A Dissertation

entitled

Synthesis and Characterization of Polymeric Ionic Liquids and Applications in Solid-Phase Microextraction Coupled with Gas Chromatography

By

Yunjing Meng

Submitted to the Graduate Faculty as partial fulfillment of the

requirements for the Doctor of Philosophy Degree in Chemistry

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August 2011

An Abstract of

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Ionic liquids (ILs) are a class of molten salts with melting points considerably lower than conventional inorganic salts. Their unique properties make them an ideal class of separation media for various sample preparation techniques. Polymeric ionic liquids (PILs) inherit many physical properties of ILs such as high thermal stability, negligible vapor pressure, multiple solvation interactions and can easily be chemically modified to tether a variety of functional groups. In addition, PILs possess high viscosity making them amenable to forming stable, thin films on the fused silica glass fibers, a requirement of solid-phase microextraction (SPME). SPME is a high speed sample preparation technique possessing a number of advantages such as simplicity, and no organic solvent requirement. The marriage of PILs with SPME opens a new avenue in the search for new sorbent coatings. This dissertation is dedicated towards the design and synthesis of PILs and employs them as SPME sorbent coatings coupled with gas chromatography (GC).

The dissertation begins with the definition of ILs. The applications of ILs in a number of sample preparation techniques are introduced. The following chapters describe the synthesis of various PILs and their application as SPME sorbent coatings for the extraction of various analytes. PILs including poly(1-vinyl-3-hexadecylimidazolium) bis[(trifluoromethyl)sulfonyl]imide (poly([ViHDIm] [NTf_2])), poly(1-(4-vinylbenzyl)-3-hexadecylimidazolium bis[(trifluoromethyl)sulfonyl]imide) (poly($VBHDIm^+$ NTf_2^-)), and poly(1-vinyl-3-hexylimidazolium chloride) (poly($ViHIm^+Cl^-$)) were synthesized.

The poly([ViHDIm] [NTf_2]) PIL provides stable SPME coatings for both headspace-SPME or direct-immersion SPME, and can be used at elevated temperature conditions to perform extractions. The poly($VBHDIm^+$ NTf_2^-) PIL exhibited high affinity towards analytes bearing aromatic groups due to the presence of benzyl-functional moieties in the PIL structure. The poly($ViHIm^+Cl^-$) PIL demonstrated high selectivity towards polar analytes with high hydrogen bond acidity, due to the high hydrogen bond basicity of the Cl^- anion in the PIL structure.

*This dissertation is dedicated to my husband **Chaochao**, and **our parents** for their love, support and encouragement throughout my life. And it is also to my son **Boyuan** for his love to his mother, although she spent so much time away from him working on this dissertation.*

Acknowledgments

I wish to express my deepest gratitude to my advisor, Dr. Anderson whose patient guidance and invaluable advice have led me to learn new knowledge and techniques in separation field. It would be impossible for me to achieve what I obtained now if he were not so intelligent, knowledgeable, enthusiastic, and patient, and if he has not cared so much about his students.

I would like to convey my gratitude to my committee members, Dr. Kirchhoff, Dr. Griffith, and Dr. Schall, as well as Dr. Pino in Spanish, for all their abundant help and constructive advice.

I would like to express my thanks to my friends and labmates, Qichao, Christa, Pamela, Manish, Tianhao, Tien, Honglian, and former labmates, Fei, Quinner, William, Leah, and Yao. My special thanks to the University of Toledo, Chemistry Department for all support during my study here.

I wish to express my love and deepest gratitude to my beloved families: my husband, my son and our parents. Without their love, support, and encouragement, I would never have been able to survive so many frustrating experiences, and eventually pursue this degree.

Contents

List of Tables

List of Figures

Chapter 1

Ionic Liquids and their Application in Sample Preparation

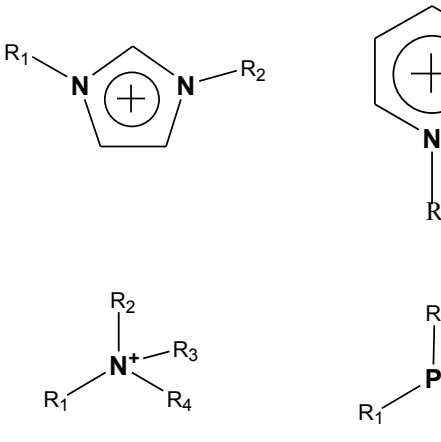
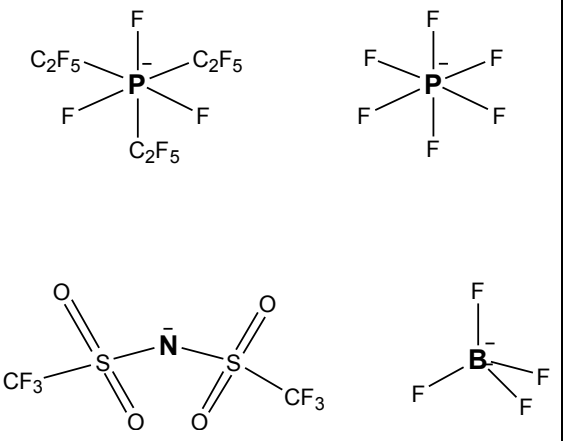
1.1. A Brief History and Definition

The most common definition of ionic liquids (ILs) describes them as a class of molten salts with melting points below 100 ºC. The root of ILs stems from the traditional inorganic molten salts which remain in a liquid state at high temperatures. Such molten salts possess some unique characteristics that cannot be provided by traditional molecular solvents. These properties include: 1) inert to thermal and chemical process, 2) possess a wide liquid range and are nonvolatile and nonflammable making them good reaction media under strict conditions, 3) high conductivity allows them to play a role in some electrochemical process. However, the high temperature needed to maintain their liquid state (for example, the melting point of NaCl is 801℃) eliminates the practical application of these inorganic molten salts. Efforts have been made to discover new materials with all the mentioned properties but remain at liquid state at lower temperature ranges.

The first observation of ILs was traced back to the 19th century. Red oil was observed in the process of toluene synthesis using a classical Friedel-Craft reaction. The red oil was identified later as a salt called sigma complex [1]. The first recognized IL, ethyl ammonium nitrate was discovered by Walden in 1914 [2]. In 1978, Osteryoung and co-workers reported that quaternary pyridinium mixed with aluminum chloride ($AlCl_3$) formed low melting point salts. This discovery was the first report of pyridinium-based ILs [3]. Imidazolium-based ILs were first reported by Wilkes and co-workers [4,5]. The pyridinium- or the imidazolium-based organic salts were blended with $AlCl_3$ in order to synthesize liquid salts at room temperature. However, these binary ILs are air- and moisture-sensitive thereby limiting their practical utility. The discovery of modern ILs was initiated by Wilkes and Zaworotko [6] who found that air- and moisture-stable imidazolium-based ILs could be formed by pairing anions that are resistant to hydrolysis, such as BF_4^-, PF_6^-, NO_3^-, SO_4^-, and acetate. This discovery opened a new avenue for the synthesis and application of modern ILs.

The asymmetric structure and bulky size of the cation or anion are essential for lowering the melting point of ILs [7]. The literature shows that the majority of ILs are quaternary ammonium, phosphonium, pyridinium, and imidazolium cations paired with bulky, charge diffusive anions. Table 1.1 shows typical structures of cations and anions that are often employed for making ILs. Typically, the physical properties of ILs such as viscosity, surface tension, thermal stability, and water solubility are all determined by

Table 1.1: Common cations and anions of ionic liquids.

Cation	Anion
	

both the cationic and anionic moieties [8]. Generally, [Cl^-] and [BF_4^-] anion-based ILs are water soluble while [PF_6^-] and [NTf_2^-] anion-based ILs are water-immiscible. For example, 1-butyl-3-methylimidazolium chloride [BMIM][Cl] and 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF_4] are all water soluble [8]. However, if the chain length of the alkyl substituents on the imidazolium cation increases, the water solubility of the IL decreases [9]. For example, 1-octyl-3-methylimidazolium tetrafluoroborate ([OMIM][BF_4]) is water immiscible.

1.2. Application of ILs in Sample Preparation Techniques

Sample preparation steps are very important for an overall analytical procedure and in many cases, are the primary source of error for the final results while consuming almost two-thirds of the overall analysis time. Most of the sample preparation techniques require the use of a large amount of hazardous organic solvent. Reducing or even eliminating the use of toxic solvents drives efforts for the search of green solvent used as the extractants. Certain classes of ILs are deemed as green solvents [10]. The unique properties of ILs have boosted a wide range of applications. Their negligible volatility prevents the loss of ILs due to evaporation. Their tunable viscosity and adjustable water solubility make them suitable as an extraction medium. The most attractive feature of ILs is the ease of structure modification which dictates their physical and chemical properties, and therefore provides different affinity and selectivity accordingly.

Research has revealed that ILs can be used as novel stationary phases for GC. The "dual nature" property of ILs allows them to interact with both polar and non-polar analytes. The high thermal and high chemical stability offers low background for GC-MS [11]. Imidazolium-based ILs exhibited high solubility towards CO_2 providing a new class of materials for CO_2 separation [12,13]. ILs have also been reported to be good matrices for matrix-assisted laser desorption ionization (MALDI) mass spectrometry [14,15]. ILs have been found to be good mobile phase additives for reverse phase high performance liquid chromatography (RP-HPLC) [16-18] and for capillary electrophoresis (CE) [19-21].

1.2.1. Liquid-Liquid Extraction (LLE)

LLE is one of the most widely used sample separation methods. It employs two immiscible or nearly immiscible solvents to separate analytes that exhibit different affinities towards the two phases. Rogers and co-workers were the first to employ ILs as extractants for organic compounds [10]. A high distribution coefficient was observed for benzoic acid in the 1-butyl-3-methylimidazolium hexaflurophosphate ($[C_4mim][PF_6]$) IL phase. Khachatryan and co-workers reported the extraction of phenolic compounds such as phenol, nitrophenols, chlorophenol and polyphenols from aqueous solution using the $[C_4mim][PF_6]$ IL [22]. Nearly quantitative recovery was achieved. The 1-octyl-3-methylimidazolium hexaflurophosphate ($[C_8mim][PF_6]$) IL was employed for the extraction of trace amounts of para red and Sudan dyes in food samples [23]. ILs have also been demonstrated to be good solvents for the separation of undesired compounds from nonaqueous solutions. For example, the 1-ethylpyridinium ethylsulfate ($[EPy][EtSO_4]$ IL was effective in the removal of benzene from alkanes (hexane or heptane) [24].

Heavy metal contamination in the environment is a major global concern. The extraction of metal ions from aqueous solutions employing ILs represents another important research area. Dai and co-workers first reported employing several ILs (1-R^1-2-R^2-3-methylimidazolium bis[(trifluoromethyl) sulfonyl]imide ($[R^1R^2MeIm][NTf_2]$), where R^1 = ethyl, propyl, or butyl and R^2 = H, or methyl, and

1-R^1-2-R^2-3-methylimidazolium hexafluorophosphate ([R^1R^2MeIm][PF_6]) blended with dicyclohexyl-18-crown-6(2,3,11,12-dicyclohexano-1,4,7,10,13,16-hexaoxacyclooctadeca ne), for the extraction of ^{90}Sr, a fission product for which there is no available extraction technique for its removal from radioactive waste sites [25]. Distribution coefficients were found to be one to four orders of magnitude higher compared to conventional organic solvents such as toluene and chloroform. Luo et al. reported using the 1-alkyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ([$C_n$mim] [NTf_2]) ILs (where n= 2, 3, 4, 6, 8) blended with calix[4]arene-bis(*tert*-octylbenzo-crown-6) to extract Cs^+ from aqueous solutions [26]. Kogelnig et al. used the trihexyl(tetradecyl)phosphonium chloride (CyphosR IL101) IL dissolved in chloroform for the separation of Fe^{3+} from Ni^{2+} in acidic solution [27].

1.2.2. Dispersive Liquid-Liquid Microextraction (DLLME)

DLLME was introduced by Assadi and co-workers [28]. It employs a small amount of extraction solvent (typically at the microliter level) and a dispersive solvent being injected into aqueous sample solutions containing the analytes of interest. A cloudy solution forms as the fine particles of the extraction solvent are dispersed throughout the aqueous solution. The extraction phase enriched with the analytes of interest is separated from the sample by centrifugation, and then subjected to analysis typically using GC or HPLC. The original DLLME method utilized small amounts of organic solvent as the

extraction phases, typically including toxic chlorinated solvents such as chloroform and chlorobenzene. A number of research groups have attempted to use ILs as a solvent system.

Fan et al. employed the [C_4mim][PF_6] IL in DLLME for the extraction of phenolic compounds from water samples [29]. The 1-hexyl-3-methylimidazolium hexafluorophosphate ([C_6mim][PF_6]) IL was also utilized by Liu et al. as the extraction phase in DLLME and combined with HPLC to detect and analyze four insecticides including fipronil, chlorfenapyr, buprofezin, and hexythiazox from water samples [30]. Metal ions have been effectively extracted by use of the IL-DLLME method. Berton et al. first used IL-DLLME to extract vanadium ions from water samples [31]. Employing ILs as the extraction solvent in DLLME can reduce the amount of organic solvent in the sample preparation step although very small amounts of organic solvent is still needed as dispersive solvent. In order to completely avoid the use of organic solvent, IL-DLLME methods were improved by modulation temperature [32], or by using sonication [33] to increase the contact area of the ILs with analytes. Yao et al. developed an in-situ metathesis IL-DLLME method to extract PAHs yielding high enrichment factors compared to the conventional IL-DLLME [34].

1.2.3. Single-Drop Microextraction (SDME)

SDME uses a microdroplet of a solvent (typically 1-3 μL) as the extraction phase,

typically suspended on a tip of a syringe. After extraction, the microdroplet is subjected to chromatographic analysis. Due to the simplicity, high efficiency, low cost, low sample and low solvent consumption, SDME has become a popular sample preparation technique. Due to their low volatility and high viscosity, there are a number of advantages when ILs are employed as solvents in SDME. ILs are able to form more stable microdroplets, permitting larger volumes and prolonged extraction time, which dramatically increases the sensitivity of the method.

Liu and co-workers first employed ILs as the extraction phase for SDME coupled with HPLC [35]. Three ILs including $[C_4mim][PF_6]$, $[C_6mim][PF_6]$, and $[C_8mim][PF_6]$ were used for the extraction of PAHs. The $[C_4mim][PF_6]$ IL was successfully used for the extraction of aromatic amines from water samples using headspace SDME [36]. Yao and co-workers reported using tris(pentafluoroethyl)trifluorophosphate (FAP) anion-based ILs to conduct SDME for the extraction of aromatic compounds, phenols, and PAHs [37]. IL-based SDME has also been utilized to extract metal ions. Xia et al. employed the $[C_4mim][PF_6]$ IL as the extraction solvent for the extraction of Co, Hg, and Pb ions from environmental water samples [38].

1.2.4. Hollow-Fiber Protected Liquid-Phase Microextraction (HF-LPME)

HF-LPME involves the use of a porous hollow fiber support, typically polypropylene with a length of 1.5-10 cm. The fiber is first soaked in an extraction

solvent (typically an organic solvent) so that the extraction phase can enter the porous support. The excess amount of the organic solvent is removed. An acceptor phase is then injected into the lumen of the fiber. During the course of extraction, analytes diffuse from the sample matrix to the extraction phase immobilized in the pores of the fiber and then to the acceptor phase inside the channel. The acceptor phase can be either the same solvent that is immobilized inside the pores or another aqueous phase. Employing an IL as the extraction phase in HF-LPME provides many superior advantages compared to conventional organic solvent based HF-LPME. Use of hydrophobic ILs prevents loss of the extractant during long extraction times, thus increasing the method reproducibility. For the extraction of polar compounds, IL-based HF-LPME has been proven to be even superior to organic solvent-based membranes due to comparatively higher polarity of ILs than conventional hydrophobic organic solvents.

Basheer et al. impregnated the $[C_4mim][PF_6]$ IL in the pores of polypropylene fiber with toluene acting as the acceptor phase for the extraction of aromatic hydrocarbons [39]. In this approach, the analytes preconcentrated in toluene were analyzed using GC/MS. Peng et al. developed a HF-LPME procedure for the extraction of polar phenolic compounds including 4-chlorophenol, 3-chlorophenol, 2, 4-dichlorophenol and 2,4,6-trichlorophenol, using the $[C_8mim][PF_6]$ IL as the extraction phase and alkaline aqueous solution as the acceptor phase [40]. Due to the higher polarity of the $[C_8mim][PF_6]$ IL compared to dichloromethane, the polar analytes were extracted with

lower detection limits. Tao and co-workers impregnated the $[C_8mim][PF_6]$ IL blended with TOPO in the pores on the wall of a polypropylene fiber and utilized alkaline aqueous solution (pH 13 of NaOH) as the acceptor phase for the extraction of sulfonamides from environmental water samples [41]. The three phase hollow fiber supported IL membrane method was able to extract the sulfonamides from water sample with higher efficiency and enrichment factors compared with the use of organic based membranes such as undecane and dihexyl ether under the same extraction conditions.

1.2.5. Solid-Phase Extraction (SPE)

SPE was introduced in the early 1970s and it did not receive common attentions until mid 1990s. It's also named as liquid-solid extraction (LSE). The principle of SPE is based on the partition of an analyte between two phases: the solid sorbent and the liquid sample matrix. SPE minimizes or eliminates many disadvantages of LLE such as the need of a large amount of organic solvents, emulsification, lengthy extraction time and the difficulty of automation. In the case of trace analysis, SPE is mainly used as a pretreatment step for isolation, purification and pre-concentration of trace environmental samples. Due to the capability of sampling a wide range of compounds, SPE has been the most popular sample preparation method. ILs supported by various materials such as silica, organic polymer, or mineral oxides have been used as the sorbents in SPE. The early work using ILs as sorbent in SPE is very recent. For example, Tian et al. reported

using imidazolium-based IL modified silica material as the sorbent of SPE for the isolation of active ingredient from *Salvia Miltiorrhiza* Bunge [42]. In another instance, Li et al. developed a silica-supported IL sorbent material for the extraction of polyunsaturated fatty acid methyl esters from fish oil [43]. Xie et al. reported a preparation of a polymer supported IL as sorbent for the removal of nitrogen-containing compounds from diesel feed [44]. Merrifield resin was functionalized with imidazolium, pyridinium, and triethylammonium chloride ILs and the high selectivity towards N-containing compounds was obtained. The advantage of using IL modified resin was that it was easily regenerated by simple washing with a protic solvent such as methanol.

The extraction of trace metal ions from environmental solutions using solvent impregnated resin (SIR) has been proposed [45]. The macroporous resins provide large surface areas allowing an extractant impregnated within their lattice to afford high capacity and provide more chelating sites. Sun et al. used Amberlite XAD resin which has uniform pore size distribution, high surface area and high chemical stability, as a support and the $[C_8mim][PF_6]$ IL containing Cyanex923 was impregnated on the surface of the resin for the extraction of rare earth metals [46]. Li et al. synthesized a series of new ILs and physically coated onto mesoporous SBA-15 for the extraction of *a*-Tocopherol [47]. The presence of these ILs dramatically enhanced the selectivity of the extraction.

ILs can also be chemically incorporated into the support to enhance the extraction

ability of the sorbent. Fontanals et al. [48] developed a polymer supported IL material for SPE of acidic pharmaceuticals from water samples. In this approach, the polymer support was first prepared by polymerization of vinyl benzyl chloride with 2% divinyl benzene (DVB). Tthen N-methylimidazole was grafted onto the polymer through the reaction between chloride and the nitrogen group on the imidazole ring forming IL. The anion was exchanged to trifluoromethyl acetate using trifluoromethyl acetic acid. The resulting material was able to selectively and quantitatively extract acidic pharmaceutical compounds from complex matrices under strong anion exchange conditions in which formic acid was employed in the elution step. Complete recoveries were obtained for the pharmaceutical compounds from water samples.

Bidentate diphenylcarbamoylmethylphosphine oxide complexing groups were synthetically included in the imidazolium-based cation part of the ILs. These were paired with halides or PF_6^- counteranions and immobilized on a solid support for SPE of acinidies and rare earth metals [49]. The integral task specific ILs (TSILs) combining all the features of the extractant and the IL served as effective sites for the separation of Pu(IV), Am(III), Eu(III), and U(VI) using carbon nanotube as support from nitric acid solutions.

Fang et al. chemically immobilized N-methylimidazolium based IL which was functionalized with a silane coupling reagent 3-chloropropyltriethoxysilane, on silica gel to prepare a material used as SPE stationary phase for the extraction of sulfonylurea

herbicides from water and soil samples [50]. Compared with the commercial C_{18} cartridge, the IL functionalized SPE cartridge demonstrated higher selectivity towards the analytes studied.

1.2.6. Solid-Phase Microextraction (SPME)

SPME is a sampling and sample preparation technique invented by Pawliszyn and co-worker in the early 1990s [51]. The general configuration of SPME device is a thin fiber coated with stationary phase housed in a syringe for protecting the coating on the outside surface of the fiber. Experiments are commenced simply by exposing the fiber into the extraction vial containing analytes of interest for an optimized period of time. After the extraction, the analytes on the SPME coating can be directly loaded into an analytical instrument such as GC or HPLC for thermal or liquid desorption. This technique offers a number of advantages and has been gaining increasing popularity. SPME is free of organic solvent, needs no clean-up steps, reducing cost and environmental concern due to the disposal of waste organic solvents, reducing sample preparation time, and is much less labor-intensive. The mechanism of SPME is based on partition of an analyte into the stationary phase [52]. SPME preconcentrating analytes in its stationary phase, is a very sensitive extraction technique. Because of the miniaturized configuration and the non-exhaustive equilibrium properties, SPME has been proved to be effective for samples in very small scales and even samples *in vivo* [53]. The

advantages of SPME are also including the ease of hyphenation to various analytical techniques, such as GC [54], high performance liquid chromatography (HPLC) [55,56], capillary electrophoresis (CE) [57], and supercritical fluid chromatography (SFC) [58], ion mobility spectroscopy (IMS) [59-62], and MALDI MS [63]. Compared to conventional extraction method, SPME is often able to provide higher sensitivity and selectivity. There are primarily two extraction modes for SPME, namely headspace SPME (HS-SPME) and direct immersion SPME (DI-SPME) (Figure 1-1). Due to the faster diffusion coefficient of gas, HS-SPME provides a faster sampling process than DI-SPME, but its application is limited to the analytes with sufficient vapor pressures. For analytes that have lower vapor pressures, DI-SPME is able to provide lower detection limits and higher sensitivity than HS-SPME. Therefore, the application scope for DI-SPME is much larger than the HS-SPME. However, DI-SPME requires the coating material to be able to tolerate the sample matrices. For more discussion about the principle of SPME and its applications, see book edited by Dr. Pawliszyn [64]. A number of reviews nicely address various aspects of SPME [65-67].

Recently, many research groups have been making the effort to develop new coating materials to extend the application scope and improve the performance of SPME. These materials include silica, carbon, and macroporous polymers [68]. Some research has been

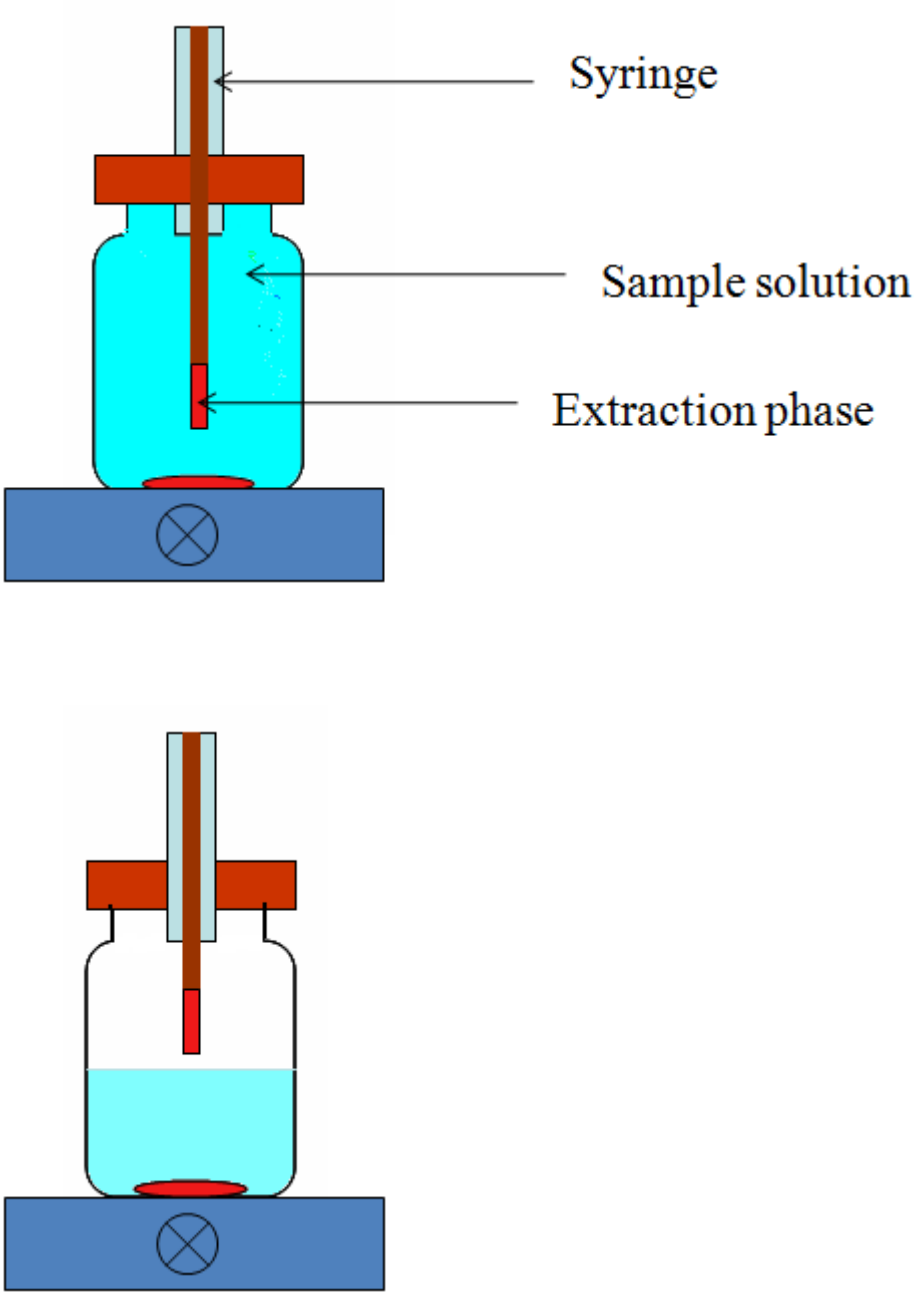


Figure 1-1: Solid-phase microextraction in direct-immersion mode (top) and headspace mode (bottom).

focused on developing SPME coatings based on ILs or PILs.

Liu et al. was the first to apply ILs as stationary phases of SPME and used GC as the following sorption and analyzing step [69]. The [C_8mim][PF_6] IL was physically deposited on the outside surface of a fused silica fiber forming a thin film and was used for the extraction of benzene, toluene, ethylbenzene, and xylenes (BTEX) from water using HS-SPME. The coating was washed out after one extraction/desorption and the fiber was re-coated for next extraction. Hsieh et al. used Nafion membrane as support to obtain an even IL-based coating on a fused silica glass fiber for the extraction of PAHs from aqueous solutions using HS-SPME [70]. Three ILs including 1-methyl-3-octylimidazolium trifluoromethanesulfonate ([C_8mim][TfO]), 1-benzyl-3-methylimidazolium trifluoromethanesulfonate ([Bemim][TfO]), and 1-methyl-3-phenylpropylimidazolium trifluoromethanesulfonate ([Phpromim][TfO]) were evaluated and the [C_8mim][TfO] IL provided the best extraction efficiency. Before the fused silica fiber was coated with the [C_4mim] [PF_6] IL, Huang et al. etched the fiber with ammonium hydrogen difluoride and the SPME fiber was employed for HS-SPME of PAHs from aqueous solutions [71]. Enhanced extraction efficiency was observed by the etched fiber due to the increased extraction areas compared with the extraction efficiency obtained using the [C_4mim] [PF_6] IL-based SPME coating but without etching. The extraction efficiency was also superior to the one obtained by the SPME coating pretreated by Nafion. He et al. synthesized 1-ethoxyethyl-3-methylimidazloium

bis(trifluoromethane) sulfonylimide ([EeMim][NTf_2]) IL and immoblized it with silicone elastomer on a fused silica fiber [72]. The resulting IL-based SPME fiber was re-usable and demonstrated good reproducibility. The IL-based fiber was successfully applied for the extraction of methamphetamine (MAP) and amphetamine (AP) in urine samples using HS-SPME.

Polymeric ionic liquids (PILs) were initially created in the search of stable film forming solid electrolytes that are needed for energy devices [73-75]. PILs inherit most of the physical properties of ILs such as high thermal stability, negligible vapor pressure, multiple solvation interactions and easily undergo chemical modification to tether a variety of functional groups. In addition, PILs possess high viscosity which makes them amenable to form stable thin films on the fused silica glass fibers. The synthesis of PILs often involves a free radical polymerization reaction on a vinyl group-containing IL monomer initiated using azobisisobutyronitrile (AIBN). After the polymerization, the PIL may undergo metathesis to exchange the halide counter-anion into other desired anions [76].

The application of PILs as SPME coating was pioneered by Dr. Anderson and co-workers [77]. In this study, a series of homologous PILs were developed and applied as SPME stationary phases for the extraction of fatty acid methyl esters from water samples. The exceptional thermal stability of PILs allows the PIL-based SPME coatings to be coupled directly with GC for thermal desorption and analysis of the analytes

extracted. The most remarkable feature of the PIL-based SPME coatings is that unlike the conventional IL-based coatings, the PIL coated SPME fiber can have prolonged lifetime and good reproducibility. Since then, a number of publications from the same group and others have been continuously contributed to the PIL-based SPME techniques.

