthesized using a previously reported procedure from the literature.$^{16}$

**Preparation of IL coated GC Columns.** Prior to coating the IL-based columns, all ILs were placed under vacuum at 60 °C overnight to remove residual water. A 0.25% (w/v)
coating solution was prepared by dissolving the neat IL in dry methylene chloride. During preparation of the IL coating solutions, no wetting agents were employed as they may alter the selectivity of the stationary phase.\textsuperscript{A17} Five-meter untreated capillary columns were coated by the static method at 40 °C.\textsuperscript{A18} The coated columns were conditioned by holding the GC oven at 30 °C for 2 h, followed by a linear temperature program from 30 °C to 100 °C at 1 °C min\textsuperscript{-1} and held at 100 °C for 2 h. A constant flow of helium at 1.0 mL min\textsuperscript{-1} was used to condition all columns. Column efficiency was determined using naphthalene at 100 °C. The coated columns had efficiencies ranging from 1800 to 3600 plates per meter. The MAOTs of the columns was determined by examining the baseline drift of the signal when the chromatographic oven was programmed from 40 °C to 350 °C at a rate of 3 °C min\textsuperscript{-1}. The chromatograms are shown in Figure A-5.

\textbf{Solvation Parameter Model.}

The solute descriptors of the forty-six probe molecules are described elsewhere.\textsuperscript{A19} The probe molecules were used as received. The probes were individually dissolved in methylene chloride and their retention factors ($k$) were determined under three different temperatures, namely, 50, 80, and 110 °C. The injection and detection ports were kept at 250 °C. Helium was used as carrier gas at a constant flow of 1.0 mL min\textsuperscript{-1}. Methane was used to measure the dead time of each column using the three different temperatures. Multiple linear regression analysis and statistical analysis were performed using Analyze-it (Microsoft, Redmond, WA, USA).
Figure A-1. Lab-designed and assembled GC×GC fitted with a two-stage cryogenic loop modulator. The system consists of a modified Agilent 6890 gas chromatograph with a split/splitless injector and a flame ionization detector.
Figure A-2. In (A) is shown a photo of the heating and cooling system. In (B) is illustrated the chromatographic oven fitted with the cryogenic loop modulator.
Figure A-3. $^1$H NMR spectra of [C$_4$MIM][Cl].
Figure A-4. $^{13}$C NMR spectra of [C$_4$MIM][Cl].
Figure A-5. Stationary phase bleed profile of (1) [C₄MIM][FeCl₄] IL, (2) [P₆₆₆₁₄][FAP] IL, and (3) [P₆₆₆₁₄][FeCl₄] IL.
Figure A-6. GCxGC-FID chromatograms of kerosene employing (A) Rtx-5 × OV-1701 and (B) Rtx-5 × [P_{66614}][NTf_2] column set.
**Table A.7.** Description of the column sets employed in this study.