Meng et al. employed the poly(1-vinyl-3-hexadecylimidazolium) bis[(trifluoromethyl)sulfonyl]imide (poly[ViHDIM] [NTf_2]) PIL as a SPME coating for the extraction of high boiling point (>380 ºC) hydrocarbons and fatty acid methyl esters using the [HMIM][FAP] IL as solvent (see Chapter 2) [78]. Lopez-Darias et al. used the poly[ViHDIM] [NTf_2] PIL as SPME sorbent coating for the extraction of eighteen pollutants in waters including PAHs and substituted phenols, followed by quantification with GC-MS [79]. At a spiked level of 5 ng mL^{-1}, the average relative recoveries of 92.5% for deionized waters and 90.8% for well waters were obtained. Reproducibility (RSD%) was 11% for deionized waters and 12% for well waters. Compared with commercial fibers, the PIL-based coating was superior to PDMS fiber (30 μm) and more suitable for the extraction of nonpolar analytes while less efficient than the PA coating in the case of polar analytes. In order to improve the selectivity of the PIL-based coatings towards the extraction of PAHs, a new PIL tethering benzyl functional groups was developed by Meng and Anderson (see Chapter 3) [80]. In this study, two PIL-based SPME coatings as well as commercial PDMS coating was evaluated by extracting 12 EPA PAHs from aqueous solutions. The results showed that the benzyl group

functionalized PIL poly(1-(4-vinylbenzyl)-3-hexadecylimidazolium bis[(trifluoromethyl)sulfonyl]imide (poly(VBHDIm^{+}NTf$_2^{-}$)) exhibited the highest extraction efficiency among the SPME coatings. Partition coefficients of the PAHs into the PIL sorbent coatings were estimated to be higher than those obtained by the PDMS coating, and the benzyl-containing PIL demonstrated the largest partition coefficients among the three coatings towards most of the analytes. The application of the newly developed poly(VBHDIm^{+}NTf$_2^{-}$) PIL for the extraction of PAHs, parabens and alkylphenols from water samples was performed by Lopez-Darias et al. [81]. Their results showed that the performance of the poly(VBHDIm^{+}NTf$_2^{-}$) PIL (12 μm film thickness) was superior to the 30 μm PDMS and 85 μm PA fibers.

The extraction of polar analytes has been a challenge. ILs provide a niche by incorporating polar functional groups or by combining anions with high hydrogen bond basicity.

Wanigasekara et al. anchored ILs including bis(hydroxyethyl) imidazolium trioxyethylene bis(trifluoromethylsulfonyl) imide ((HeIM)$_2$PEG$_3$, 2 NTf$_2$), and bis(hydroxyethyl) imidazolium trioxyethylene ((HeIM)$_2$PEG$_3$,2TfO), and two styrene group containing PILs differing by anions ([(StyrIM)$_2$C$_6$, 2 TfO^{-}]$_n$, [(StyrIM)$_2$C$_6$, 2 NTf$_2^{-}$]$_n$) on silica particle surface and employed the particle as SPME stationary phase for the extraction of polar and hydrophilic compounds from water solutions [82]. The results showed that the PIL-bonded SPME coatings had better sensitivity than the results

obtained by commercial PA and PDMS-DVB fiber. The PIL with triflate as an anion had higher sensitivity than the NTf_2^-. Meng et al. took advantage of the high hydrogen bond bacisity of the Cl^- anion in the poly(1-vinyl-3-hexylimidazolium chloride) (poly($ViHIm^+Cl^-$)) PIL to have increased the extraction efficiency of polar analytes possessing high hydrogen bond acidity, such as volatile fatty acids, phenols and alcohols (see Chapter 4) [83]. Carda-Broch et al. developed dicationic ILs as SPME coating for the extraction of polar analytes [84]. The polar oxyethylene unit in the ILs increased the affinity of the coating towards alcohols and thus yielded a comparable extraction efficiency with the commercial PA and PDMS/DVB fibers.

Carbon dioxide has been a public concern due to the greenhouse effect. The determination of CO_2 concentration by SPME was first introduced by Zhao et al. [85]. New PILs including poly(1-vinyl-3-hexylimidazolium) bis[(trifluoromethyl) sulfonyl]imide (poly(VHIM-NTf_2)) and poly(1-vinyl-3-hexylimidazolium) taurate (poly(VHIM-taurate)), were designed as SPME coatings for the selective extraction of CO_2 followed by quantification with GC-TCD. CO_2 was proposed to be chemically trapped onto the poly(VHIM-taurate) PIL by forming carbamate salts which was reversibly going back to the original forms once the fiber with the analyte was subjected for thermal desorption. Although the PILs did not provide the highest extraction efficiency towards CO_2, it showed the benefit for sample storage. Compared with the extraction efficiency obtained by commercial Carboxen-PDMS SPME fiber (75μm), the

poly(VHIM-NTf_2) PIL coated fiber demonstrated a comparable extraction efficiency at smaller film thickness (10 μm). The selectivity of the two PIL-based SPME fibers on the extraction of CO_2 was further investigated by the same group [86]. The SEM evidence strongly supported that the amine groups in the poly(VHIM-taurate) PIL coating only sampled CO_2 not CH_4 or N_2. Due to the chemical bonding interactions of the amine groups with CO_2, the extraction sensitivity was less affected by humidity of the sample. Compared with the results for sampling dry CO_2 and the one from water saturated CO_2, the poly(VHIM-taurate) PIL coating experienced 28% drop in sensitivity while the poly(VHIM-NTf_2) PIL found 40% decrease in sensitivity and the commercial Carboxen fibers underwent 75% decrease in sensitivity. The poly(VHIM-NTf_2) PIL showed best selectivity towards CO_2/CH_4 and CO_2/N_2.

In order to increase the thermal and chemical stability of an IL-based SPME coating, ILs can be chemically bonded onto the surface of a fused silica support. Liu et al. used a sol-gel technique to chemically immobilize ILs 1-allyl-3-methylimidazolium hexafluorophosphate ([Amim][PF_6]) and 1-allyl-3-methylimidazolium bis(trifluoromethanesulphonyl)imide ([Amim][NTf_2]) in silica-based porous networks [87]. The impressive feature for the chemically bonded SPME coating is the high thermal and pH stability. The [Amim][PF_6] IL-based SPME coating can be desorbed at 280 ºC and the [Amim][NTf_2] IL-based coating can be desorbed at 360 ºC. Amini et al. tethered the trimethoxylsilyl group on the imidazolium-based IL and then chemically bonded the

IL on the surface of a silica support [88]. Compared with sol-gel method, this method is easier for the SPME fiber preparation and provides a lower-cost SPME fiber. The resulting SPME coating could be used for 16 extraction/desorption cycles in HS-SPME mode without significant loss of the coating.

1.3. Summary

In this chapter, the evolution of modern ILs, and their physico-chemical properties related to their molecular structure was briefly introduced. It also provides an overview of the applications of ILs in various sample preparation techniques. IL research will continue to flourish and produce new developments in sample preparation, improving the existing techniques and/or boosting new techniques. The subsequent four chapters of this dissertation describe the use of PILs as sorbent coatings for SPME in the extraction of various analytes using GC as the analysis step. PILs with different functional groups have been designed and synthesized intending to provide different selectivities and enhance extraction efficiencies.

Chapter two describes the use of the poly(1-vinyl-3-hexadecylimidazolium) bis[(trifluoromethyl)sulfonyl]imide (poly[ViHDIM] [NTf_2]) PIL as a SPME coating for the extraction of high boiling point (>380 ºC) hydrocarbons and fatty acid methyl esters. The headspace extraction was carried out at 170±10 ℃ using the [HMIM][FAP] IL as solvent. The proposed method provides detection limits ranging from 0.3 to 0.6 mg kg^{-1},

relative recoveries from 69.9% to 106%, and precision (relative standard deviation for the overall method) from 6.9% to 16%.

Chapter three describes the synthesis of the poly(1-(4-vinylbenzyl)-3-hexadecylimidazolium bis[(trifluoromethyl)sulfonyl]imide) (poly(VBHDIm$^+$ NTf$_2^-$)) PIL and applied as a SPME coating for the extraction of PAHs from aqueous solution. Due to the enhanced $\pi-\pi$ interactions between the PIL-based SPME sorbent coating and the analytes, the newly developed PIL exhibited high extraction efficiency and lower LODs compared with a commercial PDMS fiber and the PIL without the functional groups. Partition coefficients of some of the studied PAHs to any of the PIL-based SPME sorbent coatings were estimated for the first time.

In Chapter four, a PIL poly(1-vinyl-3-hexylimidazolium chloride) (poly(ViHIm$^+$Cl$^-$)) was synthesized and applied as a coating material for SPME in the extraction of polar compounds including volatile fatty acids (VFAs) and alcohols. The results showed that the poly(ViHIm$^+$Cl$^-$) PIL coating exhibited higher selectivity and lower LODs towards more polar analytes due to the presence of the Cl$^-$ anion compared to the PIL bearing the same cation but the NTf$_2^-$ anion.

In Chapter five, the poly(ViHDIM$^+$NTf$_2^-$) PIL was utilized as SPME coating for the extraction of mono- and poly-aromatic hydrocarbons from aqueous solution using direct-immersion mode. Compared with the commercial PDMS fiber with similar film thickness, the PIL coating provided much higher extraction efficiency, higher sensitivity, wider linear range, and lower detection limits. The performance of the PIL stationary phase was also evaluated by analyzing water samples. The recoveries for the 15 analytes

were found to be in the range of 75-120% for creek water, 72 -116% for river water, and 75-120% for tap water.

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Chapter 2

Exploiting the Versatility of Ionic Liquids in Separation Science: Determination of Low-Volatility Aliphatic Hydrocarbons and Fatty Acid Methyl Esters Using Headspace Solid-Phase Microextraction Coupled to Gas Chromatography

A paper published in *Analytical Chemistry*[1]

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Abstract

The determination of high-molecular weight aliphatic hydrocarbons and fatty acid methyl esters possessing high boiling points and low vapor pressures was performed using a headspace solid-phase microextraction gas chromatography (HS-SPME-GC) method comprised entirely of ionic liquids (ILs). The method utilizes three independently structurally engineered ILs in which the imparted physical and chemical properties make

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them compatible with the requirements of each component of the method. Component one is composed of a thermally stable IL solvent used to increase the equilibrium concentration of analytes in the HS, component two is a SPME sorbent coating based on a polymeric ionic liquid (PIL) for the selective HS extraction of analytes, and component three is an IL-based low-bleed GC stationary phase that performs the selective separation of the analytes. The method demonstrates the versatility of ILs within separation science in addition to determining these analytes, for the first time, using HS extraction at elevated temperatures with detection limits ranging from 0.3 to 0.6 mg kg^{-1}, relative recoveries from 69.9% to 106%, and precision (relative standard deviation for the overall method) from 6.9% to 16%.

2.1. Introduction

Static headspace-gas chromatography (HS-GC) is a common approach used for the analysis of analytes in the vapor phase that are in equilibrium with a solid or liquid phase. In the sampling of less volatile analytes, it is often necessary to thermostat the liquid or solid phase at elevated temperatures, thereby increasing the equilibrium amount of analyte present in the headspace [1]. However, heating of the sample often causes partial vaporization of the solvent, resulting in increased pressure build-up within the sample vial. For that reason, it has been stated that the vapor pressure of the extracting solvent dramatically affects the enrichment factor achieved in HS-GC [2].

We are particularly interested in utilizing the unique properties of ionic liquids (ILs) to address challenges in separation science. ILs are an interesting class of nonmolecular solvents due to their tunable physicochemical properties, making them versatile solvents in a variety of applications [3,4]. Important properties of ILs include their low vapor pressure, high thermal stability, variable viscosity, and the ability to interact with dissolved molecules through a multitude of solvation interactions. The application of ILs as a sample solvent in HS-GC has been previously reported [5-7]. In these studies, the low vapor pressure of the ILs was exploited to avoid pressure build-up in the sample vial as well as to enhance the sensitivity when determining analytes possessing high boiling points. Once present in the headspace, a method is required to sample the analytes for subsequent analysis. Various approaches, such as headspace solid-phase microextraction (HS-SPME), can be used to preconcentrate volatile analytes from the headspace of a sample. SPME is a solvent free sampling technique first introduced by Pawliszyn and co-workers [8]. The success of SPME is due to its simplicity, speed, and sensitivity. SPME utilizes a fused silica fiber coated with a small volume of stationary phase into which analytes from the sample partition. Analytes are then thermally desorbed from the fiber coating in the injector of the GC. The utilization of HS-SPME can be problematic if a sample needs to be heated as the vaporized solvent may compete with target analytes for sorption sites within the SPME coating and thus may decrease the sensitivity and selectivity of the extraction.

In this technical note, we demonstrate the versatility of ILs in separation science by introducing a HS-SPME-GC extraction/ separation method in which carefully designed ILs are used as (1) a sample solvent for hydrocarbons and fatty acid methyl esters

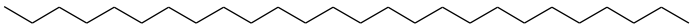
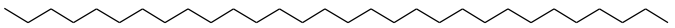
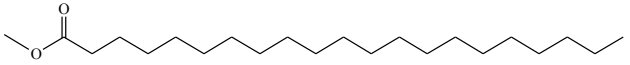
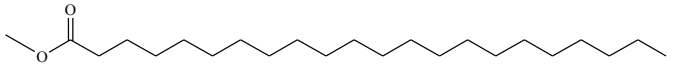
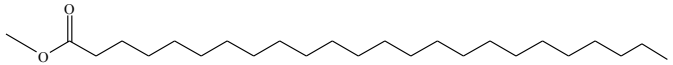
(FAMEs) possessing high boiling points (higher than 380 °C) and low vapor pressures, (2) a high selectivity SPME sorbent coating for the HS extraction of analytes, and (3) a low-bleed, high selectivity stationary phase for GC. Each IL has been independently structurally engineered so that the imparted physical and chemical properties are compatible with the requirements of each component of the method thereby producing a robust method in terms of overall analytical performance. To our knowledge, this is the first report in which these analytes have been successfully quantified by HS-GC.

2.2. Experimental

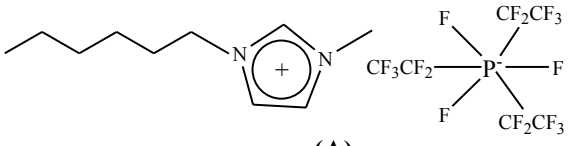
2.2.1. Materials

The six analytes determined in this work were purchased from Sigma-Aldrich (Milwaukee, WI). Their molecular structures, boiling points, and vapor pressures are shown in Table 2.1. PTFE stir bars (6 mm long) and silicone oil were obtained from Fisher Scientific (Fair Lawn, NJ). Untreated fused silica capillary tubing (0.25 mm i.d.) and glass vials (2 mL) with PTFE septa caps were purchased from Supelco (Bellefonte, PA). A model 324 direct immersion heater was purchased from Cole Parmer (Vernon Hills, IL), and a model Arrow 6000 overhead stirrer was obtained from Arrow Engineering Co., Inc. (Hillside, NJ). A Cimarec magnetic stirrer was acquired from Barnstead Thermolyne (Dubuque, IA). The IL 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate [HMIM] [FAP] was provided by Merck KGaA (Darmstadt, Germany). The molecular structure of this IL is shown in Figure 2-1.

Table 2.1: Structures, boiling point, vapor pressure of hydrocarbons and fatty acid methyl esters evaluated in this study.

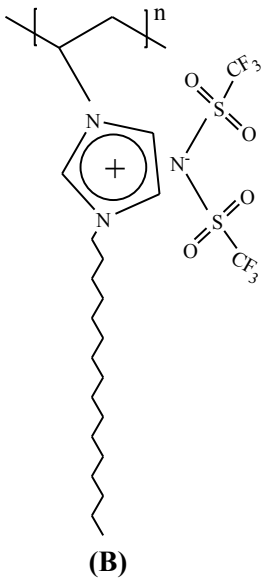
Analyte	Structure and Molecular Formula	Boiling Point (at 760 torr)[a]	Vapor Pressure (at 25)[a]
Tricosane	 ($C_{23}H_{48}$)	380 ℃	1.24×10^{-5} torr
Hexacosane	 ($C_{26}H_{54}$)	412 ℃	1.26×10^{-6} torr
Triacontane	 ($C_{30}H_{62}$)	450 ℃	7.37×10^{-8} torr
Methyl heneicosanoate	 ($CH_3(CH_2)_{19}COOCH_3$)	387 ℃	3.47×10^{-6} torr
Methyl behenate	 ($CH_3(CH_2)_{20}COOCH_3$)	398 ℃	1.52×10^{-6} torr
Methyl tetracosanoate	 ($CH_3(CH_2)_{22}COOCH_3$)	420 ℃	3.03×10^{-7} torr

[a] Calculated a using Advanced Chemistry Development (ACD/ Laboratories) Software version 9.04 for Solaris



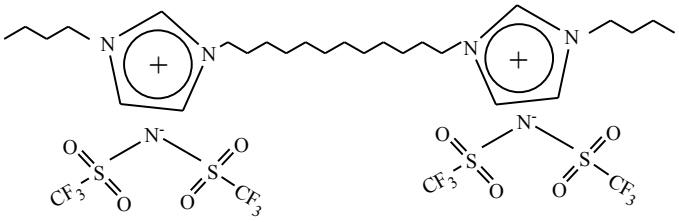
(A)

1-Hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate (HMim-FAP)



(B)

poly(1-vinyl-3- hexadecylimidazolium bis[(trifluoromethyl)sulfonyl]imide) (poly(ViHDIm^{+} NTf$_2^{-}$))



(**C**)

1,12-di-(3-butylimidazolium) dodecane -bis (trifluoromethylsulfonyl)- imide ($C_{12}(bim)_2$-NTf_2)

Figure 2-1: Structures of ILs and PIL used in HS-SPME-GC method: IL (A) was used as the high-temperature solvent to stabilize the analytes in the study, PIL (B) was used as SPME sorbent coating, IL (C) was used as a low-bleeding, highly selective stationary phase in GC.

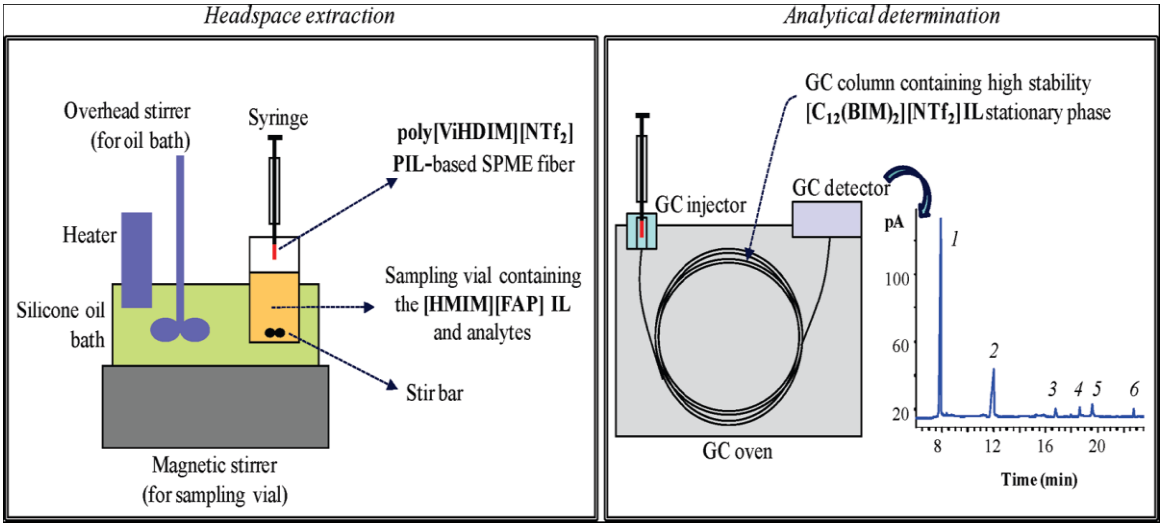


Figure 2-2: Schematic diagram demonstrating the use of [HMIM][FAP] as a headspace solvent, the poly[ViHDIM][NTf_2] PIL as the SPME sorbent coating, and the [$C_{12}(BIM)_2$][NTf_2] IL as a high stability GC stationary phase. The analytes are (1) tricosane, (2) hexacosane, (3) methyl heneicosanoate, (4) methyl behenate, (5) triacontane, and (6) methyl tetracosanoate.

2.2.2. Methods

The coating of the GC column with the high stability IL was performed using the static method on a 15 m capillary column (0.25 mm i.d.). The coating method utilized a 0.25% (w/v) solution of the dicationic IL 1,12-di-(3-butylimidazolium)-dodecane bis[(trifluoromethyl)sulfonyl]imide [$C_{12}(BIM)_2$] [NTf_2] (shown in Figure 2-1) in methylene chloride at 40 °C, following a previously published procedure [9]. The synthesis of this dicationic IL was carried out as previously reported [10]. Coated capillaries were conditioned overnight from 40 to 100 °C at 1 °C min^{-1} using a constant

flow of helium at a flow rate of 1.0 mL min^{-1}. Column efficiency was tested with naphthalene at 120 °C. The column possessed an efficiency of 1554 plates m^{-1} at 120 °C and was tested weekly to ensure that the efficiency remained constant throughout the study.

2.2.3. Instrumentation

All GC experiments were conducted using an Agilent Technologies 6890N gas chromatograph (Palo Alto, CA). The gas chromatograph was equipped with thermal conductivity (TCD) and flame ionization (FID) detectors coupled in series. Helium was used as the carrier gas with a flow rate of 1 mL min^{-1}. The inlet and detector temperatures were operated at 250 °C. Splitless injection was used during all experiments. The makeup flow of helium was maintained at 45 mL min^{-1}, the hydrogen flow at 40 mL min^{-1}, and the air flow at 450 mL min^{-1}. The following temperature program was used in the separation of the analytes: the initial temperature of 150 °C was held for 4 min, then raised to 160 °C at a ramp of 10 °C min^{-1} and held for 2 min, and then raised to 170 °C at a speed of 10 °C min^{-1} and held for 5 min. Afterward, a 10 °C min^{-1} ramp was used to increase the oven temperature to 180 °C and was held for another 5 min. Finally, the temperature of the oven was raised to 195 °C using a ramp of 15 °C min^{-1} and was held for 15 min. Agilent ChemStation software was used for data acquisition.

The preparation of the polymeric ionic liquid (PIL)-based SPME coating involved the synthesis of the poly[ViHDIM] [NTf_2] PIL (see structure in Figure 2-1) followed by the preparation of fibers using recently published procedures [11]. The film thickness of the

coating was in the range of 10-15 μm, as estimated by optical microscopy. The desorption time for the fiber in the GC injector was fixed at 5 min in all experiments.

2.2.4. SPME Procedures

A stock solution was prepared by dissolving 2 mg of each of the analytes into 40 g of the [HMIM] [FAP] IL, which was dried in a vacuum oven at 70 °C overnight before use. The stock solution was maintained at approximately 60 °C in order to ensure a homogeneous mixture. The working solution was prepared by diluting different amounts of the stock solution with pure [HMIM] [FAP] to various concentrations. The total mass of the working solution was maintained at 400 mg in the sample vial, and the volume of the headspace was 1.5 mL for all extractions. The sorption-time profiles were obtained by immersion of the PIL coated fiber into the headspace of the working standard solution containing the studied analytes at a concentration of 25 mg of analyte per kg of [HMIM] [FAP], using different extraction times (from 15 to 150 min) while stirring at 170 ± 10 °C. Figure 2-2 shows a detailed schematic of the extraction and separation system utilized in this work.

Static headspace extractions were performed by first piercing the sampling vial containing the IL/analyte mixture and stir bar with the syringe housing the SPME fiber. The sampling vial was then positioned in the heated silicone oil bath followed by stirring of the IL/analyte mixture using a magnetic stirrer. The SPME fiber was then exposed to the headspace of the sampling mixture. In order to minimize large temperature variations throughout the extraction, an overhead mechanical stirrer was used to stir the oil bath. Following the extraction, the SPME fiber was withdrawn into the syringe, the syringe

removed from the vial, and the fiber thermally desorbed in the GC injector thereby subjecting the analytes to the IL-based stationary phase for separation.

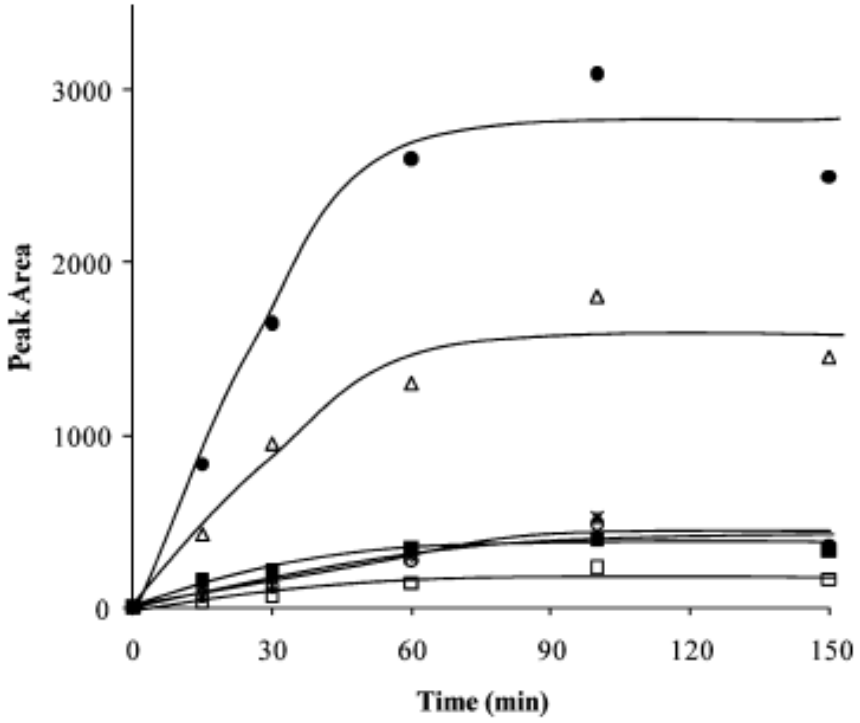


Figure 2-3: Sorption-time profiles obtained for the poly([ViHDIM][NTf_2]) PIL fiber when performing headspace extraction at 170 ±10 °C using a concentration of 25 mg of analyte per kg of [HMIM] [FAP] IL. The studied analytes are (●) tricosane, (△) hexacosane, (*) methyl heneicosanoate, (○) methyl behenate, (■) triacontane, and (□) methyl tetracosanoate.

2.3. Results and Discussion

2.3.1. IL Selection

2.3.1.1. Component 1: [HMIM] [FAP] IL as Thermally Stable Solvent for High-Temperature Extraction

To function as an effective solvent in headspace extraction studies, an IL should possess the following features: (1) be chemically unreactive with analytes being examined, (2) exhibit high thermal stability, (3) ability to dissolve the analytes in the concentration range needed for making adequate calibration curves, and (4) exhibit reasonably low viscosity to facilitate the preparation of samples and standards as well as to ensure efficient sample agitation during extraction. Merck KGaA has recently developed a class of hydrophobic ILs that exhibit much lower water uptake than commonly studied NTf_2- and hexafluorophosphate-based ILs [12-14]. ILs containing this unique anion exhibit viscosities comparable to the NTf_2-anions. Thermal gravimetric analysis of this class of ILs has revealed that imidazolium-based ILs decompose at temperatures above 280 °C. The solubility of the analytes in the [HMIM] [FAP] IL was found to be acceptable in the range up to 50 mg of analyte per kg of IL.

2.3.1.2. Component 2: Poly([ViHDIM] [NTf_2]) PIL as SPME Sorbent Coating for Selective Headspace Extraction of Analytes

Recently, a new class of sorbent coatings for SPME based on PILs was introduced [11] .The polymeric nature of these compounds provides them additional thermal stability as well as exceptional film stability, thereby producing high extraction-to-extraction reproducibility and lifetimes comparable to commercially coated fibers. The selectivity of

PIL-based coatings can be modulated by introducing functional groups to the cationic portion of the IL or by incorporating different anions to impart desired solvent characteristics. In this study, the poly[ViHDIM] [NTf_2] PIL was chosen as it undergoes stronger dispersion type interactions with the analytes thus producing high extraction efficiencies.

2.3.1.3. Component 3: [$C_{12}(BIM)_2$] [NTf_2] IL as Highly Selective and Low-Bleed GC Stationary Phase

ILs have been shown to be highly selective stationary phases for GC [9]. To fulfill the requirements of this component for this study, a relatively nonpolar stationary phase possessing low bleed at elevated temperatures was required. The dicationic IL [$C_{12}(BIM)_2$][NTf_2] was chosen as it has been shown previously to exhibit high thermal stability, a wide liquid range, and broader selectivities compared to many traditional classes of monocationic ILs [10].

2.3.1.4. Synergy of Three IL-Based Components in Extraction/Separation System

The analytes extracted in this work include three hydrocarbons, tricosane, hexacosane, and triacontane, and three fatty acid methyl esters, methyl behenate, methyl heneicosanoate, and methyl tetracosanoate. These analytes were dissolved in the [HMIM] [FAP] IL and then extracted by HSSPME-GC. In order to achieve adequate extraction efficiencies using the HS-SPME method, high temperature is required for these less volatile analytes. However, the sorption of the analytes to the SPME coating is an exothermic process, and as the temperature increases, the analyte to coating partition

coefficient decreases. Therefore, the temperature must be optimized so that the decrease of the partition coefficient is offset by the increase in the equilibrium concentration of the analytes in the headspace to achieve reasonable extraction efficiencies. The optimized extraction temperature was 170 ±10 °C. The extraction time and temperature in several previously reported studies involving headspace applications for less volatile analytes (with boiling points ranging from 152 to 228 °C) are 10 min at 110 °C [6], 15 min at 100 °C [7] and 15 min at 150 or 180 °C, depending on the analyte [5]. Sorption-time profiles were generated by performing the extraction at various time intervals to identify the equilibration time using the optimum temperature. Figure 2-3 shows the sorption time profiles obtained by plotting the analyte peak area versus the extraction time. Tricosane and hexacosane reach equilibrium at around 60 min whereas the remaining analytes reach equilibrium in around 100 min. An extraction time of 100 min was considered as the optimum extraction time. The comparison of the extraction efficiencies for the hydrocarbons and FAMEs can also be observed in Figure 2-3. With respect to the hydrocarbons, the lightest hydrocarbon (tricosane) exhibits the highest extraction efficiency whereas the lowest extraction efficiency is seen with the heaviest hydrocarbon, triacontane. The same trend is observed with the three FAMEs, although their extraction efficiencies are much lower compared to the studied hydrocarbons. The trend in the extraction efficiency is consistent with the vapor pressures and boiling points of these analytes (see Table 2.1).

2.3.2. Analytical Performance of the Method

Calibration curves were obtained using working standard solutions of analytes in the [HMIM] [FAP] IL at different concentrations while performing the extraction at the optimum extraction time and temperature. The figures of merit for the entire method, shown in Table 2.2, include the sensitivity, calibration range, correlation coefficients,

Table 2.2: Figures of merit of the calibration curves for the overall method using a three component extraction and separation system comprised of ionic liquids.

	R	Eorr of the estimate	Calibration range mg kg^{-1}	Slope ±SD[a] PA/(mg kg^{-1})	LOD[b] mg kg^{-1}
tricosane	0.998	164	1-45	137.7±3.4	0.1
hexacosane	0.996	151	1-35	123.4±4.6	0.2
triacontane	0.993	36.3	1-30	36.8±2.2	0.3
methyl behenate	0.998	28.3	2-30	25.9±0.5	0.4
methyl heneicosanoate	0.994	14.7	1-45	13.4±0.7	0.4
methyl tetracosanoate	0.990	29.6	2-45	12.6±0.7	0.6

[a] SD: error of the slope for $n = 8$ calibration levels.
[b] LOD: limits of detections calculated as 3 times the signal-to-noise ratio.

error of the estimate, and limits of detection. The obtained linearity of the overall method was found to be acceptable, with correlation coefficients (R) ranging from 0.990 to 0.998. The sensitivity, which can be evaluated by the slope, is higher for the hydrocarbons, particularly for tricosane, than for the FAMEs. It can be clearly observed that the sensitivity decreased with increasing carbon chain length of the hydrocarbons and FAMEs. The limits of detection varied from 0.1 mg kg^{-1} for tricosane to 0.6 mg kg^{-1} for methyl tetracosanoate. This constitutes the first report of a headspace extraction approach for these particular analytes. However, other analytes possessing high boiling points have been determined previously by headspace extraction. They include *N*,*N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidine (NPM), propylene glycol (PG),

formamide, tri-*n*-butylamine (tBA), and 2-ethylhexanoic acid (2EHA). The boiling points for these analytes are in the range 152-228 °C, and the reported detection limits for these analytes are 53 mgL^{-1} (ref 6) or 1-90 mg L^{-1} depending on the IL solvent [7] for DMF; 2.5 mg L^{-1} (ref 6) or 1-100 mg L^{-1} depending on IL solvent [7] for NMP; 13 mg L^{-1} for formamide [5]; 8 mg L^{-1} for tBA [5]; and 22 mg L^{-1} for 2EHA [5]. For comparison, the analytes determined in this method possess boiling points in the range 380-450 °C with detection limits less than 0.6 mg kg^{-1}.

The reproducibility of the method was evaluated by carrying out a series of extractions using working standard solutions of the analytes at two different concentration levels, namely, 4 and 20 mg of analyte per kg of [HMIM] [FAP] IL. The obtained results can be observed in Table 2.3. The relative standard deviation ranged from 11 to 22% for the lower spiking level (4 mg kg^{-1}) and from 5.9 to 16% for the higher spiking level (20 mg kg^{-1}). This precision reflects all of the errors in the overall method, including the temperature fluctuations that occur during SPME. The extraction efficiency, expressed as relative recoveries, varied from 78.5 to 122% at the lower spiking level and from 69.9 to106% at the higher spiking level. Under the extreme extraction temperatures and times used in this study, the fiber lifetime dropped to approximately 30 extractions before the extraction-to-extraction reproducibility decreased dramatically. Finally, the performance of the GC column comprised of the $[C_{12}(BIM)_2]$ $[NTf_2]$ IL stationary phase was evaluated. A sample chromatogram of the six analytes separated on this stationary phase is shown as Supporting Information. The reproducibility of the analyte retention times during the study produced RSD values ranging from 0.9 to 2.6% (n = 60).

Table 2.3: Precision and extraction efficiency at different spiking levels for the overall method.

	spiking level: 4 mg kg^{-1}		spiking level: 20 mg kg^{-1}	
analyte	RSD[a] (%)	RR[b] (%)	RSD[a] (%)	RR[b] (%)
Tricosane	15	99.1	10	75.9
Hexacosane	18	78.5	5.9	69.9
Triacontane	21	114	16	103
Methyl behenate	22	121	15	98.3
Methyl heneicosanoate	21	115	16	78.3
Methyl tetracosanoate	11	122	6.9	106

[a] RSD: relative standard deviation for $n = 4$.
[b] RR: relative recovery for $n = 4$.

2.4. Conclusions

One of the most interesting and useful characteristics of ILs lies with their vast structural tuneability which provides a wealth of opportunities in adapting the physical and chemical properties of the material for applications in separation science. Herein, an analytical method utilizing three distinct and separate IL components was used to perform high-temperature headspace extraction and separation of six analytes possessing high boiling points and low vapor pressures. The [HMIM] [FAP] IL has been shown to be an excellent solvent in that the hydrophobic and refractory nature of the IL promotes dissolution of the apolar analytes while avoiding pressure build-up within the sample vial under extreme temperatures. As a selective sorbent coating for SPME, the PIL component exhibits acceptable extraction efficiency of the studied analytes under the extreme experimental conditions. Finally, the structural design of the IL-based GC stationary phase produces a thermally stable material that exhibits high separation

selectivity of the analytes while producing minimal column bleed. The overall method nicely demonstrates the versatility of ILs within separation science for the determination of low volatility analytes using the headspace extraction mode with detection limits ranging from 0.3 to 0.6 mg kg^{-1}, relative recoveries ranging from 69.9% to 106%, and precision values between 5.9 and 22% as relative standard deviation. This method may be particularly useful for monitoring reaction products formed during catalysis experiments when ILs are used as the reaction solvent. Future work will involve the use of blended ILs and task-specific ILs to further improve the sensitivity and reproducibility of the overall method.

Acknowledgments

The authors wish to thank Dr. William R. Pitner from Merck KGaA for providing the ionic liquid sample and for useful discussions. J.L.A acknowledges funding from the Analytical and Surface Chemistry Program in the Division of Chemistry and the Separation and Purification Process Program in the Chemical, Environmental, Bioengineering, and Transport Systems Division from the National Science Foundation for a CAREER grant (Grant CHE-0748612). V.P. and J.L.A. thank the University of Toledo for a visiting faculty grant.

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Chapter 3

Tuning the Selectivity of Polymeric Ionic Liquid Sorbent Coatings for the Extraction of Polycyclic Aromatic Hydrocarbons Using Solid-Phase Microextraction

A paper published in *Journal of Chromatography A*[1]

Yunjing Meng, Jared L. Anderson

Abstract

A new generation polymeric ionic liquid (PIL), poly(1-(4-vinylbenzyl)-3-hexadecylimidazolium bis[(trifluoromethyl)sulfonyl]imide) (poly(VBHDIm$^+$ NTf$_2^-$)), was synthesized and is shown to exhibit impressive selectivity towards the extraction of 12 polycyclic aromatic hydrocarbons (PAHs) from aqueous samples when used as a sorbent coating in direct-immersion solid-phase microextraction (SPME) coupled to gas chromatography (GC). The PIL was imparted with aromatic

character to enhance $\pi-\pi$ interactions between the analytes and the sorbent coating. For comparison purposes, a PIL with similar structure but lacking the $\pi-\pi$ interaction capability, poly(1-vinyl-3-hexadecylimidazolium bis[(trifluoromethyl)sulfonyl]imide) (poly($HDIm^+$ NTf_2^-)), as well as a commercial polydimethylsiloxane (PDMS) sorbent coating were evaluated and exhibited much lower extraction efficiencies. Extraction parameters, including stir rate and extraction time, were studied and optimized. The detection limits of poly($VBHDIm^+$ NTf_2^-), poly($HDIm^+$ NTf_2^-), and PDMS coatings varied between 0.003–0.07 μ g L^{-1}, 0.02–0.6 μ g L^{-1}, and 0.1–6 μ g L^{-1}, respectively. The partition coefficients (log K_{fs}) of eight PAHs to the three studied fiber coatings were estimated using a static SPME approach. This study represents the first report of analyte partition coefficients to any PIL-based material.

3.1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a large group of organic compounds with two or more fused aromatic rings. Studies have shown that they distribute in a variety of environmental matrices worldwide [1,2]. Formation of PAHs is mainly due to incomplete combustion of organic compounds. Common sources include engine exhaust from automobiles [3] and smoke of industrial [4], municipal, and domestic origins as well [5]. Because of their toxic and carcinogenic effects, PAHs have been listed as priority pollutants in wastewater, groundwater, hazardous solid waste, soil and sediments by the United States Environmental Protection Agency (EPA) [6,7]. Due to the low

concentration of PAHs in the environment, analytical methods aimed at analyzing these compounds include isolation and pre-concentration steps prior to chromatographic separation. Conventionally, PAHs can be preconcentrated and extracted by means of liquid–liquid extraction (LLE) and solid-phase extraction (SPE). However, LLE is tedious, time consuming, and requires large amounts of organic solvent. SPE is more time efficient, but it still requires organic solvent for the elution step.

Solid-phase microextraction (SPME) has received considerable attention due to its high sensitivity, simplicity, and lacking requirement of organic solvents [8]. This technique has gained increasing utility in trace analysis within many areas of research, including environmental [9], food [10], and pharmaceutical analysis [11]. SPME has been used successfully for the determination of PAHs [12,13]. Doong et al. investigated the performance of five SPME fibers for the extraction of PAHs including: 100, 30, 7 μm polydimethylsiloxane (PDMS), 85 μm polyacrylate (PA), and 65 μm Carboxen-PDMS and found that the 100 μm PDMS fiber exhibited higher affinity to the higher-ring containing PAHs while the 85 μm polyacrylate (PA) was more suitable for PAHs possessing smaller ring structures [14]. Aguinaga et al. found the intermediate polarity polydimethylsiloxane–divinylbenzene (PDMS/DVB) sorbent coating (65 μm) to be more suitable than a 100 μm PDMS and a 85 μm PA coating due to the $\pi-\pi$ interactions imparted by the DVB copolymer [15].

In addition to commercial fibers, considerable effort has been devoted to developing new coatings capable of improving the extraction efficiency of PAHs. Bagheri et al. reported the electrochemical deposition of polyaniline films as a SPME extraction phase

in the determination of five PAHs [16]. Coupled with GC–MS, naphthalene, acenaphthylene, acenaphthene, fluorene, and anthracene were extracted with limits of detection (LODs) in the range of 0.1–6 pg mL^{-1}. The low LODs were attributed to the high surface area and $\pi - \pi$ interactions imparted by structure of polyaniline. Recently, Yan and co-workers reported the use of etched stainless steel wire to extract PAHs, and the new fiber showed much higher enrichment factors than PDMS and PDMS/DVB fibers based on donor–acceptor interactions [17]. Coupled with GC–FID, Jiang's group reported the extraction of naphthalene, fluorene, anthracene, and fluoranthene using TiO_2 nanotubes as SPME coating materials with LODs of 0.1–0.01 μg L^{-1} [18]. Carbon nanotubes were also reported to exhibit higher extraction efficiency than the commercial PDMS coating in the extraction of PAHs [19]. By incorporating phenyl groups into sol–gel solutions, Bianchi and co-workers improved the extraction of PAHs in terms of extraction efficiency, thermal and chemical stability [20]. Coupled with GC–MS, the detection limits for many PAHs were two-fold lower than those obtained by a 7 μm PDMS fiber. By introducing cyclodextrin in the PDMS network, Hu et al. fabricated a SPME membrane capable of extracting PAHs [21]. Coupled with GC–MS, detection limits ranged from 0.01 to 0.2 μg L^{-1}.

Ionic liquids (ILs) have emerged as an increasingly popular class of solvents for various applications within analytical chemistry [22]. The tunable solvation interactions make them useful as stationary phases in GC [23–25], and high performance liquid chromatography (HPLC) [26,27], matrices in matrix-assisted laser desorption/ionization (MALDI) mass spectrometry [28], liquid–liquid extraction [29,30], dispersive liquid–liquid microextraction [31], and single drop microextraction [32,33]. Their high

viscosity, high thermal stability, and tailored water-immiscibility coupled with their minimal vapor pressure promote the formation of stable coatings for SPME [34–39]. IL-based SPME coatings provide a new avenue in the search for additional classes of highly efficient and selective sorbent coating materials in SPME. Our group has recently introduced SPME coatings based on polymeric ionic liquids (PILs) [37–39]. Due to their high thermal stability and resistance to flowing at elevated temperatures, PIL-based SPME coatings can be re-used while also exhibiting long lifetimes when they are coupled with GC. In addition, the fibers exhibit exceptional extraction-to-extraction reproducibility.

One of the remarkable advantages of using ILs as separation media lies in the ease of IL/PIL functionalization, making them tunable in providing desired selectivity and sensitivity towards target analytes [32,40]. In this work, a new generation of structurally designed PIL-based SPME coatings was synthesized and used for the extraction of PAHs. To improve the extraction efficiency of these analytes, the PIL was functionalized with benzyl groups capable of imparting $\pi-\pi$ interactions between the analyte and the sorbent coating. Due to the stronger hydrophobic and enhanced $\pi-\pi$ interactions, the new PIL sorbent coating exhibits significantly higher sensitivity and lower detection limits than a similar PIL lacking benzyl groups and much higher sensitivity than a commercial PDMS fiber of similar film thickness. To further understand the unique selectivity and sorption behavior of the PIL coatings, the static SPME method [41–43] was used to estimate the partition coefficients of PAHs to the two PIL-based sorbent coatings as well the PDMS sorbent coating.

3.2. Experimental

3.2.1. Chemicals and Reagents

The following PAH standards were obtained from Supelco (Bellefonte, PA, USA): naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene and benzo(k)fluoranthene. The reagents imidazole, 1-bromohexadecane (97%), 4-vinylbenzyl chloride (97%), acrylonitrile (>99%), and 2,2'-azobis(isobutyronitrile) (AIBN) were purchased from Sigma–Aldrich (Milwaukee, WI, USA). Lithium bis[(trifluoromethyl)sulfonyl]imide was purchased from SynQuest labs (Alachua, FL, USA). Chloroform, methylene chloride, hexane, acetone, cyclohexane, and methanol (HPLC grade) were purchased from Fisher Scientific (Fair Lawn, NJ, USA). Ultrapure water was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA) and was used in the preparation of all aqueous solutions.

For SPME experiments, all of the PAHs investigated were dissolved individually in acetone to prepare standard solutions with concentrations of 2000 or 1000 μg mL^{-1}. These standard solutions were used to prepare stock solutions: solution A containing 500 μg mL^{-1} of naphthalene, acenaphthylene, acenaphthene and fluorene; solution B containing phenanthrene, anthracene and fluoranthene at concentrations of 200 μg mL^{-1}; and solution C containing pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene and benzo(k)fluoranthene at concentrations of 10 μg mL^{-1}. Acetone was used to prepare diluted working solutions. All stock solutions were stored at 4 °C. The working solutions

were prepared by spiking a certain amount of the stock solutions into 19.70 mL of deionized water within a 20 mL sampling vial.

3.2.2. Quantification of FID Response

The external calibration method was used to determine the detector response for all analytes examined in this study. All of the PAHs were dissolved individually in cyclohexane to prepare standard solutions of 20 μg mL^{-1}. Three stock solutions with concentrations of 5 μg mL^{-1} for each analyte were prepared: solution 1 containing naphthalene, acenaphthylene, acenaphthene, and fluorene; solution 2 including phenanthrene, anthracene, fluoranthene, and pyrene; solution 3 containing benzo(a)anthracene, chrysene, benzo(b)fluoranthene, and benzo(k)fluoranthene. Cyclohexane was used to prepare diluted working solutions. Calibration curves of the analyte peak area (from FID response) versus the mass of PAHs injected onto the column were generated by injecting 1 μL of a standard mixtures through an autosampler using identical inlet and column conditions as to those carried out during SPME desorption. The FID response from the direct liquid injection of the standard solutions was used to estimate the amount of analyte extracted by the three different SPME sorbent coatings examined in this study.

3.2.3. Materials

Fused silica capillary (0.10 mm I.D.) and amber glass vials (20 mL) with PTFE/Butyl septa screwcaps were obtained from Supelco (Bellefonte, PA, USA). A 7 μm PDMS fiber and a manual SPME holder were also purchased from Supelco. The

poly(1-vinyl-3-hexadecylimidazolium bis[(trifluoromethyl)sulfonyl]imide) (poly(HDIm$^+$ NTf_2^-)) PIL was prepared using previously published procedures [37]. A home-made SPME device was constructed by purchasing a 5 μL syringe from Hamilton (Reno, NV, USA) and the syringe re-assembled by discarding the stainless steel fiber on the plunger and replacing it with a fused silica capillary affixed by epoxy glue (GC Electronics, IL, USA). The end of the capillary was sealed by a microflame torch and the outer 1 cm of the polyimide coating was removed. The bare fiber segment was washed with methanol, acetone, hexane, and methylene chloride before coating. PTFE stir bars were obtained from Fisher Scientific and were used to perform all extractions at an optimized stir rate on a Corning stir plate (Nagog Park Acton, MA, USA). An auto injector (7683B Series) purchased from Agilent (Agilent Technologies, Palo Alto, CA, USA) was employed for all direct liquid injection experiments.

3.2.4. Instrumentation

All separations were performed using an Agilent 6850N gas chromatograph equipped with a flame ionization detector (FID). A 0.75 mm I.D. liner was used to introduce the sample to the column. Helium was used as the carrier gas and maintained at a constant flow rate of 1 mL min^{-1}. All separations were performed using a HP-5 capillary column (30 m × 0.25 mm I.D., 0.25 μm film thickness) purchased from Agilent Technologies. Desorption of the fibers into the injection port was carried out in the splitless mode at 250 $^{\circ}$C for 5 min. The following temperature program was used for the chromatographic separation of the mixture: initial temperature of 80 $^{\circ}$C was held for 1 min and increased to 160 $^{\circ}$C at 25°C min^{-1}, from 210 $^{\circ}$C at 10 $^{\circ}$C min^{-1} increased to 216 $^{\circ}$C at a ramp of 3 $^{\circ}$C

min^{-1}, increased to 246 °C at 10 °C min^{-1}, and then finally the oven temperature was raised to 300 °C at 3 °C min^{-1} and held for 10 min. The temperature of the detector was set at 300 °C. All scanning electron micrographs were obtained using a Hitachi S-4800 High Resolution Scanning Electron Microscope.

3.2.5. Synthesis of Benzyl-Functionalized Polymeric Ionic Liquid SPME Sorbent Coating

The poly(1-(4-vinylbenzyl)-3-hexadecylimidazolium bis[(trifluoromethyl)sulfonyl]imide) (poly(VBHDIm$^+$ NTf_2^-)) PIL was synthesized as shown in Fig. 3-1. To a 50-mL round-bottom flask, 0.1 mol of imidazole and 0.13 mol of acrylonitrile were added to 10 mL of methanol. The mixture was heated to 45 °C for 5 h under nitrogen. Methanol and excess acrylonitrile were subsequently removed under vacuum to obtain compound **1**. This compound was dissolved in 30 mL of chloroform followed by the addition of 0.1 mol of 1-bromohexadecane. The resulting solution was refluxed overnight to obtain compound **2**. Then, 40 mL of a 15% (w/w) NaOH aqueous solution was added. The mixture was stirred overnight at room temperature. The chloroform layer was separated using a separatory funnel and the organic layer was washed with water five times in order to eliminate the base and other impurities. Chloroform was subsequently removed and the residue dried under vacuum to yield compound **3**. The product was re-dissolved in chloroform and one molar equivalent of 4-vinylbenzyl chloride was added. The solution was refluxed overnight to yield compound **4**. The polymerization reaction was commenced by introducing AIBN (1% by weight) under the protection of N_2 and refluxed for 3 h. Finally, the halide counteranion

was exchanged to [NTf_2^-] by metathesis anion exchange. In this procedure, 0.1 mol of lithium bis[(trifluoromethyl)sulfonyl]imide dissolved in 30 mL of water was added to the polymer/chloroform solution. The two-phase solution was stirred at room temperature for 3 days and the chloroform layer separated by separatory funnel. The chloroform solution was then washed with water multiple times to remove all halide residues from the product followed by the removal of chloroform under vacuum to yield compound **5**. The ^{1}H NMR spectra of compounds **4** and **5** as well as the poly($HDIm^+$ NTf_2^-) PIL (produced following procedures from Ref. [37]), along with corresponding peak assignments, are shown in Fig. 3-2. Successful polymerization was evidenced by the disappearance of the proton signals originating from the vinyl group.

The IL monomer and polymer and all intermediate products were characterized using ^{1}H NMR carried out using Varian VXRS-400 MHz and UNITY INOVA-600 MHz spectrometers. ^{1}H NMR [δ , ppm relative to TMS]: Compound **1** (400 MHz, d_6-DMSO): 7.470 (s, 1 H), 7.005 (s, 1H), 6.712 (s, 1H), 4.023 (t, 2H), 2.797 (t, 2H); Compound **2** (400 MHz, $CDCl_3$): 9.984 (s, 1H), 7.945 (s, 1H), 7.244 (s, 1H), 4.750 (t, 2H), 4.060 (t, 2H), 3.198 (t, 2H), 1.712 (m, 2H), 1.036 (m, 26H), 0.647 (m, 3H); Compound **3** (400 MHz, $CDCl_3$): 7.932 (s, 1H), 7.086 (s, 1H), 6.920 (s, 1H), 3.974 (t, 2H), 1.754 (m, 2H), 1.208 (m, 26H), 0.816 (t, 3H); Compound **4** (600 MHz, d_6-DMSO): 9.401 (d, 1H), 7.857 (m, 2H), 7.541 (m, 4H), 6.773 (dd, 1H), 5.891 (d, 1H), 5.424 (m, 2H), 5.330 (dd, 1H), 4.162 (t, 2H), 1.755 (m, 2H), 1.227 (m, 26H), 0.830 (t, 3H).

3.2.6. Preparation of SPME Fibers and Extraction Procedures

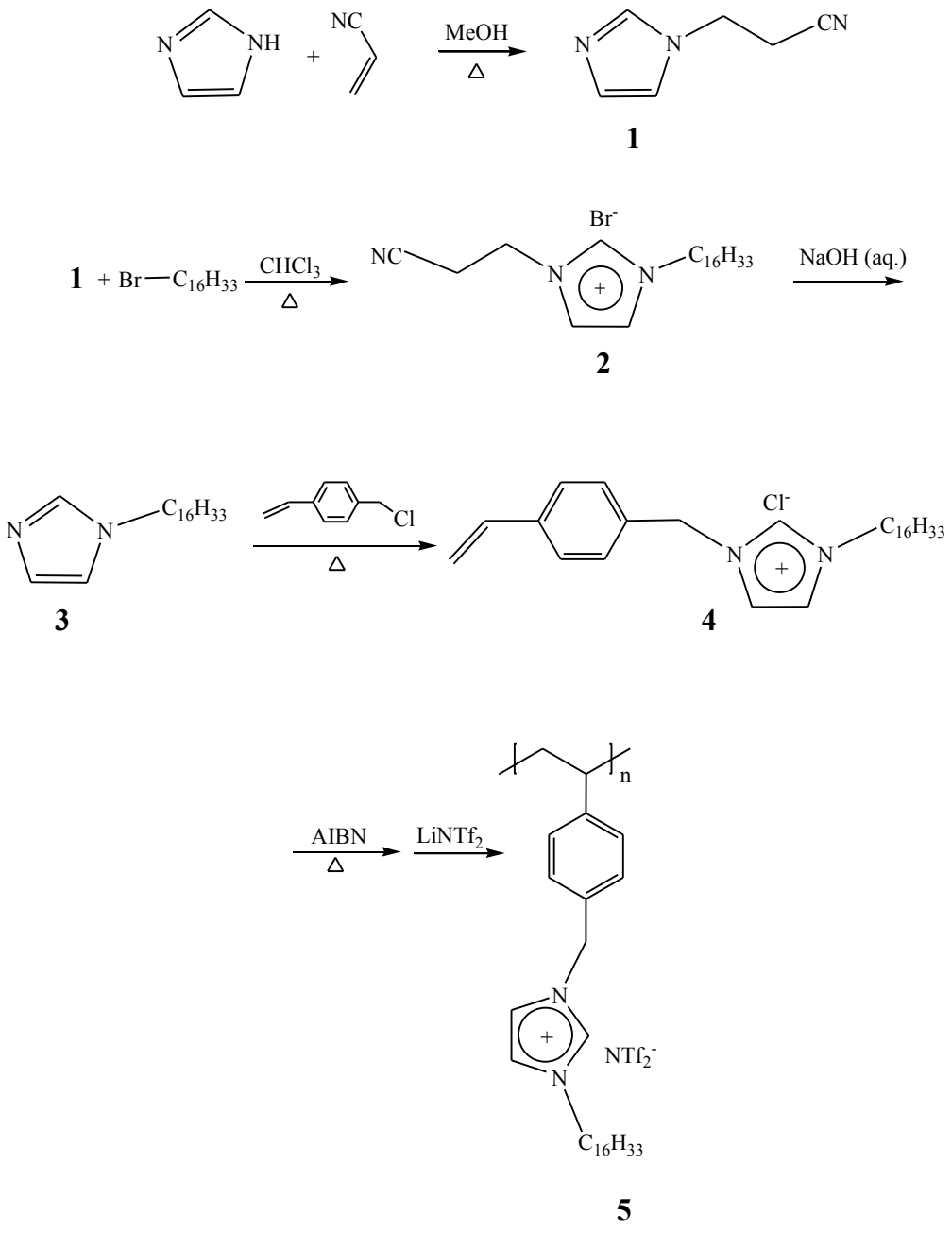


Figure 3-1: Synthetic route used to prepare the poly(1-(4-vinylbenzyl)-3-hexadecylimidazolium bis[(trifluoromethyl)sulfonyl]imide) PIL.

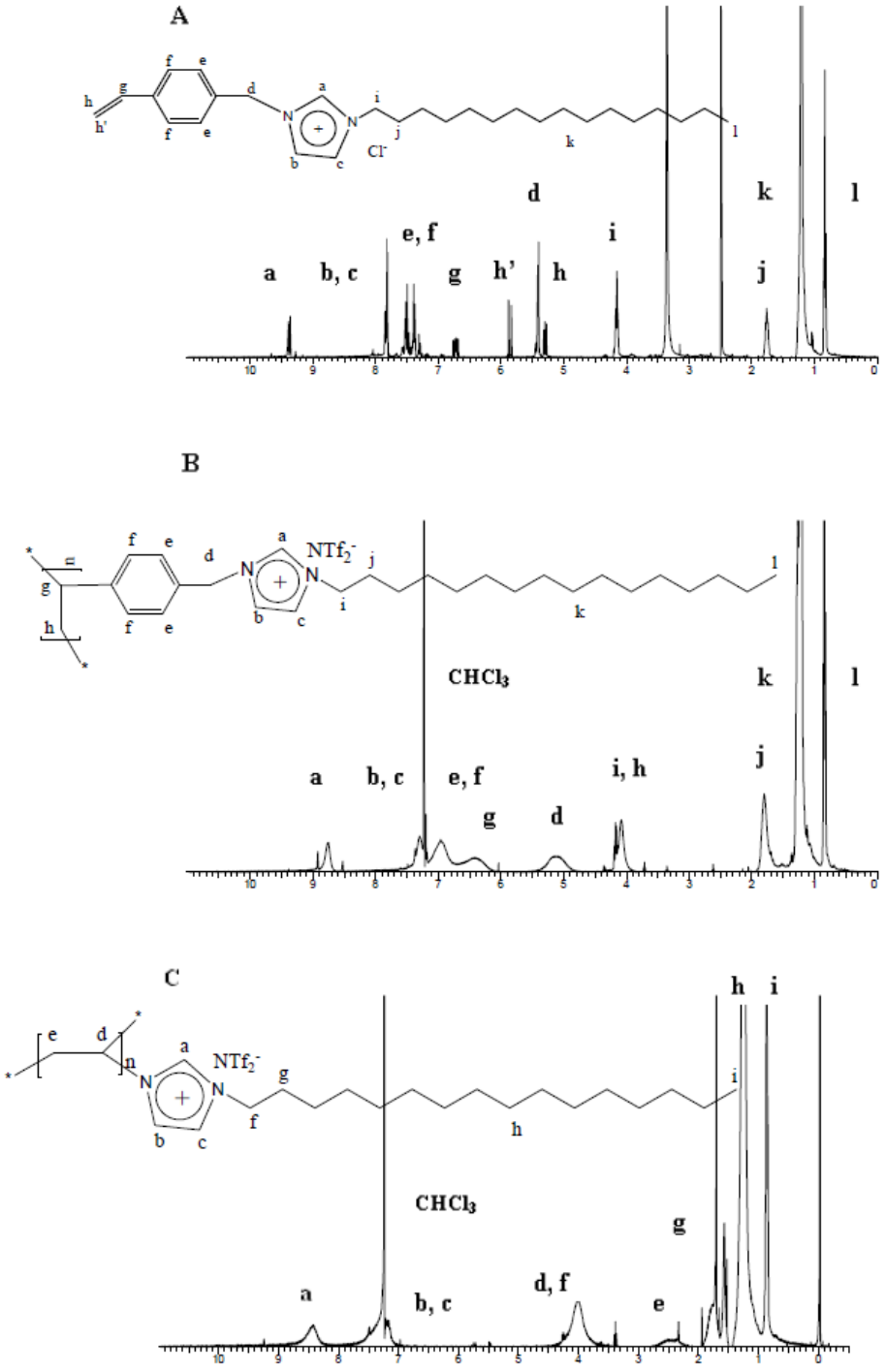


Figure 3-2**:** ^{1}H NMR spectra of (A) 1-(4-vinylbenzyl)-3-hexadecylimidazolium chloride in d_6-DMSO, (B) poly(VBHDIm^{+} NTf_2^{-}) in $CDCl_3$, and (C) poly(HDIm^{+} NTf_2^{-}) in $CDCl_3$.

The coating of the SPME fiber followed the procedures described previously [37,38]. Briefly, the poly(VBHDIm$^+$ NTf_2^-) and poly(HDIm$^+$ NTf_2^-) PILs were diluted in chloroform to prepare a coating solution with a ratio of 1:1 (v/v). The bare fiber was then dipped into the solution and slowly removed. After coating, the fiber was dried in the air for 10 min before it was retracted back into the needle. The fiber was conditioned in the GC injection port for 5 min at 250 °C prior to performing extractions.