<table>
<thead>
<tr>
<th>Column set</th>
<th>Primary column</th>
<th>Secondary column</th>
<th>MAOT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rtx-5 × SUPELcowax 10</td>
<td>Rtx-5</td>
<td>SUPELcowax 10</td>
<td>(^1D: 350 ^\circ C)</td>
</tr>
<tr>
<td></td>
<td>30 m × 250 μm</td>
<td>1.2 m × 200 μm</td>
<td>(^2D: 280 ^\circ C)</td>
</tr>
<tr>
<td></td>
<td>(d_f = 0.25 \mu m)</td>
<td>(d_f = 0.20 \mu m)</td>
<td></td>
</tr>
<tr>
<td>Rtx-5 × OV-1701</td>
<td>Rtx-5</td>
<td>OV-1701</td>
<td>(^1D: 350 ^\circ C)</td>
</tr>
<tr>
<td></td>
<td>30 m × 250 μm</td>
<td>1.2 m × 250 μm</td>
<td>(^2D: 250 ^\circ C)</td>
</tr>
<tr>
<td></td>
<td>(d_f = 0.25 \mu m)</td>
<td>(d_f = 0.15 \mu m)</td>
<td></td>
</tr>
<tr>
<td>Rtx-5 × SLB-IL60</td>
<td>Rtx-5</td>
<td>SLB-IL60</td>
<td>(^1D: 350 ^\circ C)</td>
</tr>
<tr>
<td></td>
<td>30 m × 250 μm</td>
<td>1.2 m × 100 μm</td>
<td>(^2D: 300 ^\circ C)</td>
</tr>
<tr>
<td></td>
<td>(d_f = 0.25 \mu m)</td>
<td>(d_f = 0.08 \mu m)</td>
<td></td>
</tr>
<tr>
<td>Rtx-5 × SLB-IL100</td>
<td>Rtx-5</td>
<td>SLB-IL100</td>
<td>(^1D: 350 ^\circ C)</td>
</tr>
<tr>
<td></td>
<td>30 m × 250 μm</td>
<td>1.2 m × 180 μm</td>
<td>(^2D: 230 ^\circ C)</td>
</tr>
<tr>
<td></td>
<td>(d_f = 0.25 \mu m)</td>
<td>(d_f = 0.14 \mu m)</td>
<td></td>
</tr>
<tr>
<td>Rtx-5 × SLB-IL111</td>
<td>Rtx-5</td>
<td>SLB-IL111</td>
<td>(^1D: 350 ^\circ C)</td>
</tr>
<tr>
<td></td>
<td>30 m × 250 μm</td>
<td>1.2 m × 250 μm</td>
<td>(^2D: 270 ^\circ C)</td>
</tr>
<tr>
<td>Column set</td>
<td>Primary column</td>
<td>Secondary column</td>
<td>MAOT</td>
</tr>
<tr>
<td>---------------------</td>
<td>----------------</td>
<td>------------------</td>
<td>------------</td>
</tr>
<tr>
<td>Rtx-5 × [C₄MIM][NTf₂]</td>
<td>Rtx-5</td>
<td>[C₄MIM][NTf₂]</td>
<td>¹D: 350 °Cᵃ</td>
</tr>
<tr>
<td></td>
<td>30 m × 250 µm</td>
<td>1.2 m × 250 µm</td>
<td>²D: 185 °Cᵇ</td>
</tr>
<tr>
<td></td>
<td>dₐ = 0.25 µm</td>
<td>dₐ = 0.20 µm</td>
<td></td>
</tr>
<tr>
<td>Rtx-5 × [C₄MIM][FeCl₄]</td>
<td>Rtx-5</td>
<td>[C₄MIM][FeCl₄]</td>
<td>¹D: 350 °Cᵃ</td>
</tr>
<tr>
<td></td>
<td>30 m × 250 µm</td>
<td>1.2 m × 250 µm</td>
<td>²D: 230 °Cᵇ</td>
</tr>
<tr>
<td></td>
<td>dₐ = 0.25 µm</td>
<td>dₐ = 0.15 µm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30 m × 250 µm</td>
<td>1.2 m × 250 µm</td>
<td>²D: 380 °Cᶜ</td>
</tr>
<tr>
<td></td>
<td>dₐ = 0.25 µm</td>
<td>dₐ = 0.15 µm</td>
<td></td>
</tr>
</tbody>
</table>

Table A.7. continued
\[ d_f = 0.25 \, \mu m \quad d_f = 0.15 \, \mu m \]

**MAOT:** Maximum allowable operation temperature. \(^{a}\) Provided by the manufacturer (Ref. A20); \(^{b}\) determined by the stationary phase bleed profile; \(^{c}\) obtained from Ref. A14.

**Table A.8.** System constants of gas-liquid chromatographic stationary phases examined in this study.

<table>
<thead>
<tr>
<th>Stationary phase / Temperature</th>
<th>System constants (^{a})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( c )</td>
</tr>
<tr>
<td>poly(dimethylidiphenylsiloxane) with 5% diphenylsiloxane monomer incorporation (^{b})</td>
<td></td>
</tr>
<tr>
<td>80 °C</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-</td>
</tr>
<tr>
<td>poly(ethylene glycol) (^{b})</td>
<td></td>
</tr>
<tr>
<td>80 °C</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-</td>
</tr>
<tr>
<td>poly(cyanopropylphenyldimethylsiloxane) with 14% cyanopropylphenylsiloxane monomer incorporation (^{b})</td>
<td></td>
</tr>
<tr>
<td>80 °C</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-</td>
</tr>
</tbody>
</table>
1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ([C₄MIM][NTf₂])

<table>
<thead>
<tr>
<th>Temperature</th>
<th>c</th>
<th>e</th>
<th>s</th>
<th>a</th>
<th>b</th>
<th>l</th>
<th>n</th>
<th>R²</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>80 °C</td>
<td>-</td>
<td>0</td>
<td>1.646</td>
<td>1.685</td>
<td>0.330</td>
<td>0.533</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

1-butyl-3-methyl imidazolium tetrachloroferrate ([C₄MIM][FeCl₄])