To carry out the extractions, 19.70 mL of Milli-Q water and an appropriate amount of stock solution were placed in 20 mL amber glass sampling vials. The vial was immediately closed with a screwcap after introducing a magnetic stir bar. The needle of the SPME device was pierced through the septum of the vial and the fiber then exposed directly into the solution. Immediately, the extraction was initiated by stirring the solution under the optimized conditions. After the extraction, the fiber was withdrawn back into the syringe and immediately transferred to the GC injection port for thermal desorption.

In order to remove any carryover effects of PAHs with the sampling vials used in this study, they were first cleaned by sonicating with detergent for 2 h and then with deionized water for four 1 h cleaning increments. The vials were then kilned at 500 °C for longer than 4 h before use. The stir bars used in this study were sonicated in acetone for over 30 min and then rinsed with fresh acetone. They were then air dried for over 2 h before use. Carryover was examined after performing extractions at the highest concentrations on the calibration curves, namely 1.7 mg L^{-1} of naphthalene, acenaphthylene, acenaphthene and fluorene; 130 μg L^{-1} of phenanthrene, anthracene, and fluoranthene; 9 μg L^{-1} of pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, and benzo(k)fluoranthene, by reinserting the SPME fiber in the

injector for another 5 min after each run. The highest carryover was found to be less than 4%.

3.2.7. Partition Coefficient Estimation Using SPME

The amount of analyte extracted can be determined by Eq. (1) [45],

$$n_f = \frac{K_{fs} V_f n_0}{K_{fs} + V_s} \quad (1)$$

where n_0 is the initial amount of analyte in the sample, n_f is the amount of analyte on the fiber after equilibrium, V_s is the volume of matrix, and V_f is the volume of the fiber coating. By rewriting Eq. (1), the partition coefficient (K_{fs}) can be calculated directly according to Eq. (2).

$$K_{fs} = \frac{V_s}{V_f\left(\frac{n_0}{n_f} - 1\right)} \quad (2)$$

In the determination of partition coefficients for this study, the sample volume (V_s) was maintained at 19.70 mL. The initial mass of the analyte was 118.2 ng for naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, and fluoranthene, and 59.1 ng for pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, and benzo(k)fluoranthene. For the 7 μm PDMS fiber, the volume of sorbent material (V_f) is 0.026 μL, as reported by the manufacturer. The volume of the PIL sorbent layer for the poly(VBHDIm$^+$ NTf$_2^-$) and poly(HDIm$^+$ NTf$_2^-$) PILs was calculated as a cylindrical layer of polymer on the fused silica support possessing an outer diameter of 237 μm and length of 1 cm. The film thickness for both of the PILs was estimated to be in the range

of 12–16 μm, as determined by scanning electron microscopy (SEM). Representative SEM photos of fibers containing the two PIL coatings are supplied as supplementary data. For estimation purposes, 12 μm was used as the approximate film thickness which yielded a V_f of 0.094 μL for both of the PIL-based fibers.

3.3. Results and Discussion

3.3.1. Development of PAH Selective PIL-Based Coatings

Due to the low vapor pressure and high boiling point of PAHs, direct-immersion SPME at room temperature provides higher extraction efficiency compared to headspace SPME. Therefore, sorbent coating materials must be sufficiently hydrophobic to avoid dissolution of the coating during prolonged sampling. For this reason, the PIL introduced in this study was synthetically designed to possess a long hydrocarbon chain structure in addition to containing the non-coordinating bis[(trifluoromethyl)sulfonyl]imide [NTf_2^-] anion, both of which impart the PIL with enhanced hydrophobicity. The poly($HDIm^+$ NTf_2^-) PIL (see Fig. 3-2C) has been shown previously to exhibit higher extraction efficiency of PAHs compared to the PDMS sorbent coating [44]. In order to further increase the selectivity of the sorbent coating, additional aromatic character (in the form of benzyl groups) was introduced into the PIL structure, as shown in Fig. 3-1. It was hypothesized that addition of π-electrons to the PIL could enhance the extraction efficiency of PAHs by promoting stronger $\pi - \pi$ interactions between the PIL sorbent coating and the analyte. As shown in Fig. 3-2, the only difference between the two PILs

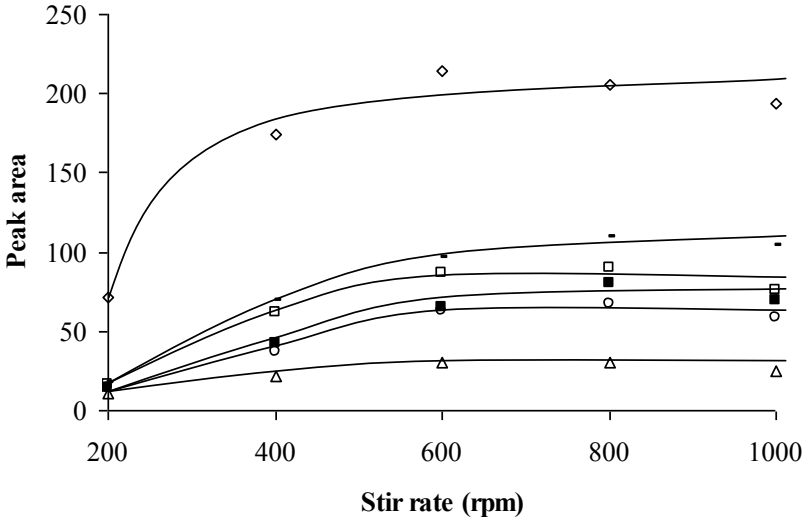
examined in this study is the presence of benzyl moieties within the chemical structure of the poly(VBHDIm$^+$ NTf$_2^-$) PIL. The imidazolium cation core, length of aliphatic hydrocarbon substituent, and anion are identical for the poly(VBHDIm$^+$ NTf$_2^-$) and poly(HDIm$^+$ NTf$_2^-$) PILs.

3.3.2. Optimization of Stir Rate and Sampling Time

Agitation is a very important factor that affects extraction in SPME. Good agitation accelerates the diffusion and mass transfer of analytes from the aqueous solution to the extraction phase and consequently reduces the extraction time. Fig. 3-3 shows the dependence of stir rate on the extraction peak areas of PAHs using a range from 200 to 1000 rpm for the poly(VBHDIm$^+$ NTf$_2^-$) PIL fiber. The extraction peak areas for all analytes reached equilibrium when the stir rate was higher than 800 rpm. Therefore, 800 rpm was chosen as the optimized stir rate for subsequent studies.

Sampling time is another decisive factor in achieving distribution equilibrium of the analyte between the sample and the extraction phase. SPME extractions were carried out at various extraction times using a stir rate of 800 rpm. Fig. 3-4 shows the peak area versus sampling time for the poly(VBHDIm$^+$ NTf$_2^-$) PIL fiber. All of the PAHs reached equilibrium in approximately 45 min. When an extraction time longer than 45 min was applied, the extraction peak areas for the PAHs slightly decreased and leveled off. Thus, 45 min was chosen as the best extraction time for the PIL fiber.

Sorption-time profiles for the poly(HDIm$^+$ NTf$_2^-$) PIL and PDMS (7 μm) fibers were also generated using a stir rate of 800 rpm, as shown in Figs. 3-5 and 3-6, respectively. Due to the lower extraction efficiencies of these two fibers for the PAHs, the



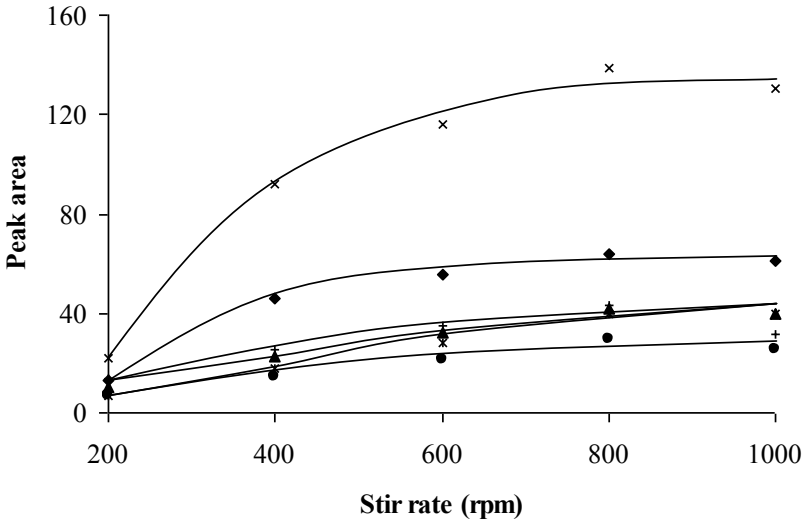
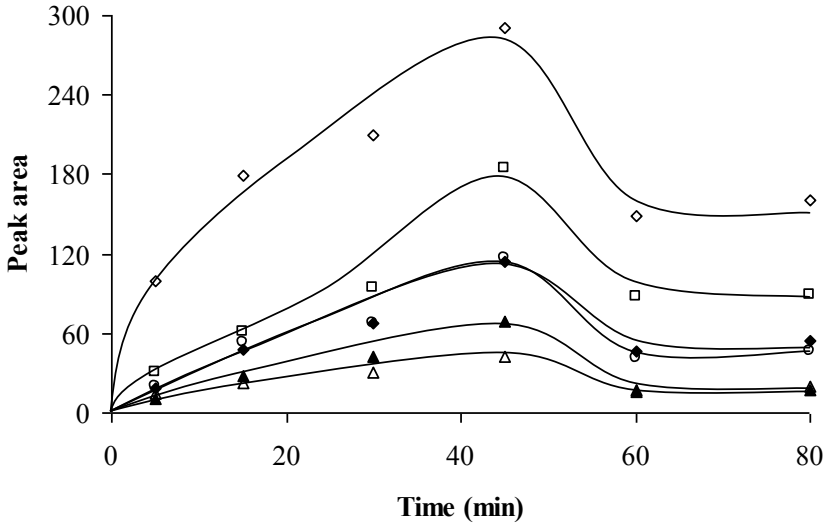


Figure 3-3: Dependence of extraction peak area on stir rate using the poly(VBHDIm^{+} NTf_2^{-}) PIL fiber. The extraction time was 30 min and the concentration of the analytes was: 1 μg L^{-1} of naphthalene (△), acenaphthylene (○), acenaphthene (■), fluorene (□), phenanthrene (♦), anthracene (–), and fluoranthene (x); 0.5 μg L^{-1} of pyrene (◆), benzo(a)anthracene (*), chrysene (▲), benzo(b)fluoranthene (+), and benzo(k)fluoranthene (●).



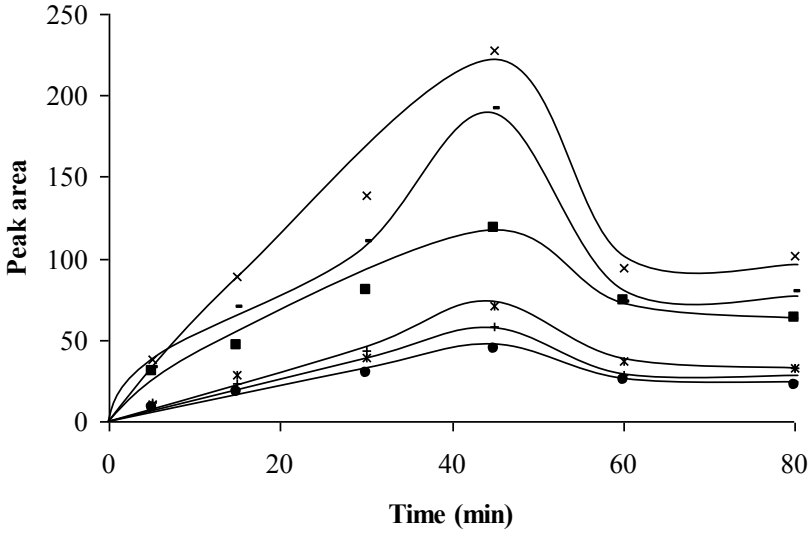


Figure 3-4: Dependence of extraction peak area on extraction time using the poly(VBHDIm$^+$ NTf$_2^-$) PIL fiber. The stir rate was 800 rpm and the concentration of the analytes was: 1 μg L^{-1} of naphthalene (Δ), acenaphthylene (○), acenaphthene (■), fluorene (□), phenanthrene (♦), anthracene (–), and fluoranthene (x); 0.5 µg L^{-1} of pyrene (◆), benzo(a)anthracene (*), chrysene (▲), benzo(b)fluoranthene (+), and benzo(k)fluoranthene (●).

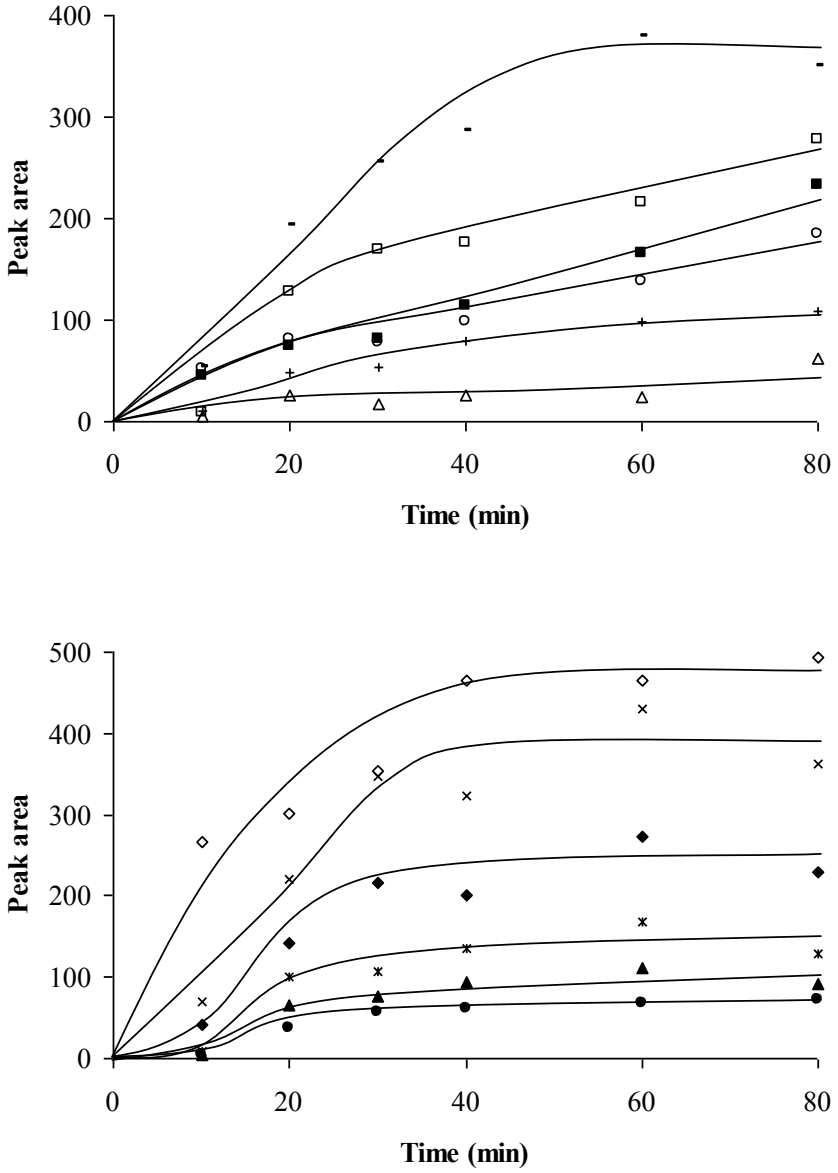


Figure 3-5: Sorption-time profile of the poly($HDIm^+$ NTf_2^-) PIL fiber. The stir rate was 800 rpm and the concentration of the analytes was: 6 µg L^{-1} of naphthalene (△), acenaphthylene (○), acenaphthene (■), fluorene (□), phenanthrene (♦), anthracene (–), and fluoranthene (x); 3 µg L^{-1} of pyrene (◆), benzo(a)anthracene (*), chrysene (▲), benzo(b)fluoranthene (+), and benzo(k)fluoranthene (●).

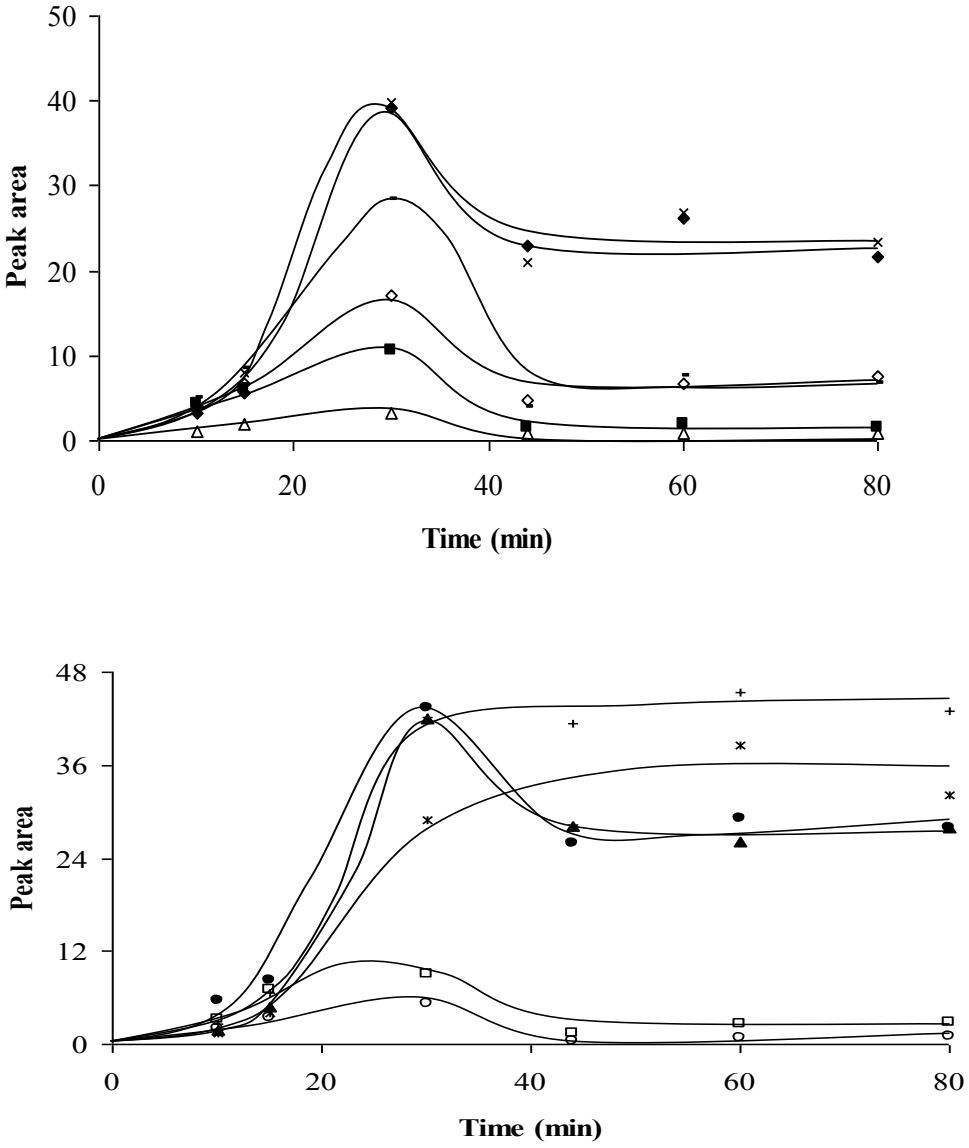


Figure 3-6: Sorption-time profile of the PDMS (7 μ m) fiber. The stir rate was 800 rpm and the concentration of the analytes was: 6 µg L^{-1} of naphthalene (△), acenaphthylene (○), acenaphthene (■), fluorene (□), phenanthrene (♦), anthracene (–), and fluoranthene (x); 3 µg L^{-1} of pyrene (◆), benzo(a)anthracene (*), chrysene (▲), benzo(b)fluoranthene (+), and benzo(k)fluoranthene (●).

concentration of the analytes was increased six-fold in order to achieve reasonable extraction for further optimization. Most of the PAHs reached equilibrium using the poly($HDIm^+$ NTf_2^-) PIL fiber (Fig. 3-5) in approximately 40 min, except for fluorene, acenaphthene and acenaphylene which required longer than 60 min to reach equilibrium. For the PDMS fiber (Fig. 3-6), most of the analytes reached equilibrium in approximately 30 min. Therefore, 40 and 30 min were chosen as the optimized fiber exposure times for the poly($HDIm^+$ NTf_2^-) PIL and PDMS fibers, respectively, and were used for subsequent calibration studies.

Different extraction behaviors were observed for the three coatings in terms of the extraction time needed for most of the analytes to reach equilibrium: approximately 45 min for the poly($VBHDIm^+$ NTf_2^-) PIL fiber, 40 min for the poly($HDIm^+$ NTf_2^-) PIL fiber, and 30 min for the PDMS fiber. This difference can be partly explained by the varying film thicknesses and properties of the sorbent coatings. The thinner film thickness of PDMS (7 μm) provided shorter equilibration times, while the slightly thicker PIL-based coatings rendered longer equilibration times. Compared with the PDMS fiber, the higher extraction peak areas for the two PIL fibers indicated the higher affinity of the fibers towards PAHs. The phenomenon in which the extraction peak areas decreased after the fiber was saturated for the poly($VBHDIm^+$ NTf_2^-) PIL fiber and PDMS fiber may be attributed to the adsorption of these PAHs on the wall of the sampling vials. Given the low concentrations of the analytes (1 and 0.5 μg L^{-1}) in the solution, the adsorption of the analytes to the wall of the sampling vial may be more pronounced for the poly($VBHDIm^+$ NTf_2^-) PIL fiber compared to the poly($HDIm^+$ NTf_2^-) PIL fiber in which the concentrations of the analytes was six-fold higher (6 and 3 μg

L^{-1}). Compared with other studies using similar analytes [14,46], the more pronounced adsorption effect observed in our work may be due to the low concentration of analytes, the low content of the organic modifier (<1%) in extraction solution, the small sample volume (20 mL) and/or the relatively low extraction temperature (22 °C).

3.3.3. Extraction Efficiency Comparison of Benzyl-Functionalized PIL Versus Non-Functionalized PIL and PDMS Sorbent Coatings

The extraction efficiencies of PAHs were examined by performing 30 min extractions at a stir rate of 800 rpm at room temperature using the two PIL and PDMS coatings. The extraction time of 30 min was chosen because at this time the PDMS fiber demonstrated the best performance for the extraction of the PAHs based on its sorption-time profiles (Fig. 3-6). A comparison of the amount of analyte extracted (in ng) for the three fibers using the same concentration of analytes is shown in Fig. 3-7. The PDMS fiber exhibited the lowest extraction efficiency for nearly all of the studied analytes compared to the two PIL fibers. The masses of acenaphthylene, acenaphthene, fluorene, phenanthrene, and anthracene extracted by the two PIL fibers were between ten and fifty times higher than that obtained by the PDMS fiber. In the case of fluoranthene, pyrene, benzo(a)anthracene, and benzo(k)fluoranthene, the amount extracted varied between two and six times higher for the PIL-based fibers compared to PDMS while similar amounts of naphthalene and benzo(b)fluoranthene were extracted. Among the two PIL fibers, except for naphthalene, fluoranthene, and benzo(b)fluoranthene, where similar amounts of analyte were extracted, the poly(VBHDIm$^+$ NTf_2^-) PIL fiber exhibited superior extraction efficiency towards all PAHs. For acenaphthylene, acenaphthene, fluorene, pyrene, chrysene, and

benzo(k)fluoranthene, the mass extracted by the poly(VBHDIm$^+$ NTf_2^-) PIL fiber was between 1.5 and 3 times higher than that obtained by the poly(HDIm$^+$ NTf_2^-) PIL fiber. In the case of benzo(a)anthracene, the poly(VBHDIm$^+$ NTf_2^-) PIL extracted nearly six times the mass extracted by the poly(HDIm$^+$ NTf_2^-) sorbent coating.

Calibration curves for all studied analytes were obtained for both PIL fibers and the PDMS fiber in deionized water. The figures of merit including linear ranges, correlation coefficients, sensitivities, and detection limits are listed in Tables 3.1. For the poly(VBHDIm$^+$ NTf_2^-) PIL fiber, the linear range was wide spanning from 2 to 4 orders of magnitude for many analytes with correlation coefficients varying between 0.981 and 0.999. Compared with the other two fibers, the poly(VBHDIm$^+$ NTf_2^-) PIL fiber generally exhibited wider linear ranges and better correlation coefficients for all studied PAHs. Limits of detection were calculated as three times the standard deviation of the lowest concentration divided by the slope of the calibration curve. Among the two PIL fibers, LODs for the poly(VBHDIm$^+$ NTf_2^-) PIL fiber were lower than the poly(HDIm$^+$ NTf_2^-) PIL fiber. LODs were in the range of 0.003–0.07 μ g L^{-1} for the poly(VBHDIm$^+$ NTf_2^-) PIL fiber, 0.02–0.6 μ g L^{-1} for the poly(HDIm$^+$ NTf_2^-) PIL fiber, and 0.1–6 μ g L^{-1} for the PDMS fiber. In the case of naphthalene, benzo(a)anthracene, benzo(b)fluoranthene, and benzo(k)fluoranthene, the obtained LODs were one order of magnitude lower for the poly(VBHDIm$^+$ NTf_2^-) PIL compared to the poly(HDIm$^+$ NTf_2^-) PIL. The LODs for chrysene were two orders of magnitude smaller using the same comparison. Sensitivities, as determined by the slopes of the calibration curves, were higher for all of the PAHs using the poly(VBHDIm$^+$ NTf_2^-) PIL fiber than those

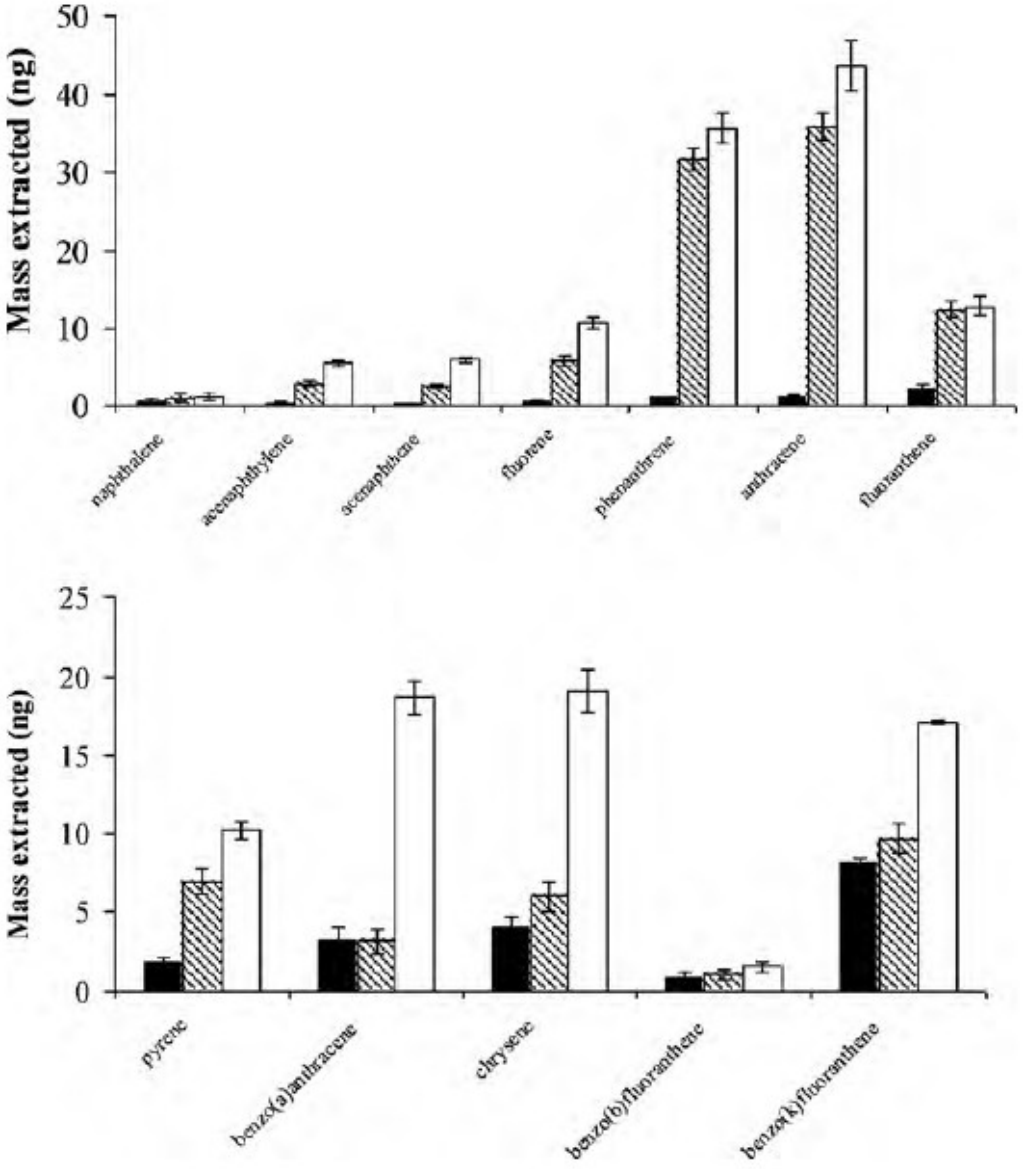


Figure 3-7: Comparison of mass extracted using the three studied fibers: 7 μm PDMS (■), 12 μm poly(HDIm$^+$ NTf$_2^-$) (▨), and 12 μm poly(VBHDIm$^+$ NTf$_2^-$) (□). The extractions were performed for 30 min with a stir rate of 800 rpm at 22 °C. The concentration of the analytes was: 6 μg L^{-1} of naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, and fluoranthene; 3 μg L^{-1} of pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, and benzo(k)fluoranthene.

measured by the other two fibers. Precision was determined by performing three consecutive extractions at a concentration of 1 μ g L^{-1} for naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, and fluoranthene, and 0.5 μ g L^{-1} for the remaining PAHs. In the case of the poly($VBHDIm^+$ NTf_2^-) PIL fiber, the %RSD values varied between 1 and 15%. For the poly($HDIm^+$ NTf_2^-) PIL and PDMS fibers (examined at concentrations of 6 μ g L^{-1} for naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, and fluoranthene; and 3 μ g L^{-1} for pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene and benzo(k)fluoranthene), %RSD values ranged from 6 to 15% and 2 to 14%, respectively.