<table>
<thead>
<tr>
<th>Temperature</th>
<th>c</th>
<th>e</th>
<th>s</th>
<th>a</th>
<th>b</th>
<th>l</th>
<th>n</th>
<th>R²</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 °C</td>
<td>-3.02</td>
<td>0.28</td>
<td>1.96</td>
<td>1.84</td>
<td>0.84</td>
<td>0.60</td>
<td>39</td>
<td>0.98</td>
<td>342</td>
</tr>
<tr>
<td></td>
<td>(0.12)</td>
<td>(0.10)</td>
<td>(0.12)</td>
<td>(0.13)</td>
<td>(0.16)</td>
<td>(0.03)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>80 °C</td>
<td>-3.18</td>
<td>0.26</td>
<td>1.89</td>
<td>1.93</td>
<td>0.70</td>
<td>0.52</td>
<td>39</td>
<td>0.98</td>
<td>430</td>
</tr>
<tr>
<td></td>
<td>(0.10)</td>
<td>(0.10)</td>
<td>(0.12)</td>
<td>(0.16)</td>
<td>(0.16)</td>
<td>(0.02)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>110 °C</td>
<td>-3.39</td>
<td>0.24</td>
<td>1.74</td>
<td>1.94</td>
<td>0.77</td>
<td>0.47</td>
<td>39</td>
<td>0.98</td>
<td>396</td>
</tr>
<tr>
<td></td>
<td>(0.09)</td>
<td>(0.09)</td>
<td>(0.11)</td>
<td>(0.15)</td>
<td>(0.15)</td>
<td>(0.02)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table A.8. continued

<table>
<thead>
<tr>
<th>Stationary phase / Temperature</th>
<th>System constants a</th>
<th>c</th>
<th>e</th>
<th>s</th>
<th>a</th>
<th>b</th>
<th>l</th>
<th>n</th>
<th>R²</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trihexyl(tetradecyl)phosphonium bis[(trifluoromethyl)sulfonyl]imide ([P₆₆₆₁₄][NTf₂]) b,c</td>
<td>70 °C</td>
<td>-3.29</td>
<td>-0.28</td>
<td>1.55</td>
<td>1.55</td>
<td>-0.15</td>
<td>0.75</td>
<td>34</td>
<td>0.99</td>
<td>536</td>
</tr>
<tr>
<td></td>
<td>(0.09)</td>
<td>(0.08)</td>
<td>(0.09)</td>
<td>(0.08)</td>
<td>(0.11)</td>
<td>(0.02)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Trihexyl(tetradecyl)phosphonium tris(pentafluoroethyl)trifluorophosphate ([P₆₆₆₁₄][FAP]) b</td>
<td>80 °C</td>
<td>-2.69</td>
<td>-0.29</td>
<td>1.39</td>
<td>0.49</td>
<td>0.25</td>
<td>0.63</td>
<td>39</td>
<td>0.99</td>
<td>744</td>
</tr>
</tbody>
</table>

101
Trihexyl(tetradecyl)phosphonium tetrachloroferrate ([P\text{66614}][\text{FeCl}_4])

<table>
<thead>
<tr>
<th>Temperature</th>
<th>(\omega)</th>
<th>(\beta)</th>
<th>(\alpha)</th>
<th>(\kappa)</th>
<th>(\gamma)</th>
<th>(\phi)</th>
<th>(\chi)</th>
<th>(\lambda)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 °C</td>
<td>-3.09</td>
<td>-0.27</td>
<td>1.51</td>
<td>1.53</td>
<td>0.12</td>
<td>0.79</td>
<td>45</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>(0.08)</td>
<td>(0.08)</td>
<td>(0.10)</td>
<td>(0.09)</td>
<td>(0.13)</td>
<td>(0.02)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>80 °C</td>
<td>-3.19</td>
<td>-0.26</td>
<td>1.43</td>
<td>1.23</td>
<td>0.02</td>
<td>0.69</td>
<td>45</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>(0.07)</td>
<td>(0.07)</td>
<td>(0.09)</td>
<td>(0.08)</td>
<td>(0.11)</td>
<td>(0.02)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>110 °C</td>
<td>-3.29</td>
<td>-0.21</td>
<td>1.31</td>
<td>1.03</td>
<td>0.04</td>
<td>0.61</td>
<td>41</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>(0.08)</td>
<td>(0.08)</td>
<td>(0.10)</td>
<td>(0.08)</td>
<td>(0.13)</td>
<td>(0.02)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(n\): number of probe molecules subjected to multiple linear regression analysis; \(R^2\): correlation coefficient; \(F\): Fischer coefficient.

\(\omega\) – non-bonding and \(\pi\)-electron interactions, \(\beta\) – dipolarity, \(\alpha\) – hydrogen bond basicity, \(\kappa\) – hydrogen bond acidity, \(\gamma\) – dispersion forces.

\(a\) Data obtained from Ref. A14 and A21, and estimated from Ref. A16 and A17.