Another meritorious feature of the poly($VBHDIm^+$ NTf_2^-) PIL are the long lifetimes exhibited by the sorbent coating. Throughout the entire course of this study, one fiber was used with no significant loss of extraction efficiency up to approximately 70 extraction/desorption steps. The stability of the poly($VBHDIm^+$ NTf_2^-) PIL sorbent coating was also examined by performing a series of 6-h extractions. For this PIL, the %RSD values ranged from 3 to 17% for three consecutive 6-h extractions.

3.3.4. Determination of PAH-PIL Partition Coefficients

In an effort to develop structure–function relationships to understand how analytes partition to PIL-based materials, partition coefficients were estimated using SPME. It is important to emphasize that the extraction time used in this study (i.e., 30 min) is shorter than the equilibrium time required by many of the PAHs; therefore, the partition coefficients determined in this study are only an estimate. The amount of analyte

Table 3.1: Figures of merit of calibration curves for 12 μm poly(VBHDIm^{+}NTf$_2^{-}$) PIL fiber. [a]

Analyte	R	Calibration range μg L^{-1}	Slope ± SD [b]	Error of the estimate[c]	LOD [d] μg L^{-1}	%RSD[e]
naphthalene	0.998	0.05-1000	14 ± 0.4	330	0.06	15
acenaphthylene	0.997	0.005-1000	36 ± 1	929	0.01	10
acenaphthene	0.992	0.05-1000	45 ± 2	1871	0.05	12
fluorene	0.994	0.005-500	51 ± 2	1012	0.01	3
phenanthrene	0.999	0.0125-100	50 ± 0.4	40	0.01	1
anthracene	0.996	0.0125-100	37 ± 1	112	0.01	6
fluoranthene	0.997	0.025-130	47 ± 1	167	0.02	8
Pyrene	0.997	0.01-9	71 ± 2	19	0.01	15
benzo(a)anthracene	0.999	0.05-5	53 ± 2	9	0.03	6
chrysene	0.995	0.003-5	452 ± 8	86	0.003	15
benzo(b)fluoranthene	0.991	0.05-9	45 ± 3	16	0.05	13
benzo(k)fluoranthene	0.981	0.05-9	8 ± 0.7	6	0.07	2

[a] Extraction conditions: sampling time, 45 min with stir rate of 800 rpm at 22 ºC; desorption for 5 min at 250 ºC; sample volume, 20 mL without headspace.
[b] Standard deviation of the slope.
[c] Standard deviation of the regression.
[d] Estimated as three times of standard deviation at the lowest concentration on the calibration curve divided by the slope of the calibration curve.
[e] Based on three extractions. The concentrations of the analytes were 1 μg L^{-1} for naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, and fluoranthene, and 0.5 μg L^{-1} for pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, and benzo(k)fluoranthene.

Table 3.2: Figures of merit of calibration curves for 12 μm poly($HDIm^+NTf_2^-$) PIL fiber.[a]

Analyte	R	Calibration range μg L^{-1}	Slope ± SD[b]	Error of the estimate[c]	LOD[d] μg L^{-1}	%RSD[e]
naphthalene	0.986	0.5-1700	4 ± 0.2	390	0.6	11
acenaphthylene	0.991	0.1-1700	17 ± 0.9	1457	0.2	7
acenaphthene	0.989	0.1-1700	24 ± 1	2201	0.06	8
fluorene	0.975	0.05-1700	27 ± 2	3586	0.02	9
phenanthrene	0.988	0.05-130	30 ± 2	259	0.06	10
anthracene	0.990	0.05-100	27 ± 2	156	0.05	15
fluoranthene	0.987	0.025-100	27 ± 2	167	0.02	8
Pyrene	0.954	0.05-4	43 ± 6	22	0.06	12
benzo(a)anthracene	0.965	0.1-5	12 ± 1	6	0.1	10
chrysene	0.958	0.1-5	9 ± 1	6	0.2	8
benzo(b)fluoranthene	0.968	0.5-5	8 ± 1	4	0.2	6
benzo(k)fluoranthene	0.973	0.5-5	5 ± 0.6	2	0.3	15

[a] Extraction conditions: sampling time, 40 min with stir rate of 800 rpm at 22 ºC; desorption for 5 min at 250 ºC; sample volume, 20 mL without headspace.
[b] Standard deviation of the slope.
[c] Standard deviation of the regression.
[d] Estimated as three times of standard deviation at the lowest concentration on the calibration curve divided by the slope of the calibration curve.
[e] Based on three extractions. The concentrations of the analytes were 6 μg L^{-1} for naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, and fluoranthene, and 3 μg L^{-1} for pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, and benzo(k)fluoranthene.

Table 3.3: Figures of merit of calibration curves for 7 μm PDMS fiber.[a]

Analyte	R	Calibration range μg L^{-1}	Slope ± SD[b]	Error of the estimate[c]	LOD[d] μg L^{-1}	%RSD[e]
naphthalene	0.984	6-500	0.08 ± 0.006	3	6	10
acenaphthylene	0.979	1-1700	0.6 ± 0.04	68	1	9
acenaphthene	0.981	1-1700	1 ± 0.09	142	1	10
fluorene	0.979	1-1700	1 ± 0.1	162	0.5	11
phenanthrene	0.990	1-100	1 ± 0.1	9	0.7	4
anthracene	0.972	1-100	2 ± 0.2	16	0.4	7
fluoranthene	0.994	0.5-100	6 ± 0.3	25	0.3	9
pyrene	0.971	0.1-8	30 ± 3	23	0.1	2
benzo(a)anthracene	0.972	0.1-8	10 ± 0.9	7	0.2	10
chrysene	0.971	0.1-5	15 ± 2	7	0.1	8
benzo(b)fluoranthene	0.991	0.5-4	27 ± 2	5	0.1	14
benzo(k)fluoranthene	0.946	0.5-8	2 ± 0.3	2	0.4	10

[a] Extraction conditions: sampling time, 30 min with stir rate of 800 rpm at 22 ºC; desorption for 5 min at 250 ºC; sample volume, 20 mL without headspace.
[b] Standard deviation of the slope.
[c] Standard deviation of the regression.
[d] Estimated as three times of standard deviation at the lowest concentration on the calibration curve divided by the slope of the calibration curve.
[e] Based on three extractions. The concentrations of the analytes were 6 μg L^{-1} for naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, and fluoranthene, and 3 μg L^{-1} for pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, and benzo(k)fluoranthene.

Table 3.4: Estimated partition coefficients (K_{fs}) of PAHs to three different sorbent coatings.

Analyte		log K_{fs} ± Error				
		poly(VBHDIm^{+}NTf$_2^{-}$) (12 μm)	poly(HDIm^{+}NTf$_2^{-}$) (12 μm)	PDMS (7 um)	PDMS (7 μm, literature)	PDMS (100 μm, literature)
naphthalene	3.35	3.30 ± 0.16	3.34 ± 0.16	3.49 ± 0.29	2.73[c]	3.02,[a] 3.01,[b] 2.85[c]
acenaphthylene	3.27	3.99 ± 0.07	3.87 ± 0.05	3.24 ± 0.27	na	3.40[a]
acenaphthene	3.92	3.92 ± 0.06	3.93 ± 0.04	2.90 ± 0.16	na	3.63,[a]
fluorene	4.18	4.26 ± 0.04	4.13 ± 0.02	3.44 ± 0.22	na	3.71,[a]
phenanthrene	4.52	5.04 ± 0.11	4.67 ± 0.05	3.85 ± 0.05	4.42,[c] 3.25[d]	3.96,[a] 3.40,[c] 3.45[d]
anthracene	4.50	4.85 ± 0.06	4.56 ± 0.07	3.90 ± 0.04	3.97,[c] 3.20[d]	3.98,[a] 4.10,[b] 3.14,[c] 3.46[d]
fluoranthene	5.20	4.50 ± 0.07	4.20 ± 0.05	4.18 ± 0.10	4.38,[c] 3.72[d]	4.71,[a] 4.11,[c] 3.79[d]
pyrene	5.00	4.57 ± 0.08	4.26 ± 0.07	4.38 ± 0.06	4.44,[c] 3.80[d]	4.86,[a] 4.07,[c] 3.82[d]

nd, not determined; na, not available

[a] Ref 46
[b] Ref 47
[c] Ref 48
[d] Ref 41

extracted by the fiber (n_f) was determined based on the linear relation of GC–FID response versus mass of analyte injected onto the chromatographic column. Partition coefficients ($\log K_{fs}$) for the two PILs and PDMS coatings are listed in Table 3.4. To ensure the accuracy of the methods used in this study, a comparison of literature $\log K_{fs}$ values for the same PAHs using 7 and 100 μm PDMS coatings are also included.

The partition coefficients of PAHs to the 7 μm PDMS coating are in reasonably good agreement with those reported in the literature, especially considering that some of the analytes are not under complete equilibrium. The larger errors in the obtained partition coefficients of naphthalene, acenaphthylene, acenaphthene, and fluorene can be ascribed to the low extraction peak areas (which are close to the detection limit of the method) for the 7 μm PDMS sorbent coating. Compared to the PAH-PDMS partition coefficients, the two PIL-based sorbent coatings exhibited larger $\log K_{fs}$ values for acenaphthene, acenaphthylene, fluorene, phenathrene, and anthracene. The results indicate a higher affinity of the PILs towards these PAHs. The impressive selectivity enhancement of the poly(VBHDIm$^+$ NTf_2^-) PIL over the PDMS sorbent coating can be observed by comparing the $\log K_{fs}$ values of acenaphthylene (3.99 versus 3.24), acenaphthene (3.92 versus 2.90), fluorene (4.26 versus 3.44), phenanthrene (5.04 versus 3.85), and anthracene (4.85 versus 3.90). A comparison of $\log K_{fs}$ values for the two PILs reveals that the poly(VBHDIm$^+$ NTf_2^-) PIL exhibits higher affinity towards all PAHs except for naphthalene and acenaphthene, in which similar $\log K_{fs}$ values were obtained.

3.4. Conclusions

The structural tune ability of polymeric ionic liquids was exploited in this study to design a new class of SPME sorbent coatings for the selective extraction of PAHs. The enhanced $\pi - \pi$ interaction imparted to the sorbent coating, in addition to its ultrahydrophobic nature, resulted in increased extraction selectivity of PAHs and long fiber lifetimes. Both of the PIL fibers demonstrated much higher extraction efficiencies towards the PAHs than the commercial PDMS fiber. This preliminary study provides, for the first time, an estimation of partition coefficients for 8 PAHs to PIL-based SPME coatings. The observed results clearly show that the benzyl-functionalized poly(VBHDIm$^+$ NTf$_2^-$) PIL exhibits higher extraction efficiency towards many of the PAHs compared to a similar PIL lacking such functionalization. This work demonstrates that by imparting specific functional groups into the structure of the PIL, the selectivity and extraction efficiency of the SPME sorbent coating can be effectively tuned and manipulated.

Acknowledgements

J.L.A. acknowledges funding from the Analytical and Surface Chemistry Program in the Division of Chemistry and the Separation and Purification Processes Program in the Chemical, Environmental, Bioengineering, and Transport Systems Division from the National Science Foundation for a CAREER grant (CHE-0748612).

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Chapter 4

Role of Counteranions in Polymeric Ionic Liquid-Based Solid-Phase Microextraction Coatings for the Selective Extraction of Polar Compounds

A paper published in *Analytical Chimica Acta*[1]

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Abstract

A polymeric ionic liquid (PIL) poly(1-vinyl-3-hexylimidazolium chloride) (poly(ViHIm^{+}Cl^{-})) was designed as a coating material for solid phase microextraction (SPME) to extract polar compounds including volatile fatty acids (VFAs) and alcohols. The extracted analytes were analyzed by using gas chromatography (GC) coupled with flame ionization detection (FID). Extraction parameters of the HS–SPME–GC–FID method, such as ionic strength, extraction temperature, pH and extraction time were

[1] Reprinted from *Analytical Chimica Acta* 2011, *687*, 141-149.

optimized. Calibration studies were carried out under the optimized conditions to further evaluate the performance of the PIL-based SPME coating. For comparison purposes, the PIL poly(1-vinyl-3-hexylimidazolium bis[(trifluoromethyl)sulfonyl]imide) (poly($ViHIm^+NTf_2^-$)) was also used as the SPME coating to extract the same analytes. The results showed that the poly($ViHIm^+Cl^-$) PIL coating had higher selectivity towards more polar analytes due to the presence of the Cl^- anion which provides higher hydrogen bond basicity than the NTf_2^- anion. The limits of detection (LODs) determined by the designed poly($ViHIm^+Cl^-$) PIL coating ranged from 0.02 μg L^{-1} for octanoic acid and decanoic acid and 7.5 μg L^{-1} for 2-nitrophenol, with precision values (as relative standard deviation) lower than 14%. The observed performance of the poly($ViHIm^+Cl^-$) PIL coating was comparable to previously reported work in which commercial or novel materials were used as SPME coatings. The selectivity of the developed PIL coatings was also evaluated using heptane as the matrix solvent. This work demonstrates that the selectivity of PIL-based SPME coatings can be simply tuned by incorporating different counteranions to the sorbent coating.

4.1. Introduction

Combining pre-concentration and sample preparation into a single step, solid-phase microextraction (SPME) has gained widespread popularity in routine laboratory and industrial applications [1]. The success of SPME lies with its simplicity, solvent-free characteristics, and the ease of coupling to various analytical separation techniques, including gas chromatography (GC), high performance liquid chromatography (HPLC),

capillary electrophoresis (CE), and supercritical fluid chromatography (SFC). This technique is based on the partitioning of target analytes between the sample matrix and a stationary phase coated on the surface of a fiber. The stationary phase coating plays an important role in SPME analysis. The limited number of commercially available SPME coatings has stimulated the development of laboratory-made materials with the goal of increasing the extraction efficiency and selectivity of wider classes of analytes.

It is well known that analysis of polar compounds remains as a challenge due to the strong interactions of these compounds with the aqueous matrix. In many cases, in situ or post fiber- derivatization is employed in order to accelerate the extraction of polar compounds [2,3]. There are two commercial SPME fibers that demonstrate high selectivity towards polar analytes, namely polyacrylate (PA) and carbowax-divinylbenzene (CW-DVB). The sensitivity and selectivity of SPME coatings for the extraction of polar compounds has been a focus of further improvement. Zeng and co-workers developed a calyx(4) open-chain crown ether as the SPME coating (~ 75 μ m film thickness) for the extraction of polar aromatic compounds and fatty acids [4]. Due to the hydrogen bonding and hydrophobic interactions provided by the crown ether moieties, this coating demonstrated higher extraction efficiency than the commercial PA coating. The same group also reported using titania-hydroxyl-terminated silicone materials [5] as SPME coating to extract phenols and aromatic amines, and alumina [6] materials hybridized with silica to fabricate SPME fibers for the extraction of polar compounds such as fatty acids, phenols and alcohols with higher efficiency than commercial sorbent coatings such as polydimethylsiloxane (PDMS), PDMS-divinylbenzene (DVB), and PA. The high extraction efficiency of these coatings

towards polar analytes was attributed to strong donor–acceptor interactions. Cyclodextrin, another important group of macrocycles, was imbedded in the silica-based material to extract phenols [7]. Comparable extraction efficiency for phenolic compounds to those obtained by using a commercial PA fiber was ascribed to the hydrogen bonding interactions between the phenols and the cyclodextrin functionalized coating. Recently, Zeng and co-workers reported the use of methacrylic acid trimethylolpropanetrimethacrylate co-polymers as SPME coatings to extract triazines [8]. Through hydrogen bonding interactions between the co-polymer and the triazines, much higher extraction efficiency was obtained compared to the commercial PDMS-DVB coating. Biajoli and co-workers developed 3-aminopropyltrimethoxysilane/PDMS material as a SPME coating and succeeded in extracting fatty acids [9]. Li and co-workers reported single-walled carbon nanotubes as a SPME coating for the extraction of phenols by using direct immersion SPME–HPLC-UV method [10]. Multiwalled carbon nanotubes combined with nafion as a SPME coating provided higher extraction efficiency of phenols than the PA fiber [11]. Hashemi et al. used 3-[bis(2-hydroxyethyl)amino] propyl-triethoxysilane (HPTES) functionalized nanoporous silica SPME coating (~ 20 μ m thickness) [12]. Wang et al. developed perfluorinated ion doped polyaniline based coating for SPME which was used to extract phenols with high extraction efficiency compared to the PA coating [13]. Electrospun SU-8 coating and the corresponding pyrolyzed coatings also exhibited comparable results for the extraction of phenolic compounds compared with the commercial PA fiber [14].

Room temperature ionic liquids (RTILs) are a class of solvents composed entirely of ions. Compared with molecular-based solvents, ILs possess unique properties such as

negligible vapor pressure, good thermal stability, tunable viscosity and miscibility with water. ILs were revealed to exhibit "dual nature" solvation characteristics when used as gas chromatographic stationary phases [15]. That is, they interact with nonpolar compounds like a nonpolar stationary phase while interacting with polar compounds like a polar stationary phase. ILs can be designed to exhibit high solubility of organic compounds while also being tuned to be water immiscible. Liu et al. first reported the use of ILs to perform microextractions coupled with HPLC [16]. Since then, ILs have been reported to be good extraction media for microextractions [17,18]. The same research group also applied ILs for the first time as SPME coatings coupled with GC [19]. In order to stabilize the IL film on the fused silica glass fiber, Hsieh used nafion to assist the IL coating for SPME extraction [20]. More recently, by using etched fused-silica fiber coated with ILs, Huang et al. were able to enhance extraction efficiency towards PAHs [21]. Thus far, only one example was found in the literature addressing the extraction of polar analytes with the use of ILs [22]. The limited research on the application of ILs in SPME inspired our research group to develop task-specific polymeric ionic liquid (PIL)-based SPME coatings for the extraction of various compounds. Unlike the monomer IL-based SPME coatings, PIL SPME sorbent coatings do not need to be re-coated after every extraction, exhibit long lifetimes as well as provide good reproducibility [23–27].

The advantage of using ILs/PILs as SPME coatings is that the selectivity of these coatings towards the target analytes can be imparted by including different functional groups into the cationic moiety or by introducing different counteranions. It has been reported that ILs paired with chloride counteranions exhibited high hydrogen bond

basicity which offers strong interactions with compounds that possess high hydrogen bond acidity, a feature for polar and hydrogen bond donating compounds [28,29].

The focus of the present study is to exploit the hydrogen bond accepting property of the chloride anion to extract polar analytes including phenols, volatile fatty acids (VFAs), and alcohols. For comparison purposes, a PIL containing the same cation but paired with bis[(trifluoromethyl)sulfonyl]imide (NTf_2^-) anion, known to possess significantly low hydrogen bond basicity, was also used to extract the same analytes. In addition to performing the extraction in an aqueous matrix, heptane was also employed as the extraction solvent to investigate the selectivity of the PIL coatings towards different analytes using headspace extraction.

4.2. Experimental

4.2.1. Chemicals and Reagents

The following chemical standards (purity ≥97%) were obtained from Sigma–Aldrich (Milwaukee, WI, USA): valeric acid, hexanoic acid, heptanoic acid, octanoic acid, decanoic acid, phenol, p-cresol, 2-fluorophenol, 2-nitrophenol, 1-pentanol, 1-hexanol, vinyl imidazole, 2, 2'-azo-bis(isobutyronitrile) (AIBN), and hexyl chloride. Lithium bis[(trifluoromethyl)sulfonyl]imide ($LiNTf_2$) was purchased from SynQuest Labs (Alachua, FL, USA). Sodium chloride, sodium hydroxide, and hydrochloric acid were purchased from Fisher Scientific (Fair Lawn, NJ, USA). HPLC-grade methanol, hexane, acetone, methylene chloride, isopropanol, chloroform, and heptane were also acquired from Fisher Scientific. Ultrapure water was obtained from a Milli-Q water purification

system (Millipore, Bedford, MA, USA) and was used in the preparation of all aqueous solutions.

4.2.2. Preparation of Standards

Analytes were individually dissolved in Milli-Q water with the addition of methanol to prepare standard solutions with concentration values ranging from 1000 to 2000 μg mL^{-1}. A stock solution mixture of 125 μg mL^{-1} including valeric acid, hexanoic acid, heptanoic acid, octanoic acid, decanoic acid, phenol, p-cresol, 2-fluorophenol, 2-nitrophenol, 1-pentanol, and 1-hexanol, was prepared with a methanol content of 25% (v/v). The stock solution was stored at 4 $^{\circ}$C. Working solutions were prepared by spiking a given amount of the stock solution into 10 mL of ultrapure water (with or without NaCl). The methanol content in the working solutions was always lower than 4% (v/v). The pH of the solution was adjusted by using HCl or NaOH. The optimum pH value with working solutions was 4. Standard solutions with a concentration of 4.4 mg mL^{-1} in heptanes were also individually prepared for all analytes. A stock solution mixture of 400 μg mL^{-1} containing valeric acid, hexanoic acid, heptanoic acid, octanoic acid, decanoic acid, phenol, p-cresol, 2-fluorophenol, 2-nitrophenol, 1-pentanol, and 1-hexanol, was prepared in heptane and stored at 4 $^{\circ}$C. Working solutions were prepared by diluting an appropriate amount of the stock solution up to 10 mL of heptane.

4.2.3. Materials

Fused silica capillary (0.10 mm I.D.), and amber glass vials (20 mL) with PTFE/Butyl septa screw caps were purchased from Supelco (Bellefonte, PA, USA). PTFE stir bars

were obtained from Fisher Scientific and were used to perform all extractions at a constant stir rate of 900 rpm using a Corning stir plate (Nagog Park Acton, MA, USA). A 10 μL syringe purchased from Hamilton was used for manual direct liquid injection. The homemade SPME device was constructed by using a previously published procedure [25]. Briefly, a 5 mL syringe purchased from Hamilton (Reno, NV, USA) was reassembled by discarding the stainless steel fiber on the plunger and replacing it with a fused silica capillary by using epoxy glue (GC Electronics, IL, USA). The other end of the capillary was sealed with a microflame torch and the outer polyimide protecting film was removed from 1 cm of the fiber. The bare fiber segment was washed with methanol, acetone, hexane and methylene chloride before coating the PIL-based sorbent coating.

4.2.4. Instrumentation

The analysis was performed with an Agilent 6890 gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID), coupled in series. An injection port containing a 0.75 mm I.D. SPME liner was used in this study. The helium carrier gas was maintained at a constant flow of 2 mL min^{-1}. All separations were performed using a DB-WAXETER (polyethene glycol (PEG)) capillary column (30 m × 0.25 mm I.D. with 0.25 μm film thickness) purchased from Agilent Technologies. Desorption of the fibers into the injection port was carried out in splitless mode at 200 °C for 4 min, opening the split valve after 4 min. The following temperature program was used for the separation of the mixture: initial temperature of 40 °C, which was held for 2 min, then increased to 125 °C at 10 °C min^{-1}, and then raised to 200 °C at 5 °C min^{-1}, being held for 10 min. The

temperatures of both detectors were set at 250 °C. Hydrogen flow was set at 40 mL min^{-1}, and air flow was 450 mL min^{-1}.

All scanning electron micrographs were obtained using a JEOL JSM-6100 (Peabody, MA, USA) scanning electron microscope (SEM). An Accumet AB15 pH meter purchased from Cole-Parmer (Vernon Hills, IL, USA) was used for all pH measurements. Thermal gravimetric analyses (TGA) was carried out using a TA Instruments SDT 2960 Simultaneous TG-DTA (Schaumburg, IL, USA) in the temperature range of 23–450 °C, using nitrogen with a flow rate of 100 mL min^{-1} and a heating rate of 10 °C min^{-1}. The amount of the PIL used for the TGA measurement was 6.9632 mg for the Cl-based PIL and 7.5968 mg for the NTf_2-based PIL.

4.2.5. Synthesis of the PILs and Preparation of the PIL-Based SPME Fibers

The synthesis of the poly(1-vinyl-3-hexylimidazolium chloride) (poly($ViHIm^+Cl^-$)) PIL, the poly(1-vinyl-3-hexylimidazolium bis[(trifluoromethyl)sulfonyl]imide) (poly($ViHIm^+NTf_2^-$)) PIL, and the fabrication procedures of the PIL-based SPME fibers were described previously [25]. The poly($ViHIm^+Cl^-$) PIL was dissolved in chloroform at a ratio of approximately 1:1 (v/v), and the poly($ViHIm^+NTf_2^-$) PIL was diluted with acetone at a ratio of 3:1 (v/v). More dilute PIL solutions were employed in order to obtain thinner coatings. Bare fused silica glass fibers were washed with methanol, hexane, dichloromethane, and acetone and then air dried. They were dipped into the PIL solutions and removed slowly to obtain smooth PIL coatings. The fibers were then air-dried for approximately 10 min before they were withdrawn back into the needle of the SPME device. The film thickness of the PIL coatings was estimated to be

approximately 8 μm for the poly(ViHIm^{+}Cl^{-}) PIL coating and 14 μm for the poly(ViHIm^{+}NTf$_2^{-}$) coating, based on SEM images. The fibers were conditioned in the GC injection port for 5 min at 200 °C prior to performing extractions.

4.2.6. HS–SPME Extraction Procedure

All extractions were performed in the headspace of 20 mL amber vials containing 10 mL of the aqueous solution (with or without NaCl) or heptane working solutions. The volume of the headspace was maintained at 10 mL. The vial was sealed with a screw cap after introducing a magnetic stir bar. Vials were then placed in a water bath with a temperature controlled at 48 ± 2 °C. The solution was stirred at a constant stir rate of 900 rpm for 5 min before the needle of the SPME syringe pierced the septum of the cap. Once the extraction is conducted at a prefixed time, the fiber was removed from the sample vial and immediately inserted into the heated injector of the GC for thermal desorption. Desorption time was optimized to be 4 min at 200 °C. Possible carryover was removed by reinserting the fiber into the GC injection port for another 4 min when the concentrations of the analytes in the vial solution were higher than 10 μg mL^{-1}.

4.2.7. Determination of Enrichment Factors

The enrichment factor (EF) was used to evaluate the preconcentration of the analytes to the PIL coatings, and is defined as the ratio of the chromatographic peak area response for the SPME extraction to that from direct liquid injection [30]. The concentration of the analytes was 1 μg mL^{-1} in 30% (w/v) NaCl aqueous solutions or heptane solutions for both PIL coatings. The SPME extraction time used was 15 min. The direct liquid

injection experiments were carried out by injection of 1 μL of the standard solution in heptanes containing 1 μg mL^{-1} of each analyte using splitless injection mode and the same SPME inlet liner. All GC separation conditions were identical to the SPME experiments. All injections carried out by SPME and by direct liquid injection to calculate EF were performed by triplicate.

4.3. Results and Discussion

4.3.1. Optimization of the HS–SPME Procedure Using Poly(ViHIm$^+$Cl$^-$) PIL Coating

Many variables can affect the extraction efficiency in HS–SPME. The extraction performance of the poly(ViHIm$^+$Cl$^-$) PIL coating was optimized using a factor-by-factor optimization in terms of ionic strength, pH of the aqueous solution, extraction temperature, and extraction time.

The extraction temperature is an important parameter to be optimized in any HS-application. High temperatures favor the tendency of the analytes to occupy the headspace by increasing the Henry constants and diffusion coefficients of the analytes studied. On the other hand, the sorption process on the SPME coating is not favored at high temperatures. Hence, a compromise temperature must be found. Temperature was studied from room-temperature to 60 °C. Higher temperatures were not tried to avoid losses of water in the water bath, and to avoid complication of the sampling device [23]. In the range studied, a temperature of 48 ± 2 °C was found adequate. It is necessary to highlight here that the ultimate purpose of this work was to evaluate the performance of

PIL fibers in HS–SPME as well as its applicability with volatile polar analytes of different nature, rather than to establish a method to characterize the selected analytes at ultratrace levels in waters.

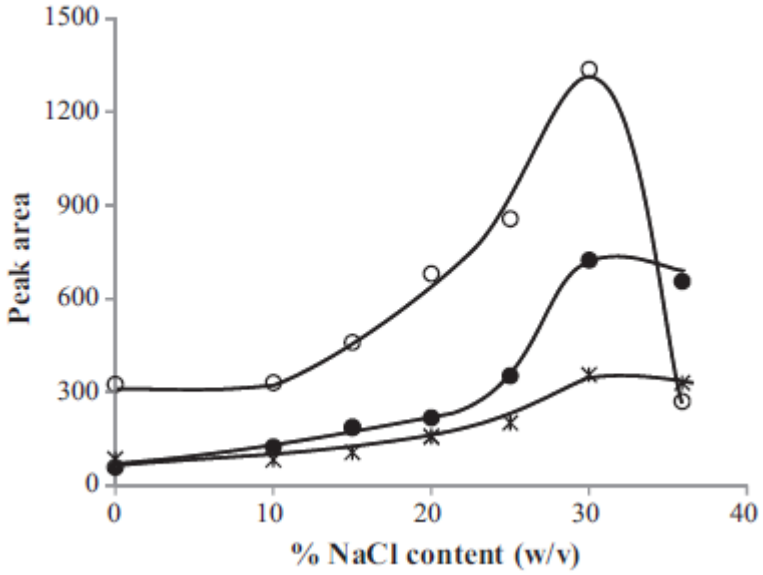

Figure 4-1: Influence of the NaCl content of the aqueous solution on the HS–SPME extraction efficiency for representative analytes: (○) heptanoic acid; (●) 1-hexanol; and (*) phenol. The extractions were carried out using the poly(ViHIm^{+}Cl^{-}) PIL sorbent coating (film thickness: ~8 μm) for 15 min using a concentration of 1 μg m L^{-1} for each analyte, and the rest of experimental conditions as described in Section 4.2.

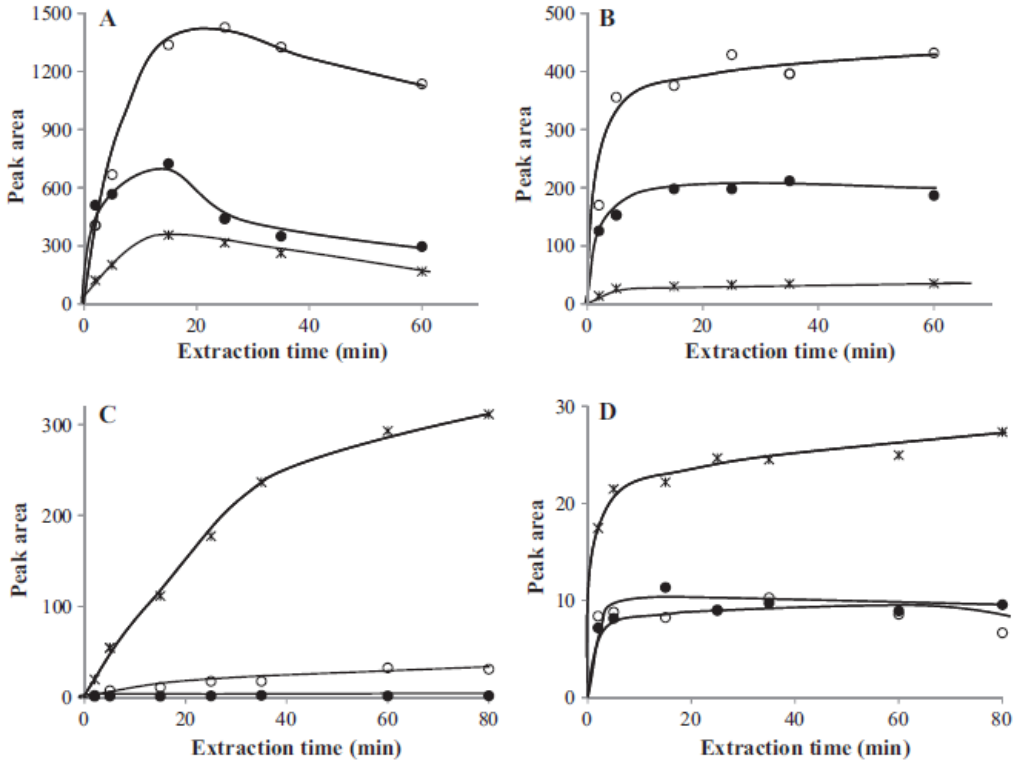

Figure 4-2: Sorption-time profiles using: (A) the poly(ViHIm^{+}Cl^{-}) PIL sorbent coating with aqueous standards; (B) the poly(ViHIm^{+}NTf$_2^{-}$) PIL sorbent coating with aqueous standards; (C) the poly(ViHIm^{+}Cl^{-}) PIL sorbent coating with heptane standards and (D) the poly(ViHIm^{+}NTf$_2^{-}$) PIL sorbent coating with heptane standards, for the following representative analytes: (○) heptanoic acid; (●) 1-hexanol and (*) phenol. The concentration of the analytes was 1 μg mL^{-1}, and the rest of conditions as described in Section 4.2.

Generally, due to the large negative Gibbs energy of hydration, the presence of kosmotropic salts in aqueous solutions can promote competition for analyte hydration and thus decrease the solubility of more hydrophobic analytes [31]. In this study, sodium chloride was employed to decrease the solubility of the analytes in the aqueous solution

and so to favor an increased equilibrium concentration in the headspace. The dependence of the headspace solid-phase microextraction with the concentration of NaCl from 0 to 36% (w/v) is shown in Fig. 4-1 for several analytes (as examples). The extraction efficiency is expressed as extraction peak area. It can be observed from the figure that there is increasing extraction efficiency with the NaCl content up to a value of 30% (w/v). Further increases in the salt concentration resulted in a decrease in the amount of analyte extracted for all analytes examined in this study. Based on this result, an ionic strength value of 30% (w/v) of NaCl was used for further experiments.

The pH of the aqueous solution is another important parameter in SPME when the analytes to be extracted are in ionic form. Given the fact that only the neutral species are going to be present in the headspace to be efficiently extracted by the SPME coating, it is necessary to adjust the pH of the solution to ensure the neutral form of the analytes studied. The differences in the pK_a values of the studied analytes can be observed in Table 4.1. Several experiments were carried out at different pH values, using aqueous solutions containing 30% (w/v) NaCl. This data is shown in Supplemental information. The utilization of lower pH values favored analytes such as octanoic acid and decanoic acid. Nevertheless, a pH value of 4 was found as the most acceptable one in order to reach adequate efficiencies for the overall group of analytes. It must be commented that a pH value of 1 was more efficient for all analytes studied when utilizing deionized water samples. However, the utilization of pH 1 and 30% (w/v) NaCl content was not efficient for alcohols (including phenols) if compared to the selected pH value of 4 (and NaCl content of 30%). This effect could be linked to the fact that the presence of more acidic species (like HCl) can compete with the analytes for the hydrogen bonding sites on the

PIL fiber. The effect is more pronounced in the case of the phenol and alcohols which have very weak hydrogen bond acidity compared to VFAs.

Sorption-time profiles of all analytes using the poly($ViHIm^+Cl^-$) PIL SPME coating were constructed by performing extractions in 30% (w/v) NaCl solutions at pH 4 and 48 ± 2 °C at various time intervals. Some of the obtained profiles are shown in Fig. 4-2(A). The extraction reached equilibrium after approximately 15 min for most VFAs. Decanoic acid was an exception; it did not reach equilibration even after an extraction time of 60 min. Alcohols, including phenols, reached equilibrium in approximately 15 min, while the efficiency decreased and leveled off at sampling times longer than 15 min. Based on the sorption-time profiles, 15 min was chosen as an adequate extraction time for the studied analytes and the poly($ViHIm^+Cl^-$) PIL SPME coating.

For comparative purposes, sorption-time profiles were also obtained for the poly($ViHIm^+NTf_2^-$) PIL SPME coating, under the same extraction conditions. Some of them are shown in Fig. 4-2(B). The obtained profiles show that all analytes reach equilibration at around 15 min, with the exception of decanoic acid, whose equilibrium time was longer than 60 min. These results are totally in agreement with the ones obtained using the poly($ViHIm^+Cl^-$) PIL SPME coating.

Considering all profiles obtained for all analytes, the superior performance of the poly($ViHIm^+Cl^-$) PIL SPME coating is clear compared to the poly($ViHIm^+NTf_2^-$) PIL SPME coating (see examples in Fig. 4-2(A) and (B)), in terms of higher peak-areas. The comparison here is only qualitative, as only one spiked concentration is used in the profiles (1 μ g mL^{-1}).

4.3.2. Enrichment Factors Obtained with the PIL Coatings

Given the fact that SPME is not an exhaustive extraction method, the calculation of the enrichment factor (E_F), defined in Section 4.2.7, is a useful tool to evaluate the extraction performance. A comparison of the E_F values obtained for the studied analytes using the poly(ViHIm$^+$Cl$^-$) PIL and the poly(ViHIm$^+$NTf$_2^-$) PIL sorbent coatings under the optimized conditions is shown in Fig. 4-3. It can be observed that the poly(ViHIm$^+$Cl$^-$) PIL sorbent coating exhibited much higher E_F values towards all VFAs, 2-fluorophenol, phenol, and p-cresol than the poly(ViHIm$^+$NTf$_2^-$) PIL coating. The enrichment factors obtained for 1-pentanol, 1-hexanol, and 2-nitrophenol were similar with both PIL coatings. E_F values oscillated from 2.4 to 176 for the poly(ViHIm$^+$Cl$^-$) PIL coating, and from 0.6 to 109 for the poly(ViHIm$^+$NTf$_2^-$) PIL coating. Xu et al. utilized a hydrofluoric acid etched stainless steel wire for HS–SPME obtaining an E_F value (calculated with the same approach) of 220 ± 3 for octanol, using an extraction time of 30 min, whereas phenol and butanol could not be extracted [30].

To better understand the extraction behavior of the studied analytes with the two PIL sorbent coatings, various physical properties of the analytes including pK_a, vapor pressure, and octanol/water partition coefficient (log $K_{o/w}$) should be considered. These properties are listed in Table 4.1. It is necessary to point out that the two PILs exhibit similar dispersive interactions, but the poly(ViHIm$^+$Cl$^-$) PIL possesses higher hydrogen bond basicity character [29]. The low pK_a values for VFAs indicates strong hydrogen bond acidity and thus they are capable of forming hydrogen bonds with the poly(ViHIm$^+$Cl$^-$) PIL coating containing the hydrogen bond basic Cl$^-$ anion. As a result, these VFAs were extracted more favorably by the poly(ViHIm$^+$Cl$^-$) PIL sorbent coating

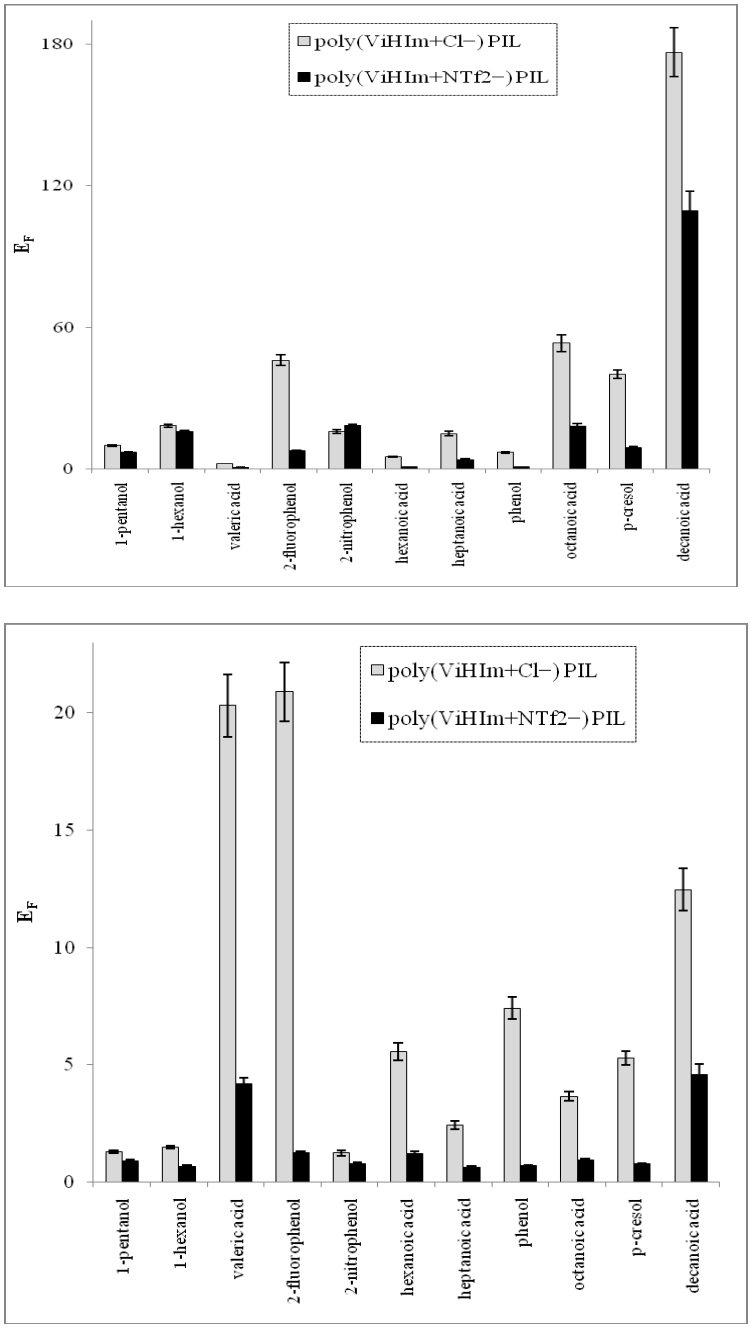

Figure 4-3: Enrichment factor values obtained for the studied analytes using both PIL coatings with (A) aqueous standards and (B) heptane standards. The concentration of analytes was 1 μ g mL^{-1}, and the rest of conditions as described in Section 4.2.

compared to the poly(ViHIm$^+$NTf$_2^-$) PIL sorbent coating, which contains the weak hydrogen bond basic NTf$_2^-$ anion [29]. The same rationale seems to apply in the extraction of phenols containing low pK$_a$ values including 2-fluorophenol, phenol, and p-cresol. However, an exception was observed for 2-nitrophenol which possesses the lowest pK$_a$ value among the phenols studied. Instead of showing higher affinity to the poly(ViHIm$^+$Cl$^-$) PIL sorbent coating, it was extracted with a similar E_F by both PIL sorbent coatings, even slightly higher for the poly(ViHIm$^+$NTf$_2^-$) PIL coating. Studies on intramolecular interactions for 2-nitrophenol carried out by Kovács et al. showed evidence of strong intramolecular hydrogen bonds between the nitro and hydroxyl functional groups [32]. Taking into account the strong intramolecular hydrogen bond, the hydrogen is bonded by the –NO$_2$ group perhaps rendering it less available to interact with the poly(ViHIm$^+$Cl$^-$) PIL coating. As a result, it appears that 2-nitrophenol was extracted more like a nonpolar analyte by interacting with the PIL sorbent coatings primarily through dispersive interactions and, therefore, similar EF values were obtained by the two PIL coatings. The intramolecular hydrogen bond does exist in 2-fluorophenol but it is much weaker than 2-nitrophenol [33]. Therefore, this compound was still able to be favorably extracted by the poly(ViHIm$^+$Cl$^-$) PIL through hydrogen bonding interactions. Due to the high pK$_a$ values of 1-pentanol and 1-hexanol, the predominant interactions of these compounds with the PIL coatings are via dispersive interactions. Thus, similar E_F values were obtained for both PIL coatings.

4.3.3. Analytical Performance of PIL Coatings

Calibration curves were generated for the poly($ViHIm^+Cl^-$) PIL and poly($ViHIm^+NTf_2^-$) PIL coatings at the above optimized conditions: 48 ± 2 °C, 30% (w/v)

Table 4.1: Physical properties of the analytes studied.

Analyte	pK_a (error)[1]	Vapor pressure at 25 ºC (Torr)[1]	Log $K_{o/w}$ (error)[1]
2-nitrophenol	7.14 (0.14)	$9.87 \cdot 10^{-2}$	1.671 (0.208)
2-fluorophenol	8.71 (0.10)	2.86	1.822 (0.288)
phenol	9.86 (0.13)	0.614	1.540 (0.185)
p-cresol	10.21 (0.13)	0.211	2.066 (0.192)
1-pentanol	15.24 (0.10)	2.81	1.348 (0.176)
1-hexanol	15.37 (0.10)	0.947	1.858 (0.177)
valeric acid	4.78 (0.20)	0.452	1.207 (0.184)
hexanoic acid	4.78 (0.10)	0.158	1.716 (0.184)
heptanoic acid	4.78 (0.10)	$5.78 \cdot 10^{-2}$	2.226 (0.184)
octanoic acid	4.78 (0.10)	$2.20 \cdot 10^{-2}$	2.735 (0.184)
decanoic acid	4.79 (0.10)	$3.55 \cdot 10^{-3}$	3.754 (0.185)

[1]Data obtained from SciFinder Scholar 2007

NaCl content, pH value of 4, and an extraction time of 15 min. The figures of merit of the calibration curves generated using the two PIL coatings are listed in Tables 4.2 and 4.3.

For the poly($ViHIm^+Cl^-$) PIL coating, calibrations exhibited a linear range with correlation coefficients (R) ranging from 0.993 to 0.998. Precision values (as relative standard deviation (RSD)) oscillated between 3.5 and 15%. Limits of detection (LODs) were calculated measuring by triplicate an aqueous standard spiked at the lowest level of the calibration range. The obtained LODs ranged from 0.02 μg L^{-1} for octanoic and

decanoic acid to 7.5 μg L^{-1} for 2-nitrophenol. It is worth mentioning that the obtained LOD for phenol was 2.1 μg L^{-1}. These LODs demonstrated that the performance of the poly(ViHIm$^+$Cl$^-$) PIL coating was quite comparable with the commercial polyacrylate (PA) SPME coating, in which the literature LODs for phenol and 2-nitrophenol were reported to be 30 μg L^{-1} and 11 μg L^{-1}, respectively, using a SPME–GC–FID approach with 40 min for the extraction time [34]. It is also important to highlight the differences in film thickness between the two coatings: 95 μm for the PA coating and 8 μm for the poly(ViHIm$^+$Cl$^-$) PIL coating. It is well-known that higher coating thicknesses in SPME are accompanied by higher extraction efficiencies. A poly(dimethylsiloxane)/β-cyclodextrin sorbent used in a HS–SPME–GC–FID approach, with 40 min for the extraction time, also reported comparable LOD values, being 2 μg L^{-1} for phenol and 13 μgL^{-1} for 2-nitrophenol [7]. Another work which utilized amino ethyl-functionalized nanoporous silica as a fiber sorbent (~ 20 μm) in a HS–SPME–GC–MS approach, with 12 min for the extraction time at 44 °C, reported limits of detection of 13 μg L^{-1} for phenol and 0.9 μg L^{-1} for 2-nitrophenol [12]. The performance of the poly(ViHIm$^+$Cl$^-$) PIL coating was also comparable to that of the calyx(4) open-chain crown ether-based SPME coatings [4]. In that case, the 75 μm fiber exhibited LOD values for valeric acid, hexanoic acid, heptanoic acid, octanoic acid, and decanoic acid of 0.2, 0.4, 0.1, 0.03, and 0.03 μg L^{-1}, respectively, using 30 min for the extraction time and 60 °C for the extraction temperature, in a HS–SPME–GC–FID approach.

Table 4.2: Figures of merit of calibration curves for the poly(ViHIm^{+}Cl^{-}) PIL sorbent coating under the optimized conditions described in the text.

Analyte	R	Calibration range (μg L^{-1})	(Slope ± SD[a])×10^3	Error of the estimate[b]	LOD[c] (μg L^{-1})	RSD[d] (%)
2-nitrophenol	0.995	25-7000	20.8 ± 0.6	4.61	7.5	12
2-fluorophenol	0.995	3.0-7000	90.9 ± 2.1	17.9	0.9	10
phenol	0.997	7.0-7000	61 ± 1	10.6	2.1	13
p-cresol	0.993	10-9000	216 ± 7	74.0	3.0	7.5
1-pentanol	0.998	16-9000	5.0 ± 0.1	0.98	4.8	4.6
1-hexanol	0.995	7.0-7000	28.9 ± 0.8	6.10	2.1	14
valeric acid	0.997	200-9000	27.8 ± 0.7	5.14	6.0	12
hexanoic acid	0.996	3.0-7000	173 ± 4	31.2	0.9	15
heptanoic acid	0.995	1.0-9000	685 ± 15	173	0.3	14
octanoic acid	0.995	0.08-9000	1971 ± 43	503	0.02	8.9
decanoic acid	0.997	0.08-5000	3231 ± 55	350	0.02	3.5

[a] Error of the slope. [b] Standard deviation of the regression. [c] LODs were calculated as three times the standard deviation of an aqueous standard spiked at the lowest value of the calibration range, and subjected to the optimized HS–SPME procedure by triplicate.
[d] Precision calculated by triplicate with an aqueous standard of 0.6 μ g mL^{-1} for each analyte.

Table 4.3: Figures of merit of calibration curves for the poly($ViHIm^+NTf_2^-$) PIL sorbent coating under the optimized conditions described in the text.

Analyte	R	Calibration range ($\mu g\ L^{-1}$)	(Slope ± SD[a]) $\times 10^3$	Error of the estimate[b]	LOD[c] ($\mu g\ L^{-1}$)	RSD[d] (%)
2-nitrophenol	0.998	3.0-20000	106 ± 1	35.8	0.9	8.4
2-fluorophenol	0.999	3.0-17000	48.0 ± 0.5	11.8	0.9	2.4
phenol	0.996	25-17000	21.9 ± 0.4	10.7	7.5	6.0
p-cresol	0.997	15-17000	77.5 ± 2.0	40.0	4.5	13
1-pentanol	0.998	5.0-20000	61.2 ± 0.7	22.4	1.5	13
1-hexanol	0.999	3.0-20000	249 ± 2	40.6	0.9	12
valeric acid	0.998	15-17000	23.7 ± 0.3	8.19	4.5	11
hexanoic acid	0.998	3.0-20000	112 ± 1	34.9	0.9	6.9
heptanoic acid	0.998	1.0-17000	428 ± 5	130	0.3	5.7
octanoic acid	0.996	1.0-17000	1426 ± 24	633	0.3	6.4
decanoic acid	0.991	0.5-400	940 ± 44	18.7	0.2	11

[a]Error of the slope. [b]Standard deviation of the regression. [c]LODs were calculated as three times the standard deviation of an aqueous standard spiked at the lowest value of the calibration range, and subjected to the optimized HS-SPME procedure by triplicate. [d]Precision calculated by triplicate with an aqueous standard of 1 $\mu g\ mL^{-1}$ for each analyte.

Table 4.4: Several figures of merit of the calibration curves obtained for both PIL sorbent coatings with standards in heptane.

	poly(ViHIm^{+}Cl^{-}) PIL sorbent coating (film thickness: ~8 μm)			poly(ViHIm^{+}NTf$_2^{-}$) PIL sorbent coating (film thickness: ~14 μm)		
Analyte	R	(Slope ± SD[a])·10^{-3}	RSD[b] (%)	R	(Slope ± SD[a])·10^{-3}	RSD[b] (%)
2-nitrophenol	0.997	0.45 ± 0.01	6.3	0.995	1.02 ± 0.04	16
2-fluorophenol	0.994	78.6 ± 1.9	15	0.996	14.6 ± 0.4	7.7
phenol	0.997	225 ± 4	7.8	0.996	27.5 ± 0.6	5.4
p-cresol	0.996	79.6 ± 1.8	6.5	0.996	13.5 ± 0.3	5.3
1-pentanol	0.997	2.08 ± 0.05	12	0.997	13.7 ± 0.3	7.1
1-hexanol	0.994	1.47 ± 0.05	5.3	0.994	10.9 ± 0.3	17
valeric acid	0.995	76.9 ± 2.3	13	0.996	21.6 ± 0.5	2.7
hexanoic acid	0.992	28.2 ± 1.3	8.3	0.994	10.6 ± 0.3	8.7
heptanoic acid	0.990	22.0 ± 1.2	8.0	0.994	5.01 ± 0.18	7.1
octanoic acid	0.993	7.66 ± 0.26	14	0.997	4.61 ± 0.10	13
decanoic acid	0.992	2.22 ± 0.08	8.8	0.994	0.90 ± 0.04	9.8

[a]Standard deviation of the slope.
[b]Precision calculated by triplicate with an aqueous standard of 5 μg mL^{-1} for each analyte

The linear range for phenol and 2-nitrophenol determined by the poly(ViHIm^{+}Cl^{-}) PIL coating was three and two orders of magnitude which was comparable with the ones obtained with the commercial PA fiber [34], whose linear range for phenol and 2-nitrophenol was reported to be 2 orders of magnitudes. The linear ranges of the VFAs (except for valeric acid) for the PIL were also comparable with or even better than the calyx(4) open-chain crown ether coating [4], whose linear range was reported to be three orders of magnitude for these same acids.

Considering the studied analytes, the use of the poly(ViHIm^{+}Cl^{-}) PIL coating showed higher sensitivities for VFAs, and increased with the increase of log $K_{o/w}$ values within the same class of compounds. The same trend was observed for the sensitivities of both the alcohols and phenols, with the exception of 2-nitrophenol.

Calibrations obtained with the poly(ViHIm^{+}NTf$_2^{-}$) PIL sorbent coating presented correlation coefficients (R) varying from 0.991 to 0.999, and precision values (as RSD) ranging from 2.4% to 13%. The limits of detection varied from 0.2 μ g L^{-1} for decanoic acid to 7.5 μ g L^{-1} for phenol. In this sense, it can be observed that the LOD values increased with the increase of the log $K_{o/w}$ value among the same class of compounds in aqueous solutions. Compared to the poly(ViHIm^{+}Cl^{-}) PIL coating, lower limits of detection for 1-pentanol, 1-hexanol, valeric acid and 2-nitrophenol were obtained by the poly(ViHIm^{+}NTf$_2^{-}$) PIL. However, for the rest of the analytes studied, the poly(ViHIm^{+}Cl^{-}) PIL coating exhibited lower LODs for phenol, p-cresol, octanoic acid, and decanoic acid, and similar LODs values for 2-fluorophenol, hexanoic acid, and heptanoic acid in aqueous solutions. The sensitivity, which can be also evaluated by the calibration slope, also points out the superior performance of the poly(ViHIm^{+}Cl^{-}) PIL

coating, with higher slopes for 2-fluorophenols, phenol, p-cresol, and all VFAs. Even though the poly(ViHIm$^+$Cl$^-$) PIL coating was thinner (8 μm compared to 14 μm), it was still superior to the poly(ViHIm$^+$NTf$_2^-$) PIL coating for the extraction of analytes with higher hydrogen bond acidity. Nevertheless, it should be also noted that the performance of the poly(ViHIm$^+$NTf$_2^-$) PIL coating is also comparable to that of commercial SPME fibers or of new developed fibers [4,7,12,34] for the studied group of volatile analytes.

4.3.4. Impact of Heptane as Solvent on the Sorption of the Poly(ViHIm$^+$Cl$^-$) and Poly(ViHIm$^+$NTf$_2^-$) PIL Coatings

In order to further understand the selectivity features of the two PIL sorbent coatings, heptane was used instead of water as the matrix solvent for headspace SPME experiments. Heptane was used because of its nonpolar and aprotic characteristics, which largely eliminate the solvent competition for hydrogen bonding sites on the PIL coating (compared to that of water). Thus, more hydrogen bonding interactions between the PIL coating and the analytes should be expected.

Sorption-time profiles were obtained for both fibers using heptanes as the matrix solvent. Several examples are shown in Fig. 4-2C and D. Analytes such as 1-pentanol, 1-hexanol, or 2-fluorophenol reached equilibration in less than 30 min with the poly(ViHIm$^+$Cl$^-$) PIL sorbent coating. The rest of analytes required an equilibration time of 50 min. In the case of the poly(ViHIm$^+$NTf$_2^-$) PIL coating, nearly all of the analytes reached equilibrium around 20 min except for valeric acid, which took approximately 60 min.

The comparison of E_F values between the two PIL coatings in heptane solution is shown in Fig. 4-3(B). Compared to aqueous solutions, the E_F values decreased dramatically for almost all of the analytes investigated. The only exception was valeric acid, which was extracted more efficiently in heptane than in aqueous solutions by both PIL coatings, and mainly by the poly(ViHIm$^+$Cl$^-$) PIL coating. The enhanced E_F values for valeric acid in heptane may be due to its low log $K_{o/w}$ and high pK_a value which renders this acid to be retained less by heptane molecules but adhered more strongly by water molecules. As a result, the equilibrium concentration of valeric acid in the headspace was higher in heptane than in aqueous solutions.

As is the case with aqueous solutions and due to stronger hydrogen bonding interactions, the VFAs, 2-fluorophenol, phenol, and p-cresol were extracted more efficiently by the poly(ViHIm$^+$Cl$^-$) PIL coating compared to the poly(ViHIm$^+$NTf$_2^-$) PIL sorbent coating. This can be observed in Fig. 4-3(B). For 2-nitrophenol, 1-pentanol, and 1-hexanol, no remarkable difference in the E_F values was observed for the two PIL fibers, probably due to the weaker hydrogen bonding interactions of these compounds with the poly(ViHIm$^+$Cl$^-$) PIL coating. In spite of the small differences, the E_F values were always slightly higher for the poly(ViHIm$^+$Cl$^-$) PIL coating. It can be argued that when the solvent was changed from water to heptane, the difference in E_F values between the two PIL sorbent coatings for the analytes capable of forming relatively strong hydrogen bonds was enhanced. For example, the E_F value of 2-fluorophenol obtained by the poly(ViHIm$^+$Cl$^-$) PIL coating was approximately sixteen-fold of that obtained by the poly(ViHIm$^+$NTf$_2^-$) PIL sorbent coating in heptane solutions, while in aqueous solutions, the E_F value of the former PIL was approximately five-fold of that for the latter PIL

coating. In the case of phenol and p-cresol, the E_F values obtained by the poly($ViHIm^+Cl^-$) PIL coating were nearly ten- and six-times of that achieved by the poly($ViHIm^+NTf_2^-$) PIL sorbent coating in heptane solutions, while in aqueous solutions the difference was only two-fold for both analytes. The observed enhancement in the E_F values between the two PIL coatings in heptane solutions provides an additional evidence that hydrogen bonding interactions play an important role in the high affinity of the poly($ViHIm^+Cl^-$) PIL coating towards these polar analytes.

Calibrations curves were also obtained with both PIL coatings using heptane as matrix solvent. Several figures of merit of such calibrations are included in Table 4.4, only to highlight the sensitivity comparison among the fibers. The calibrations were not constructed with any particular application in mind. It can be observed that the sensitivity (evaluated by the calibration slope) decreased with the increasing value of the log $K_{o/w}$ within the same class of compounds. This trend was consistent with previous discussions in that the more hydrophobic analytes (with high log $K_{o/w}$ values) resulted in higher concentrations in the headspace when using water as the solvent matrix (and so the more hydrophobic analytes exhibited higher sensitivity). Once the solvent was changed to heptane, however, the analytes possessing higher hydrophobicities were retained more strongly by heptane. Therefore, the concentrations of the analytes in the headspace decreased, resulting in a decrease in the sensitivities The sensitivities in heptane were lower for most of the analytes than those in aqueous solutions, with the exception for phenol and valeric acid whose sensitivities increased compared to those in aqueous solutions (mainly when compared to the poly($ViHIm^+Cl^-$) PIL coating).

4.3.5. Stability of the PIL Coatings

PIL-based coatings containing the NTf_2^- anion have previously been shown to exhibit reasonably long lifetimes [23–27]. The poly(ViHIm$^+$Cl$^-$) PIL coating could be used approximately 30–40 times under the conditions of this work without significant loss of extraction efficiency. The lifetime of the poly(ViHIm$^+$Cl$^-$) PIL fiber was shorter than the NTf_2-based PILs, which can be explained by the role of the chloride anion. The chloride-based ILs are inherently less thermally stable or more volatile than ILs paired with the NTf_2^- anions [29,35]. As a result, the desorption temperature for the poly(ViHIm$^+$Cl$^-$) PIL coating had to be lowered in order to increase the fiber lifetime. Thermal stability of both poly(ViHIm$^+$Cl$^-$) and poly(ViHIm$^+$NTf$_2^-$) PIL were examined using thermogravimetric analysis (TGA) and the results are shown in Fig. 4-4. For poly(ViHIm$^+$Cl$^-$) PIL, the starting point of decomposition or volatilization (T_{onset}) was approximately 230 $^\circ$C with weight loss of approximately 3%, while the poly(ViHIm$^+$NTf$_2^-$) PIL started to decompose or volatilize at approximately 350 $^\circ$C (T_{onset}) without any weight loss. Based on these results, the desorption temperature was set at 200 $^\circ$C in order to maintain reasonable lifetime of the poly(ViHIm$^+$Cl$^-$) PIL fiber.