\(b\) The capillary was pretreated with sodium chloride prior static coating.
Table A.9. Separation performance metrics of selected pairs of analytes from kerosene by GC×GC-FID comparing the conventional PEG-based stationary phase and the structurally tailored IL-based stationary phase.

<table>
<thead>
<tr>
<th>Analyte pair</th>
<th>Rtx-5 × SUPELCOWAX 10 2D Selectivity</th>
<th>Rtx-5 × [P&lt;sub&gt;66614&lt;/sub&gt;][FeCl&lt;sub&gt;4&lt;/sub&gt;] 2D Selectivity</th>
<th>△S</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 and 2</td>
<td>1.08</td>
<td>1.08</td>
<td>0.18</td>
</tr>
<tr>
<td>2 and 3</td>
<td>1.38</td>
<td>1.41</td>
<td>0.66</td>
</tr>
<tr>
<td>4 and 5</td>
<td>1.37</td>
<td>1.37</td>
<td>0.73</td>
</tr>
<tr>
<td>6 and 7</td>
<td>1.25</td>
<td>1.29</td>
<td>0.60</td>
</tr>
<tr>
<td>8 and 9</td>
<td>1.15</td>
<td>1.16</td>
<td>0.38</td>
</tr>
</tbody>
</table>

△S: 2D separation capacity (adapted from Ref. A22).
Table A.10. Second dimension peak asymmetry factor ($\tilde{2}A_s$) of selected analytes from kerosene by GC×GC-FID employing the Rtx-5 × [P$_{66614}$][FeCl$_4$] column set.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>$\tilde{2}A_s$$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.06$^a$</td>
</tr>
<tr>
<td>2</td>
<td>0.97</td>
</tr>
<tr>
<td>3</td>
<td>0.97</td>
</tr>
<tr>
<td>4</td>
<td>0.70$^a$</td>
</tr>
<tr>
<td>5</td>
<td>0.92</td>
</tr>
<tr>
<td>6</td>
<td>1.00</td>
</tr>
<tr>
<td>7</td>
<td>1.03</td>
</tr>
<tr>
<td>8</td>
<td>0.85$^a$</td>
</tr>
<tr>
<td>9</td>
<td>0.95</td>
</tr>
</tbody>
</table>

$^a$ Measurements strongly affected by peak overlap.

$^b$ Accepted values range from 0.9 to 1.2.
Table A.11. Comparison of selected peak areas of \( n \)-alkanes analyzed by GC×GC-FID employing the reference Rtx-5 × SUPELCOWAX 10 column set and the best performing Rtx-5 \( \times [P_{66614}][FeCl_4] \) column set (\( n = 4 \)).

<table>
<thead>
<tr>
<th>( n )-alkane</th>
<th>SUPELCOWAX 10 Average peak area</th>
<th>( [P_{66614}][FeCl_4] ) Average peak area</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_8H_{18} )</td>
<td>5.9±0.4</td>
<td>6.5±0.2</td>
</tr>
<tr>
<td>( C_9H_{20} )</td>
<td>6.0±0.3</td>
<td>6.5±0.2</td>
</tr>
<tr>
<td>( C_{10}H_{22} )</td>
<td>6.1±0.4</td>
<td>6.6±0.3</td>
</tr>
<tr>
<td>( C_{11}H_{24} )</td>
<td>6.2±0.3</td>
<td>6.7±0.3</td>
</tr>
<tr>
<td>( C_{12}H_{26} )</td>
<td>6.2±0.3</td>
<td>6.7±0.2</td>
</tr>
<tr>
<td>( C_{13}H_{28} )</td>
<td>6.2±0.3</td>
<td>6.7±0.2</td>
</tr>
<tr>
<td>( C_{14}H_{30} )</td>
<td>6.2±0.3</td>
<td>6.6±0.2</td>
</tr>
<tr>
<td>( C_{15}H_{32} )</td>
<td>6.3±0.3</td>
<td>6.6±0.2</td>
</tr>
<tr>
<td>( C_{16}H_{34} )</td>
<td>6.5±0.3</td>
<td>6.5±0.2</td>
</tr>
<tr>
<td>( C_{17}H_{36} )</td>
<td>6.5±0.2</td>
<td>6.5±0.3</td>
</tr>
<tr>
<td>( C_{18}H_{38} )</td>
<td>6.3±0.3</td>
<td>6.4±0.2</td>
</tr>
<tr>
<td>( C_{19}H_{40} )</td>
<td>3.7±0.1</td>
<td>3.7±0.2</td>
</tr>
<tr>
<td>( C_{20}H_{42} )</td>
<td>6.2±0.2</td>
<td>6.3±0.3</td>
</tr>
</tbody>
</table>

The means values are not statistically different at a 95 % confidence interval.
References