In addition, unlike the NTf_2^--based PIL, the chloride-based PILs suffer from swelling through absorption of water, especially when working at elevated temperatures. Therefore, the coating can be easily stripped from the fused silica support. To avoid damage of the sorbent coating by the needle wall when the fiber was withdrawn back and forth, a thinner coating was employed.

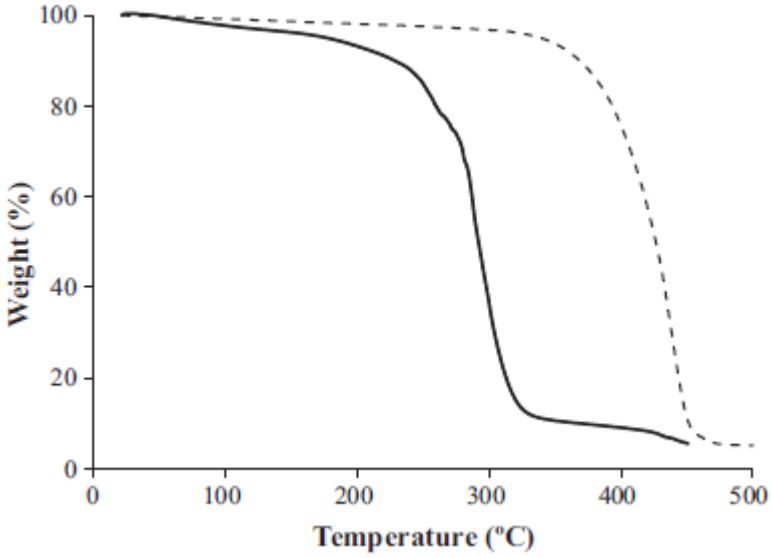

Figure 4-4: Thermal gravimetric analysis (TGA) results for the poly($ViHIm^+Cl^-$) PIL (—) and poly($ViHIm^+NTf_2^-$) PIL (– – –).

4.4. Conclusions

The polymeric ionic liquids poly($ViHIm^+Cl^-$) and poly($ViHIm^+NTf_2^-$) have been used as SPME coating materials to extract polar analytes. The PIL coating designed to have Cl^- anion possessed high hydrogen bond basicity and was able to undergo hydrogen bonding interactions with the polar analytes. This was further evidenced using heptane as solvent matrix instead of water. Polar compounds could be extracted with higher efficiency and selectivity with poly($ViHIm^+Cl^-$) compared to the PIL containing the same cation but paired with the NTf_2^- anion possessing weak hydrogen bond basicity.

The extraction conditions using the poly($ViHIm^+Cl^-$) PIL coating were optimized, and the calibration studies were carried out under such optimized conditions. The quality

parameters of the method presented detection limits ranging from 0.02 to 7.5 μ g L^{-1}, and precision values oscillating from 3.5 to 14% (as RSD). The performance of the PIL coatings was comparable to commercial fibers for the same group of analytes. This work demonstrates that the selectivity of PIL-based SPME coatings can be simply tuned by varying the anion in the sorbent coating. The results from this work suggest that if a PIL can be tailor-synthesized to incorporate a specific composition of two (or more) different anions, the extraction selectivity for various analytes can be varied significantly.

Acknowledgements

J.L.A. acknowledges funding from the Analytical and Surface Chemistry Program in the Division of Chemistry and the Separation and Purification Processes Program in the Chemical, Environmental, Bioengineering, and Transport Systems Division from the National Science Foundation for a CAREER grant (CHE-0748612). V.P. thanks the Spanish Ministry of Innovation and Science (MICINN) for theRamóny Cajal contract with the University of La Laguna (ULL).

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Chapter 5

Sorbent Coatings Based on Polymeric Ionic Liquids for the Analysis of Benzene, Toluene, Ethylbenzene, Xylenes, and Polycyclic Aromatic Hydrocarbons Using Solid-Phase Microextraction

A paper submitted to *Chromatographia*

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Abstract

The polymeric ionic liquid (PIL) poly(1-vinyl-3-hexadecylimidazolium bis[(trifluoromethyl)sulfonyl]imide) was employed as a sorbent coating for solid-phase microextraction (SPME) in the extraction of mono- and polycyclic aromatic hydrocarbons from aqueous solutions using a direct-immersion SPME-GC method. Parameters affecting the extraction efficiency of the analytes including stir rate and extraction time were optimized. Calibration curve linearity of three to four orders of

magnitude was obtained with the PIL-based coating with correlation coefficients better than 0.990. Detection limits for the studied analytes ranged from 60 to 140 ng L^{-1} for polycyclic aromatic hydrocarbons and 0.4-12.8 μg L^{-1} for monoaromatic hydrocarbons with precision lower than 14.6%. Compared to the commercial PDMS fiber with similar film thickness, the PIL sorbent coating provided much higher extraction efficiency, higher sensitivity, wider linear range and lower detection limits for all studied analytes. The performance of the PIL sorbent coating was also evaluated by analyzing water samples. The recoveries for the 15 analytes were found to be in the range of 75-120% for creek water, 72-116% for river water, and 75-120% for tap water.

Keywords: polymeric ionic liquid; solid-phase microextraction; polycyclic aromatic hydrocarbons; gas chromatography; environmental analysis

5.1. Introduction

Pioneered by Pawliszyn and coworkers, solid-phase microextraction (SPME) has gained popularity in the analysis of aqueous, solid and gaseous samples while avoiding the use of organic solvent. SPME can also be coupled to various analytical techniques such as gas chromatography (GC) [1], high performance liquid chromatography (HPLC) [2,3], capillary electrophoresis (CE) [4], and supercritical fluid chromatography (SFC) [5]. Since its introduction in the early 1990s, SPME has been successfully applied in the analysis of samples of environmental interest [6], food [7,8], and pharmaceuticals [9,10]. The general configuration of SPME is a fused glass fiber or stainless steel wire coated with a specially designed material and housed in a syringe-like device to protect the fiber

and sorbent coating material. The mechanism of extraction is based on the partitioning of analytes into the extraction phase. Because of its miniaturized configuration and non-exhaustive extraction properties, SPME can also be exploited to perform *in vivo* analysis [11]. Compared to conventional extraction methods, SPME is often capable of providing higher sensitivity and selectivity. SPME can be operated by direct immersion or headspace sampling modes. Due to the larger analyte diffusion coefficients in gaseous samples, headspace SPME (HS-SPME) provides faster sampling than direct-immersion SPME (DI-SPME), but its application is limited to analytes with sufficient vapor pressures. For analytes that possess lower vapor pressures, DI-SPME is often able to provide lower detection limits and, higher sensitivity than HS-SPME. Therefore, the application scope for DI-SPME is much larger than HS-SPME. However, DI-SPME requires that the coating material be tolerant of the sample matrix.

Ionic liquids (ILs) are a class of compounds that consist of organic cations with various anions. The unique properties of ILs include high viscosity, tunable solvent miscibility, broad liquid range, high thermal stability, negligible volatility, and good wetting ability on fused silica capillaries. Extensive investigations have explored the use of ILs in separation science including GC stationary phases [12,13], liquid-liquid microextraction (LLME) [14,15], and solid-phase extraction (SPE) [16]. The remarkable advantage of using ILs as separation media lies in the ease of derivatization, making them tunable in selectively separating target analytes [17,18]. Several research groups have described the use of ILs as sorbent coatings for SPME [19,20]. Their results indicated that the extraction efficiency of IL-based SPME coatings were comparable and sometimes superior to commercial coating materials. However, these fibers require that the sorbent

coating be re-coated after every extraction, thereby reducing its overall convenience and limiting the method's reproducibility. Our group has described SPME absorbent coatings based on polymeric ionic liquids (PILs) [21]. Due to their high thermal stability and high viscosity, PIL–based materials produce coatings that can be used up to and over 100 extractions (depending on the extraction conditions) when coupled with gas chromatography (GC) [21,22]. In addition, the fibers exhibit exceptional extraction-to-extraction reproducibility. The selectivity of PIL-based coatings can be modulated by introducing functional groups to the cationic portion of the PIL or by incorporating different anions into the polymer.

Monoaromatic hydrocarbons (MAHs), namely benzene and its alkyl derivatives including toluene, ethylbenzene and xylenes (BTEX) and polyaromatic hydrocarbons (PAHs) are known as ubiquitous contaminants. They are fuel components and commonly found in contaminated waters. They are considered as priority pollutants by the U.S. Environmental Protection Agency (EPA) due to their carcinogenic effect on humans [23]. Recent studies have found a positive association between the PAH-DNA adduct and breast cancer incidence [24,25]. Consequently, the development of a fast, reproducible, and highly selective and sensitive analytical method for the determination of these compounds is greatly needed. Due to the non-polar properties of MAHs and PAHs, the PDMS fiber has been found to be a suitable SPME sorbent coating for the extraction of these analytes [26]. In this paper, the poly(ViHDIm$^+$ NTf_2^-) PIL-based SPME coating was used in direct-immersion SPME to extract several MAHs and PAHs from aqueous solutions. The results were compared with those obtained using the commercial PDMS fiber. The versatility and analytical performance of the PIL-based SPME coating was

evaluated through the analysis of real water samples.

5.2. Experimental

5.2.1 Reagents

HPLC-grade acetonitrile was purchased from Fisher Scientific (Fair Lawn, NJ, USA). Deionized water was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA) and was used to prepare all working solutions. The analytes examined in this study include benzene, toluene, ethyl benzene, m-xylene, p-xylene, o-xylene (BTEX), naphthalene, fluorene, phenanthrene, biphenyl, anthracene, acenaphthene, acetophenone, and nitrobenzene supplied by Sigma-Aldrich (St. Louis, MO, USA), and ethyl benzoate from J. T. Baker (Philipsburg, NJ, USA). These compounds were individually dissolved in acetonitrile to make standard solutions with concentrations ranging from 1000 to 20000 mg L^{-1}, depending on the solubility of the analytes. The standard solutions were used to prepare stock solutions. Two stock solutions were prepared: one contained naphthalene (200 mg L^{-1}), biphenyl (200 mg L^{-1}), acenaphthene (200 mg L^{-1}), fluorene (200 mg L^{-1}), phenanthrene (200 mg L^{-1}), anthracene (100 mg L^{-1}), o-xylene (2000 mg L^{-1}), m-xylene (2000 mg L^{-1}), p-xylene (2000 mg L^{-1}), ethyl benzene (2000 mg L^{-1}); while the other stock solution contained benzene, toluene, acetophenone, nitrobenzene, and ethyl benzoate at concentrations of 4000 mg L^{-1}. These solutions were used to prepare daily working solutions. In the working solution, the content of acetonitrile was maintained a constant value of 1% (v/v).

Three water samples including tap water, river water and creek water were examined in this study. Tap water was taken from the laboratory tap after continual flow for 10 minutes. River water was collected from the Maumee River located at Side Cut Park in Maumee, Ohio. Creek water was collected from the Ottawa River in Toledo, Ohio. All water samples were collected according to Ground Water Rule (GWR) sample collection and transport reference guidelines posted by the EPA. These samples were filtered through nylon membranes with a pore size of 0.45 μm (Fisher Scientific) and stored in the refrigerator prior to analysis.

5.2.2. Materials

Fused silica capillary (0.10 mm I.D.), amber glass vials (20 mL) with PTFE/Butyl septa screw caps, PDMS (7 μm) SPME fiber and the holder for manual injection were all purchased from Supelco (Bellefonte, PA, USA). The home-made SPME device was constructed by using previous published procedures [21]. Briefly, a 5 mL syringe purchased from Hamilton (Reno, NV, USA) was re-assembled by discarding the stainless steel fiber on the plunger and gluing a 0.10 mm ID fused silica capillary. The other end of the capillary was sealed by using a microflame torch and the outer polyimide protecting film was removed at a length of 1 cm from the end. The bare fiber segment was washed with methanol, acetone, hexane and methylene chloride before coating. PTFE stir bars were obtained from Fisher Scientific and were used to perform all extractions at a constant stir rate on a Corning stir plate (Nagog Park Acton, MA, USA).

5.2.3. Instrumentation

The analysis was performed with an Agilent 6850 Network GC system (Agilent Technologies, Palo Alto, CA, USA) equipped with a flame ionization detector (FID), a split-splitless injection port, and a 0.75 mm I.D. liner. The helium carrier gas was maintained at a constant flow of 1 mL min^{-1}. All separations were performed using a HP-1 capillary column (25 m × 0.250 mm I.D., 0.25 μm film thickness) purchased from Agilent Technologies. Desorption of the fibers into the injection port was carried out in the splitless mode at 250 °C for 4 minutes. The following temperature program was used for the separation of the analytes: initial temperature of 40 °C was held for 1 minute, increased to 214 °C at 6 °C min^{-1}, increased to 300 °C at 30 °C min^{-1} and held for 5 minutes. The temperature of the FID was maintained at 280 °C. Under the separation conditions used in this study, m- and p-xylene co-eluted.

5.2.4. Synthesis of the Polymeric Ionic Liquid and SPME Fiber Coating

The synthesis of poly(1-vinyl-3-hexadecylimidazolium-bis[(trifluoromethyl)sulfonyl]imide (poly($ViHDIm^+$ NTf_2^-)) and the SPME fiber coating was performed according to published procedures [21]. The coated fiber, with a film thickness of approximately 12 μm estimated by scanning electron microscopy (SEM) was conditioned in the GC injection port for 10 minutes at 250 °C prior to performing extractions.

5.2.5. SPME Extraction Procedures

To a 20 mL amber extraction vial, 19.70 mL of water was spiked with a certain amount of stock solution and an appropriate amount of acetonitrile added to maintain the total

content of acetonitrile in the sample at 1% (v/v). A stir bar was placed in the vial and capped with a screw cap bearing a PTFE/Butyl septa. The needle of the SPME device was used to pierce the septa and the fiber exposed to the sample solution for a certain period of time at room temperature. Agitation for all extractions was performed using PTFE stir bar and a Corning stir plate. After extraction, the fiber was retracted back into the syringe and then transferred to the injection port of the GC to thermally desorb the analytes into the GC column. The desorption time was optimized at 4 minutes at 250 ºC. The extraction solution was changed after each extraction.

For the analysis of water samples, two levels of standard mixtures were spiked into a volume of 19.70 mL of the water samples, which include a low concentration level containing 600 μg L^{-1} of benzene, toluene, acetophenone, nitrobenzene, and ethyl benzoate; 300 μg L^{-1} of m, p-xylene; 150 μg L^{-1} of ethyl benzene, and o-xylene, 15 μg L^{-1} of naphthalene, biphenyl, acenaphthene, fluorene, and phenanthrene; 7.5 μg L^{-1} of anthracene; and a high concentration level containing 4000 μg L^{-1} of benzene, toluene, acetophenone, nitrobenzene, and ethyl benzoate; 2000 μg L^{-1} of m, p-xylene; 1000 μg·$L^{-1}$of ethyl benzene, and o-xylene; 100 μg $L^{-1}$of naphthalene, biphenyl, acenaphthene, fluorene, and phenanthrene; 50 μg $L^{-1}$of anthracene. An additional volume of acetonitrile was added to maintain a total percentage of acetonitrile at 1% (v/v).

The precision of the extractions is expressed as the percentage relative standard deviation (%RSD) and were obtained by performing a series of three 30 min extractions at a stir rate of 700 rpm for the working solution containing 4000 μg L^{-1} of benzene, toluene, acetophenone, nitrobenzene, and ethyl benzoate; 2000 μg L^{-1} of m, p-xylene; 1000 μg L^{-1} of ethyl benzene, and o-xylene; 100 μg $L^{-1}$of naphthalene, biphenyl,

acenaphthene, fluorene, and phenanthrene; 50 μg L^{-1} of anthracene.

5.3. Results and Discussion

Due to the relatively nonpolar characteristics of MAHs and PAHs, the poly(ViHDIm$^+$ NTf_2^-) PIL was chosen as the sorbent coating to carry out all extractions. In previous work by our group, the PIL was shown to exhibit high affinity towards nonpolar analytes due to the long carbon chain substituent on the imidazolium ring of the PIL [22]. In addition, the hydrophobic nature of the NTf_2^- counter anion should also impart the PIL sufficient hydrophobic character to allow it to be stable enough when contacting the aqueous sample matrix. The film thickness of the PIL fiber was estimated to be approximately 12 μm by SEM.

5.3.1. Optimization of Extraction Conditions

5.3.1.1. Stir Rate

Agitation is a very important factor that affects extraction in SPME. Good agitation can accelerate the diffusion of analytes from water to the extraction phase and therefore reduce extraction time and increase extraction efficiency. Fig. 5-1 shows the results of the dependence of extraction peak area on stir rate in the range of 200 to 900 rpm using the poly(ViHDIm$^+$ NTf_2^-) PIL fiber. The extraction peak areas for m, p, o-xylene, ethyl benzene, biphenyl and naphthalene increased with the increase of stir rate and reached equilibrium after 700 rpm while acenaphthalene reached equilibrium after approximately

500 rpm. Benzene, toluene, fluorene, phenathrene and anthracene didn't reach equilibrium even after the stir rate approached 900 rpm. The extraction peak areas of ethyl benzoate, nitrobenzene and acetophenone appeared to drop with an increase in stir rate. The different behavior exhibited by the analytes with varying stir rate could be explained by their different affinities to the sorbent coating. BTEX and PAHs are nonpolar whereas ethyl benzoate, nitrobenzene and acetophenone are comparatively more polar due to the electron withdrawing groups in their structures. The poly(ViHDIm$^+$ NTf_2^-) PIL has been found to exhibit greater affinity to nonpolar analytes [22]. With an increased stir rate, the fast mass transfer of the analytes from the sample matrix to the SPME sorbent coating allows for sorbent site competition between the analytes. As a result, the extraction efficiency for the more polar analytes with lower affinity to the coating drop at faster stir rate due to the displacement by the nonpolar analytes with higher affinity to the fiber. The results were consistent with previous studies from our group [22].

5.3.1.2. Extraction Time

Fiber exposure time to the sample is another important factor in achieving distribution equilibrium of the analyte between the aqueous sample and extraction phase. SPME extractions were carried out at various time intervals at a stir rate of 700 rpm. Fig. 5-2 shows the dependence of analyte extraction peak area on the fiber exposure time. Toluene exhibited the highest extraction efficiency at 15 min followed by a drop and leveling at longer extraction times. Benzene, ethyl benzene and xylenes exhibited the highest

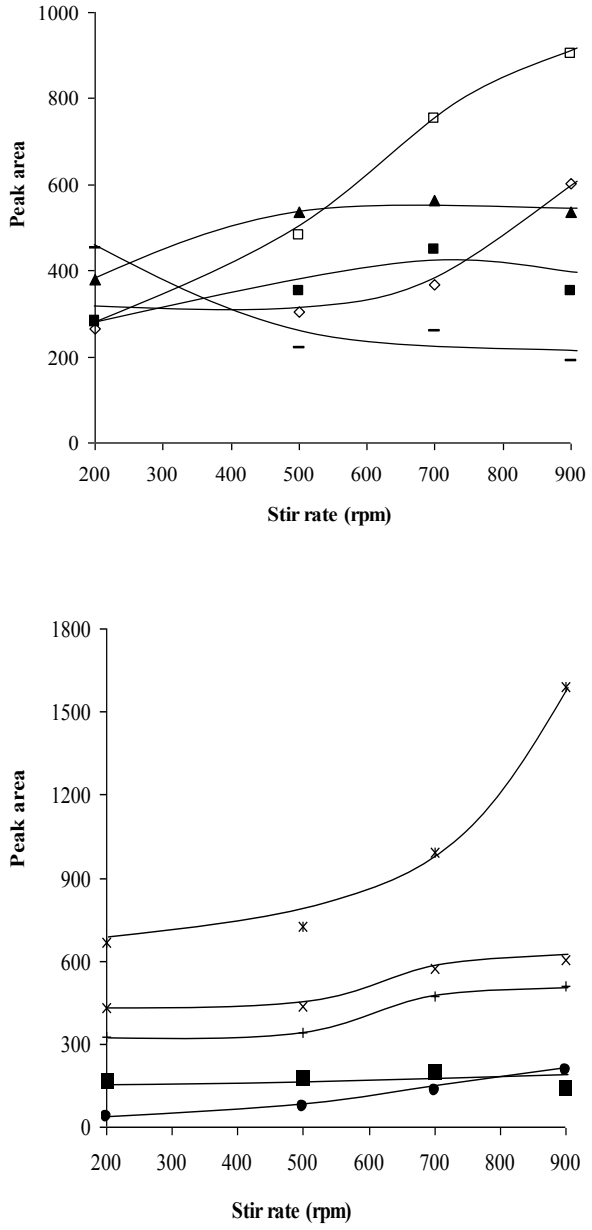

Figure 5-1: Dependence of extraction peak area on stir rate using the poly(ViHDIm^{+} NTf_2^{-}) PIL fiber at room temperature. The extraction time was 30 min. The analytes shown in the graph are: 4000 µg L^{-1} of benzene (◊), toluene (*), nitrobenzene (--); 1000 µg $L^{-1}$of ethyl benzene (+), and o-xylene (×), 100 µg $L^{-1}$of naphthalene (■), biphenyl (■), acenaphthene (▲), and phenanthrene (□); 50 µg L^{-1} of anthracene (●).

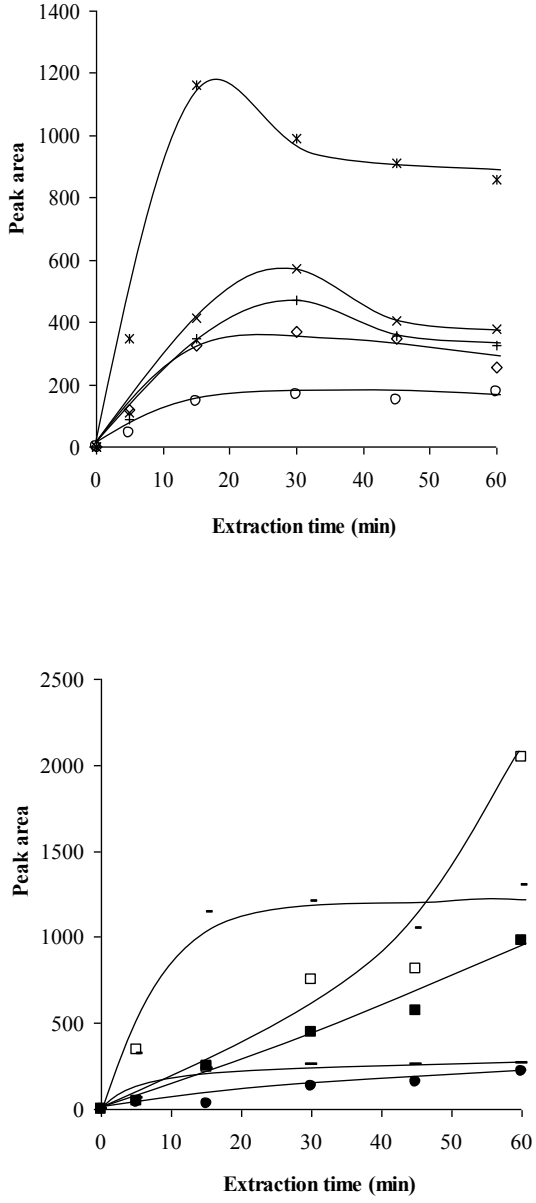

Figure 5-2: The dependence of extraction peak area on the exposure times of the poly(ViHDIm^{+}NTf$_2^{-}$) PIL fiber. The extractions were carried out with a stir rate of 700 rpm. The studied analytes are: 4000 µg L^{-1} of benzene (◊), toluene (*), acetophenone (○), and nitrobenzene (--); 1000 µg L^{-1}of ethyl benzene (+), and o-xylene (×), 100 µg L^{-1}of biphenyl (■), acenaphthene (▲), and phenanthrene (□); 50 µg L^{-1} of anthracene (●).

extraction efficiency at an extraction time of 30 min. At longer extraction time, the extraction efficiency of benzene decreased, and the extraction efficiency of ethyl benzene, m, p-xylene, and o-xylene dropped and leveled off. Ethyl benzoate, nitrobenzene, and acetophenone reached equilibrium after 30 min. Biphenyl, fluorene, acenaphthene, naphthalene, phenanthrene and anthracene did not reach equilibrium even after 60 min, which is normal behavior for such large molecules that possess lower diffusion coefficients. Therefore, 30 min was chosen as the optimal extraction time.

For comparison purposes, the commercial PDMS fiber (7 μm) was also employed for the extraction of the same analytes. PDMS is an ideal coating for extracting nonpolar analytes, and the 7 μm fiber possesses a film thickness most similar to the PIL coating used in this study. An extraction efficiency comparison of these analytes by the PIL and PDMS fiber under the same conditions is shown in Fig. 5-3. The extraction efficiencies for all analytes were higher for the PIL fiber compared to the PDMS fiber. Aside from the extraction efficiency, the selectivity of both the PIL and PDMS fibers towards these analytes were quite similar. For example, the extraction efficiency increased in the extraction of naphthalene, biphenyl, acenaphthene, fluorene and phenanthrene for both of the fibers. The results indicate that the poly($ViHDIm^+$ NTf_2^-) PIL possesses similar polarity to the PDMS coating and that the long hydrocarbon substituent on the imidazolium cation imparts the coating significant nonpolar character.

In order for the PDMS fiber to achieve the best performance, the extraction conditions for the PDMS fiber in terms of stir rate and fiber exposure time were also optimized before the calibration study and are shown in Fig. 5-4 and 5-5, respectively. The dependence of the extraction peak areas for all analytes on the stir rate (shown in Fig.

5-4) was carried out at an extraction time of 30 min at room temperature. The extraction efficiency of BTEX, acetophenone and nitrobenzene increased with the increase of stir rate up to 700 rpm. When the stir rate exceeded 700 rpm, the efficiency dropped. Ethyl benzoate achieved the maximum extraction efficiency at 500 rpm, followed by a decrease in the extraction efficiency at higher stir rates. All PAHs tended to equilibrate after 700 rpm. Based on these observations, 700 rpm was chosen as the optimized stir rate for future studies.

The sorption-time profiles (Fig. 5-5) were carried out at room temperature with the optimized stir rate at various extraction times. Benzene, acetophenone and nitrobenzene achieved highest extraction efficiencies with extraction time up to 30 min. Further increase in the extraction time resulted in a decrease of efficiencies. Toluene, ethyl benzene, m, p-xylene, acenaphthene and fluorene also obtained the highest extraction efficiency at 30 min followed by a drop and leveling of the extraction efficiency at times longer than 45 min. Naphthalene was extracted more efficiently in approximately 15 min. O-xylene, ethyl benzoate, biphenyl, phenanthrene, and anthracene reached equilibrium after an extraction time of 30 min. From these results, 30 min was chosen as the optimized extraction time for the calibration study.

5.3.2. Analytical Performance

Calibration studies for the PIL and PDMS fibers were carried out under the optimized conditions (30 min extraction time and a stir rate of 700 rpm). The calibration curves were constructed by including 8-17 calibration levels depending on the linear ranges for the various analytes.

The figures of merit for the entire method, including the calibration range, correlation coefficients (R), limits of detection (LODs), error of estimate and reproducibility for the fifteen analytes in aqueous solutions using the poly($ViHDIm^+ NTf_2^-$) PIL and PDMS coatings are shown in Tables 5.1 and 5.2, respectively. Using the PIL coating, all analytes exhibited good linearity ($R > 0.990$) in the range of three to four orders of magnitude. For the PDMS fiber, the linear ranges of the analytes were within two orders of magnitude with correlation coefficients ranging from 0.979 to 0.993. The linear ranges obtained by the PDMS fiber were much narrower than those achieved by the PIL fiber. The sensitivity, defined as the slope of the calibration curve, obtained using the PIL sorbent coating were higher for all analytes compared to those from the PDMS fiber. The sensitivities achieved by the PDMS fiber for all fifteen analytes were at least 6 times smaller than those from the PIL fiber. For the PIL fiber, the sensitivities of PAHs were higher than for the MAHs, which indicates the high affinity of the PIL-based coating toward the PAHs. LODs of all analytes were calculated as three times the signal to noise ratio. As can be seen from Table 5.1, the LODs ranged from 0.06 μg L^{-1} for naphthalene and phenanthrene to 12.8 μg L^{-1} for nitrobenzene. PAHs exhibited the lowest LODs compared to the other analytes. For the PDMS fiber (Table 5.2), LODs ranged from 0.8 μg L^{-1} for phenanthrene to 309.4 μg L^{-1} for nitrobenzene, which were more than 10 times higher than those obtained by the PIL fiber for corresponding analytes. The PIL fiber demonstrated the lowest sensitivity for acetophenone, nitrobenzene and ethyl benzoate since these molecules are slightly more polar compared to the other analytes examined in this study. The lower sensitivity for the BTEX analytes is likely due to the slightly higher polarity of these analytes compared to the PAHs. The overall results indicated that the

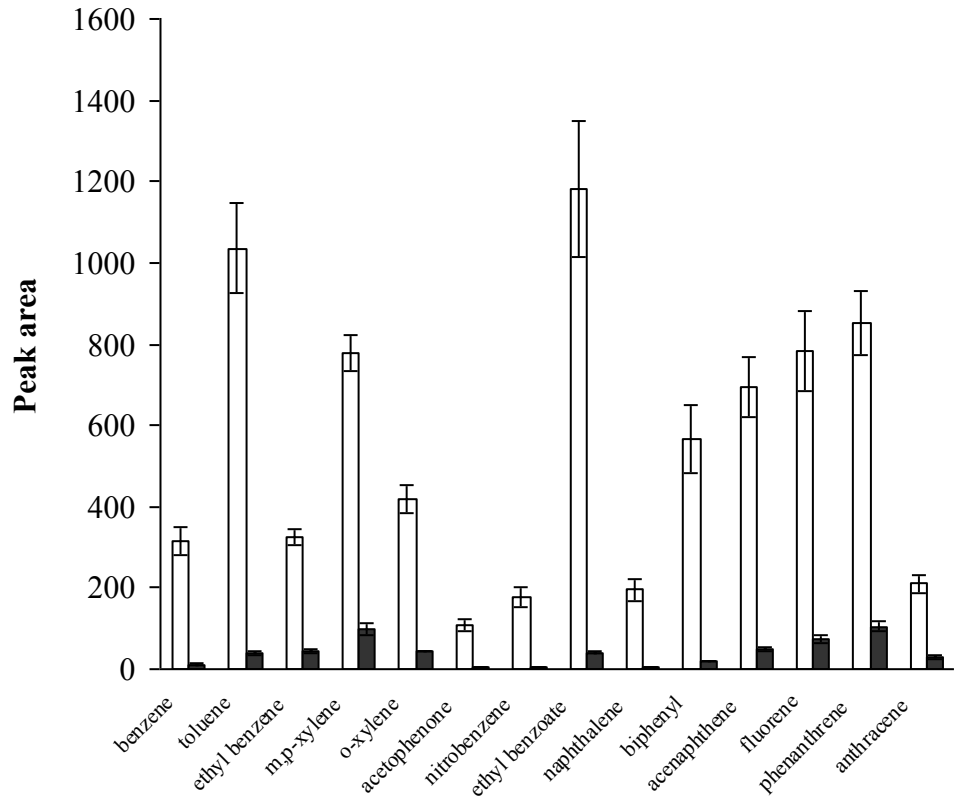

Figure 5-3: Extraction efficiency comparison between the poly($ViHDIm^+NTf_2^-$) PIL (12 μm) (□) and PDMS (7 μm) (■). The extractions were carried out with a 700 rpm stir rate for 30 min. The concentrations of the studied analytes are: 4000 μg L^{-1} of benzene, toluene, acetophenone, nitrobenzene, and ethyl benzoate; 2000 μg L^{-1} of m, p-xylene; 1000 μg $L^{-1}$of ethyl benzene, and o-xylene, 100 μg $L^{-1}$of naphthalene, biphenyl, acenaphthene, fluorene, and phenanthrene; 50 μg L^{-1} of anthracene.

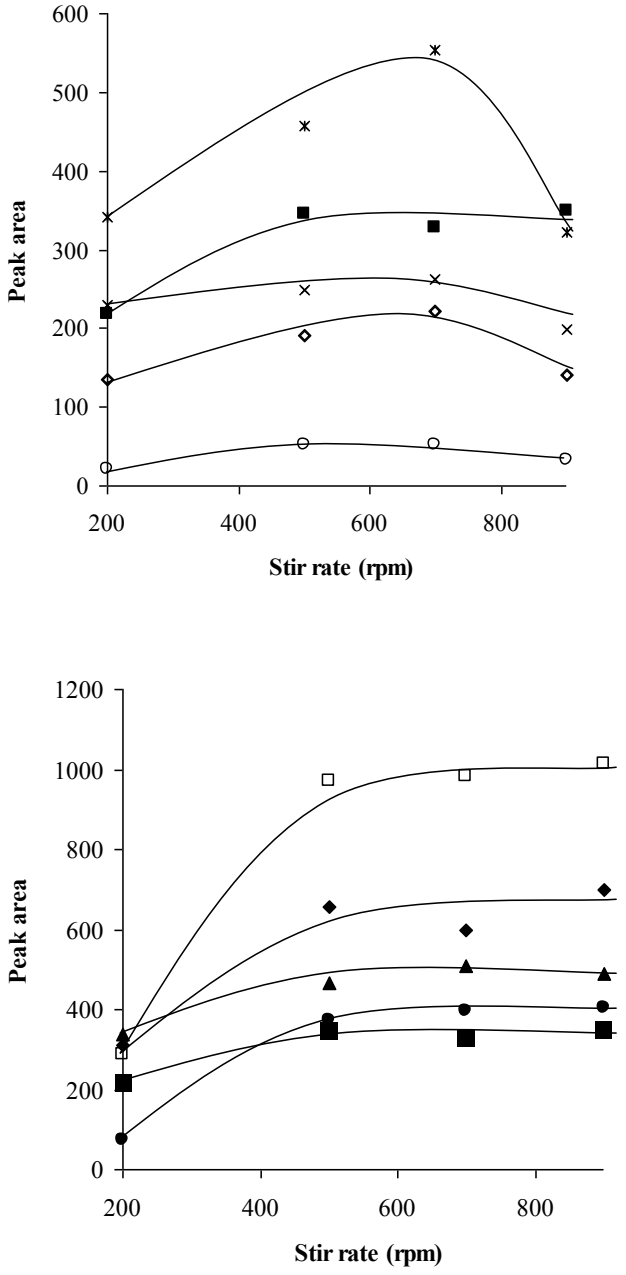

Figure 5-4: Dependence of extraction peak area on stir rate using the PDMS fiber at room temperature and an extraction time of 30 min. The studied analytes are: 24000 μg L^{-1} of benzene (◊), toluene (*), and acetophenone (○); 6000 μg $L^{-1}$of o-xylene (×), 600 μg $L^{-1}$of naphthalene (■), biphenyl (■), acenaphthene (▲), fluorene (♦), and phenanthrene (□); 300 μg $L^{-1}$of anthracene (●).

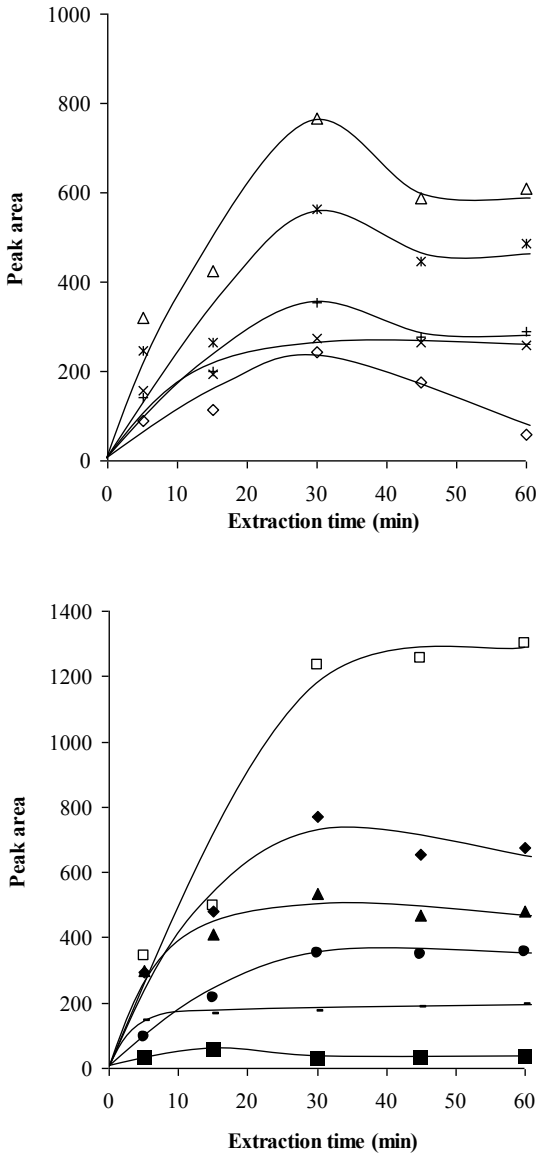

Figure 5-5: Dependence of extraction peak area on fiber exposure times using the PDMS fiber at room temperature. The extractions were carried out by employing a 700 rpm stir rate. The studied analytes are: 24000 μg L^{-1} of benzene (◊), toluene (*), and ethyl benzoate (-); 12000 μg L^{-1} of m, p-xylene (Δ); 6000 μg $L^{-1}$of ethyl benzene (+), and o-xylene (×), 600 μg $L^{-1}$of naphthalene (■), acenaphthene (▲), fluorene (♦), and phenanthrene (□); 300 μg $L^{-1}$of anthracene (●).

PIL has a higher affinity towards very non-polar analytes. The reproducibility of the PIL-based fiber, expressed as percentage relative standard deviation (%RSD), ranged from 5.7 to 14.6%. The results were similar with those obtained by the PDMS fiber whose %RSD was in the range of 1.9 to 14.8%. Based on these results, it can be clear that the extraction performance of the poly(ViHDIm$^+$ NTf_2^-) PIL SPME coating is often superior to the commercial PDMS fiber for the extraction of most analytes examined in this study.

5.3.3. Applications to Real Water Samples

The feasibility of using the poly(ViHDIm$^+$ NTf_2^-) PIL SPME fiber for real world sample analysis was demonstrated by determining the recoveries of the studied analytes from three water samples, including tap water, river water, and creek water. None of the studied analytes were detected in the three water samples. The recovery study was carried out by spiking two different concentration levels of the standard solutions to the water samples in order to investigate matrix effects. Representative chromatograms for the analytes spiked in Milli-Q water and tap water are shown in Fig. 5-6. Due to the non-exhaustive extraction behavior of SPME, the relative recovery was calculated based on GC peak area ratios of the analytes extracted from the spiked water sample to those extracted from spiked Milli-Q water with the same spiking concentration for each analyte [27]. The obtained recoveries are listed in Table 5.3. Using the low concentration level, the recoveries ranged from 75 to 120% for creek water, 72 to 116% for river water, and 74 to 117% for tap water. At the high concentration spiking level, recoveries varied from 75 to 117% for creek water, 73 to 108% for river water, and 80 to 120% for tap water.

Table 5.1: Calibration curve figures of merit for the poly(ViHDIm^{+} NTf$_2^{-}$) PIL fiber.

analyte	R	Calibration range µg L^{-1}	Slope ± SD ($\times 10^{-3}$) [a]	Error of the estimate	LOD [b] µg L^{-1}	%RSD [c]
benzene	0.991	320-12000	0.1 ± 5.6	65.7	nd [d]	11.3
toluene	0.991	3.2-14000	0.4 ± 17.2	306.8	2.8	10.7
ethyl benzene	0.993	0.8-4500	1.4 ± 48.9	279.5	0.6	6.2
m,p-xylene	0.991	1.6-9000	1.7 ± 66.8	720.8	0.6	5.7
o-xylene	0.994	0.8-4500	1.6 ± 51.6	267.1	0.4	8.2
acetophenone	0.996	20-32000	0.1 ± 3.3	131.0	12.3	12.9
nitrobenzene	0.996	20-32000	0.2 ± 5.2	212.3	12.8	12.9
ethyl benzoate	0.995	3.2-32000	0.9 ± 21.7	940.6	1.2	14.2
naphthalene	0.999	0.08-800	5.8 ± 68.8	71.4	0.06	13.8
biphenyl	0.998	0.3-900	13.1 ± 211.8	251.6	0.2	14.6
acenaphthene	0.996	0.3-900	15.9 ± 394.5	485.7	0.1	10.5
fluorene	0.993	0.08-900	15.1 ± 461.3	595.9	0.08	12.4
phenanthrene	0.995	0.08-800	17.0 ± 420.0	416.0	0.06	9.5
anthracene	0.990	0.15-450	7.3 ± 256.8	159.1	0.1	10.4

[a] SD: error of the slope.
[b] LOD: limits of detection calculated as three times of the signal to noise ratio.
[c] Results obtained by three replicate extractions.
[d] At lower concentrations, the signal was overlapped with the background, therefore the LOD wasn't determined.
[e] Conditions: sample volume of 20 mL; 30 min extraction time; stir rate, 700 rpm.

Table 5.2: Calibration curve figures of merit for the PDMS fiber.

analyte	R	Calibration range μg L^{-1}	Slope ± SD ($\times 10^{-3}$)[a]	Error of the estimate	LOD [b] μg L^{-1}	%RSD [c]
benzene	0.982	6000-24000	0.013 ± 1.0	16.0	nd [d]	11.2
toluene	0.986	6000-32000	0.027 ± 1.9	42.8	nd [d]	13.3
ethyl benzene	0.982	40-8000	0.051 ± 2.9	24.7	28.2	12.1
m,p-xylene	0.984	80-16000	0.058 ± 3.0	55.7	16.2	14.8
o-xylene	0.980	40-8000	0.041 ± 2.3	19.5	14.7	1.9
acetophenone	0.979	600-18000	0.002 ± 0.2	2.7	29.6	14.4
nitrobenzene	0.987	320-28000	0.0013 ± 0.07	2.1	309.4	10.9
ethyl benzoate	0.985	320-28000	0.0074 ± 0.4	14.0	149.0	3.4
naphthalene	0.982	15-1000	0.046 ± 3.3	2.9	13.1	9.3
biphenyl	0.983	4-1000	0.55 ± 36.7	29.6	2.2	2.7
acenaphthene	0.986	4-1000	0.75 ± 33.0	40.1	1.1	9.0
fluorene	0.987	4-700	1.28 ± 65.2	53.6	1.5	12.2
phenanthrene	0.981	1-600	2.0 ± 125.5	90.8	0.8	13.0
anthracene	0.993	2-450	1.13 ± 35.4	19.0	1.3	13.7

[a] SD: error of the slope.
[b] LOD: limits of detection calculated as three times the signal to noise ratio.
[c] Results obtained by three replicate extractions.
[d] At lower concentrations, the signal was overlapped with the background, therefore the LOD wasn't determined.
[e]Conditions: : sample volume of 20 mL; 30 min extraction time; stir rate, 700 rpm.

Table 5.3: Recovery of the investigated analytes from water samples using the poly(ViHDIm^{+} NTf$_2^{-}$) PIL fiber.[a]

Compound	Creek water		River water		Tap water	
	Recovery ± Error		Recovery ± Error		Recovery ± Error	
	Low concentration [b]	High concentration [c]	Low concentration [b]	High concentration [c]	Low concentration [b]	High concentration [c]
Benzene	75 ± 1	85 ± 4	89 ± 11	83 ± 5	74 ± 1	80 ± 4
Toluene	75 ± 10	110 ± 3	89 ± 15	108 ± 5	88 ± 15	86 ± 8
ethyl benzene	90 ± 8	80 ± 1	114 ± 6	96 ± 2	117 ± 11	97 ± 12
m,p-xylene	82 ± 6	75 ± 3	99 ± 5	91 ± 3	99 ± 12	96 ± 14
o-xylene	82 ± 7	78 ± 2	91 ± 9	88 ± 1	100 ± 11	95 ± 12
Acetophenone	116 ± 4	116 ± 7	88 ± 3	79 ± 2	75 ± 8	112 ± 13
Nitrobenzene	95 ± 13	115 ± 2	76 ± 11	78 ± 7	76 ± 14	93 ± 9
ethyl benzoate	110 ± 2	107 ± 9	72 ± 6	76 ± 14	112 ± 15	87 ± 11
Naphthalene	105 ± 10	105 ± 5	75 ± 10	73 ± 8	112 ± 8	119 ± 13
Biphenyl	98 ± 3	111 ± 10	88 ± 3	86 ± 15	107 ± 10	103 ± 12
Acenaphthene	96 ± 4	100 ± 12	89 ± 7	76 ± 16	117 ± 10	112 ± 14
Fluorine	95 ± 2	113 ± 16	86 ± 5	97 ± 15	115 ± 8	120 ± 11
Phenanthrene	120 ± 13	117 ± 2	116 ± 12	108 ± 15	116 ± 10	120 ± 2
Anthracene	87 ± 10	111 ± 16	81 ± 7	96 ± 2	108 ± 14	112 ± 13

[a] Relative recovery for n=3. [b] low concentration level: 600 μg L^{-1} of benzene, toluene, acetophenone, nitrobenzene, and ethyl benzoate; 300 μg L^{-1} of m, p-xylene; 150 μg L^{-1} of ethyl benzene, and o-xylene, 15 μg L^{-1} of naphthalene, biphenyl, acenaphthene, fluorene, and phenanthrene; 7.5 μg L^{-1} of anthracene; [c] high concentration level: 4000 μg L^{-1} of benzene, toluene, acetophenone, nitrobenzene, and ethyl benzoate; 2000 μg L^{-1} of m, p-xylene; 1000 μg L^{-1}of ethyl benzene, and o-xylene, 100 μg L^{-1} of naphthalene, biphenyl, acenaphthene, fluorene, and phenanthrene; 50 μg L^{-1} of anthracene.

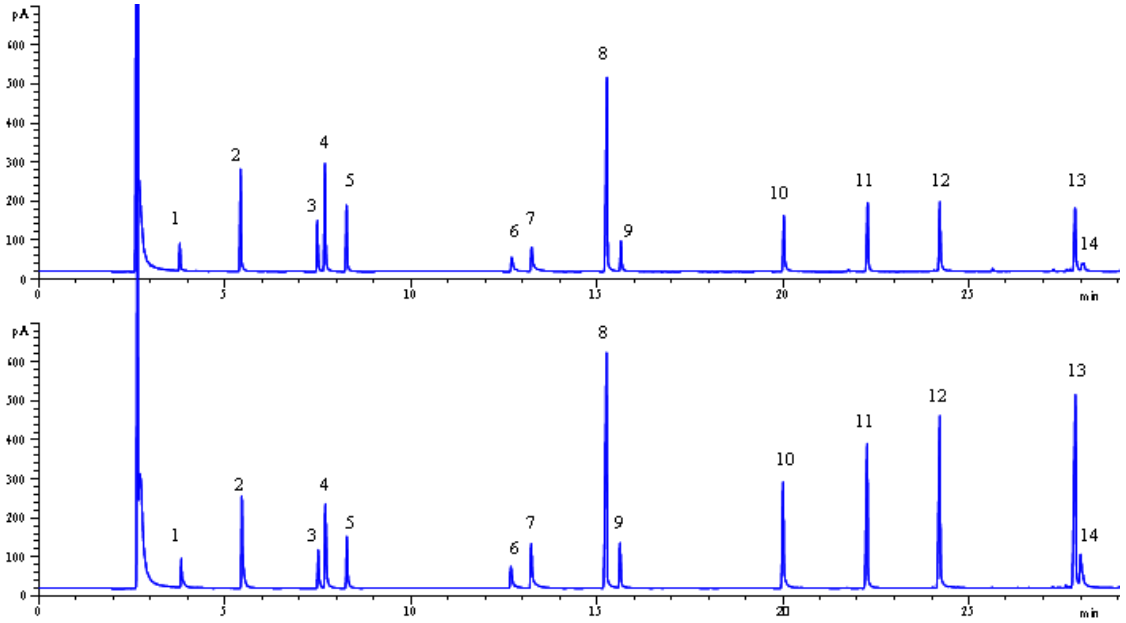

Figure 5-6: GC chromatograms of 15 analytes extracted by direct-immersion SPME using the poly(ViHDIm^{+} NTf$_2^{-}$) PIL coating in Milli-Q water (top) and tap water (bottom) under the optimized conditions: stir rate, 700 rpm; extraction time 30 minutes. Peaks and the spiking concentration are: (1) benzene (4000 µg L^{-1}); (2) toluene (4000 µg L^{-1}); (3) ethyl benzene (1000 µg L^{-1}); (4) m, p-xylene (2000 µg L^{-1}); (5) o-xylene (1000 µg L^{-1}); (6) acetophenone (4000 µg L^{-1}); (7) nitrobenzene (4000 µg L^{-1}); (8) ethyl benzoate (4000 µg L^{-1}); (9) naphthalene (100 µg L^{-1}); (10) biphenyl (100 µg L^{-1}); (11) acenaphthene (100 µg L^{-1}); (12) fluorene (100 µg L^{-1}); (13) phenanthrene (100 µg L^{-1}); (14) anthracene (50 µg L^{-1}).

There was no remarkable difference in the recoveries of the analytes from the three different matrices indicating the utility of the PIL-based coating in direct immersion extraction of analytes from analytical samples with varied matrix complexity.

5.4. Conclusions

The poly(ViHDIm^{+}NTf$_2^{-}$) PIL was used as a SPME sorbent coating for the extraction of aromatic hydrocarbons utilizing direct-immersion sampling mode. The parameters that affect extraction efficiency including stir rate and fiber exposure time were investigated. Compared to the commercial PDMS fiber with similar film thickness, the PIL sorbent coating demonstrated higher extraction efficiency, wider linear range, higher sensitivity, and lower detection limits for all analytes studied. The PIL fiber exhibited good reproducibility with the precision below 14.6% which was comparable with the commercial PDMS fiber. The performance of the PIL fiber was also evaluated by analyzing three water samples. The relatively high analyte recoveries validated the accuracy of the method. The results presented in this work demonstrate that PIL-based SPME sorbent coatings with sufficient hydrophobicity are excellent sorbent coating materials for direct-immersion SPME.

Acknowledgments

The authors wish to thank Ms. Pannee Burckel for her assistance in using SEM.

J.L.A. acknowledges funding from the Analytical and Surface Chemistry Program in the Division of Chemistry and the Separation and Purification Process Program in the Chemical, Environmental, Bioengineering, and Transport Systems Division from the National Science Foundation for a CAREER grant (CEH-0748612).

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Appendix A

Supplemental Figures Accompanying Chapter 2

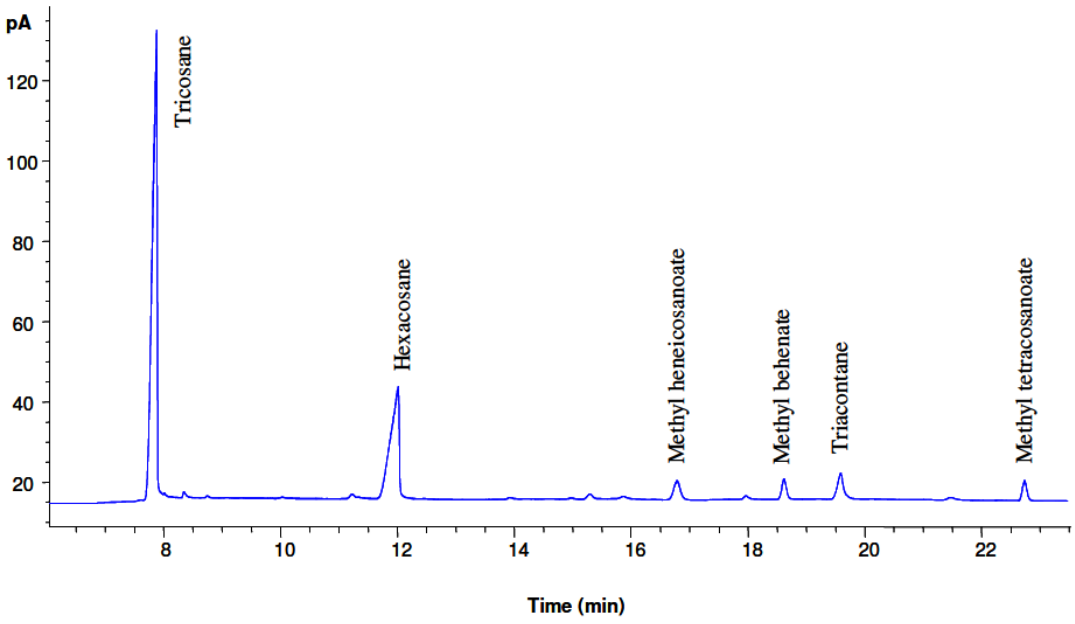

Figure A-1: Chromatogram obtained by HS-SPME of 25 mg of analyte per kg of [HMIM] [FAP] IL using a poly[ViHDIM] [NTf_2] PIL fiber (30 minute extraction time and extraction temperature of 170 ± 10 °C) and a GC stationary phase composed of the [$C_{12}(BIM)_2$] [NTf_2] IL.

Appendix B

Supplemental Figures Accompanying Chapter 3

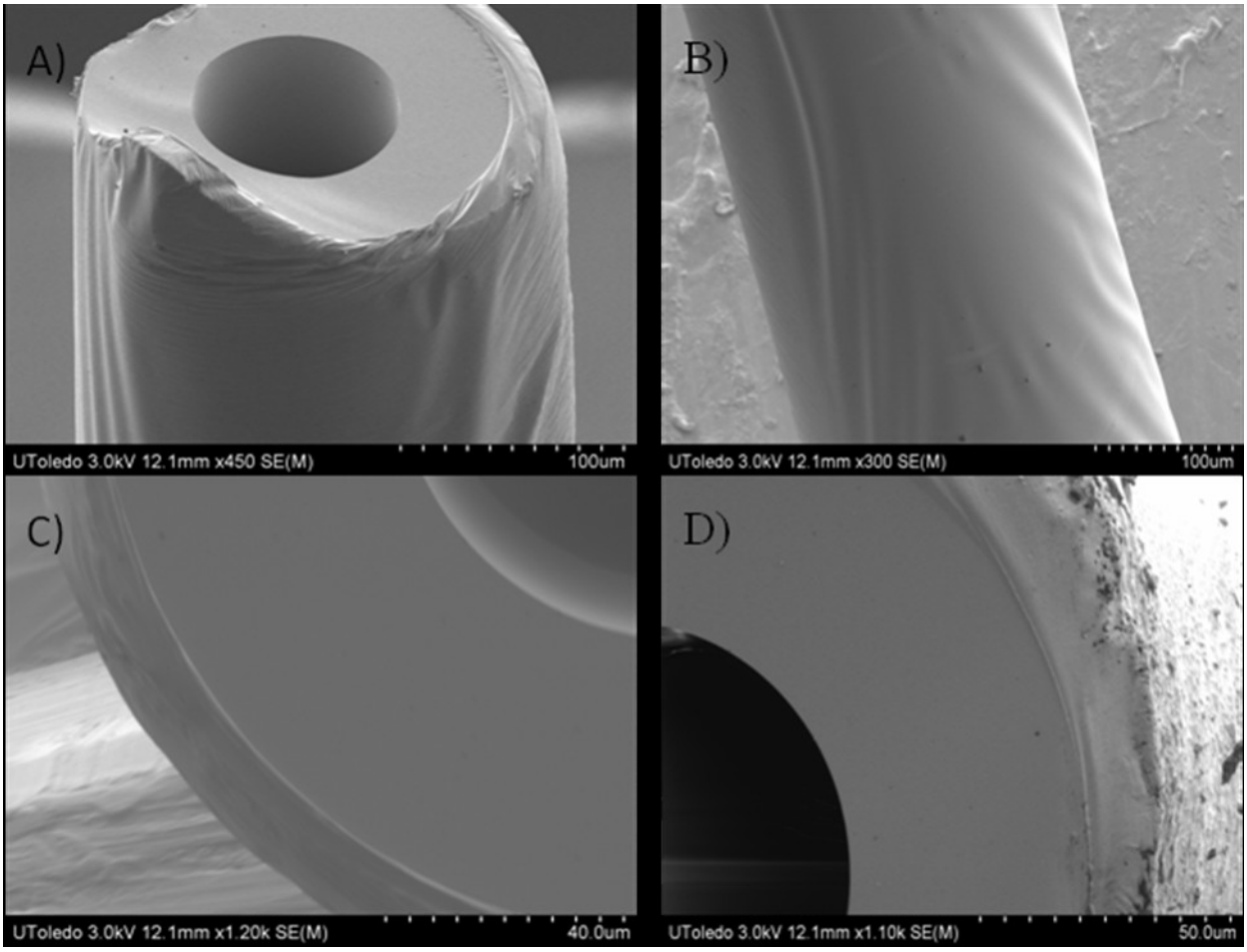

Figure B-1: Scanning electron micrographs of poly(VBHDIm$^+$ NTf$_2^-$) PIL. (A-C) and poly(HDIm$^+$ NTf$_2^-$) PIL (D) coated fibers.

Appendix C

Supplemental Figures Accompanying Chapter 4

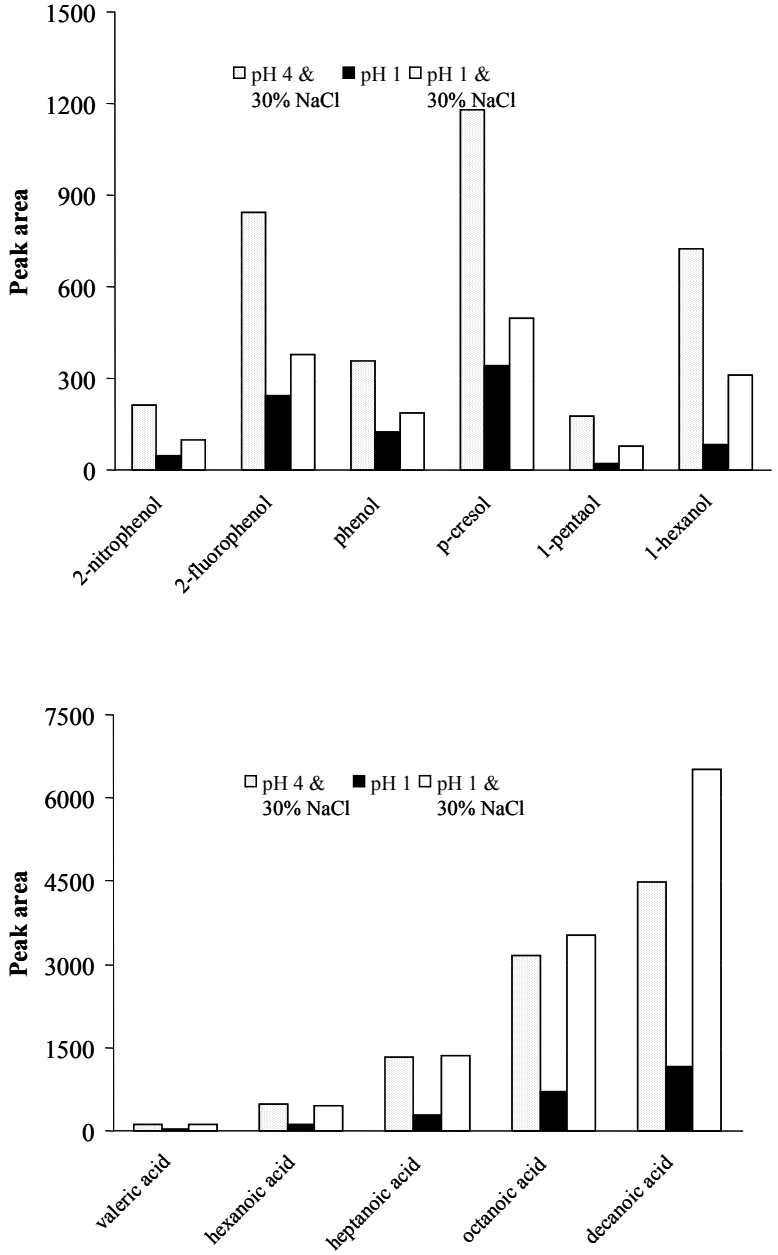

Figure C-1: Extraction efficiency comparison under different conditions for poly(ViHIm^{+}Cl^{-}) PIL SPME coating.