CPIL modified Pt wire as
SPME fiber

General structure of CPIL
polymer

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4 **Conductive Polymeric Ionic Liquids for Electroanalysis**
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7 **And Solid-Phase Microextraction**
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Abstract

Three novel electropolymerizable thiophene-based ionic liquids (ILs) were synthesized and characterized as potential candidates for developing selective extraction media for chemical analysis. Electropolymerization of the bis[(trifluoromethyl)sulfonyl]imide ([NTf₂]⁻) analogues successfully produced uniform polymeric thin-films on macro- and microelectrode substrates from both vinyl and methylimidazolium IL monomer derivatives. The resultant conducting polymer IL (CPIL) films were characterized by electrochemical methods and found to exhibit attractive behavior towards anionic species while simultaneously providing an exclusion barrier toward cationic species. Thermogravimetric analysis of the thiophene-based IL monomers established a high thermal stability, particularly for the methylimidazolium IL, which was stable until temperatures above 350 °C. Subsequently, the methylimidazolium IL was polymerized on 125 μm platinum wires and utilized for the first time as a sorbent coating for headspace solid-phase microextraction (HS-SPME). The sorbent coating was easily prepared in a reproducible manner, provided high thermal stability, and allowed for the gas chromatographic analysis of polar analytes. The normalized response of the poly[thioph-C₆MIm][NTf₂]-based sorbent coating exhibited higher extraction efficiency compared to an 85 μm polyacrylate fiber and excellent fiber-to-fiber reproducibility. Therefore, the electropolymerizable thiophene-based ILs were found to be viable new materials for the preparation of sorbent coatings for HS-SPME.

1. Introduction

Ionic liquids (ILs), salts which are liquids under 100 °C, typically consist of an organic cation and an inorganic or organic anion. Since their discovery, ILs have been shown to possess many unique features such as tunable viscosity and solubility, low vapor pressure, and excellent thermal stability, which have facilitated their ever increasing use in many applications including chromatography, SPME, catalysis, mass spectrometry, and electrochemistry. [1-4] ILs are often used in electrochemical applications as solvents due to their inherently wide potential window, especially when compared to aqueous systems. This advantage is often exploited for the electrodeposition of water-sensitive metals such as aluminum. [3] Other popular electrochemical applications include the use of ILs as binding agents in carbon paste electrodes, leading to interesting properties such as enhanced sensitivity and selectivity for analyte detection not observed with conventional binding agents, and novel sensor devices. [2,5-7]

The art of altering electrode surfaces with specific molecules has opened the door for the development and application of chemically modified electrodes (CMEs) for a range of applications. [8-10] Electropolymerization is one type of modification method that has the advantage of controlling deposition parameters to produce uniform thin-films that strongly adhere to electrode surfaces of different shapes and sizes. The resultant films can then be used as exclusion barriers or conducting matrices for entrapping additional catalytic materials. The use of conducting organic polymers in analytical applications has been very popular with applications ranging from all-plastic batteries and electrochromic devices to immobilization matrices for CMEs. [11-15] For the latter application, the most popular conducting polymers are polyheterocycles from pyrrole, aniline, thiophene, and their various derivatives. [11] Around the year 2000, electrochemical methods were also used for the preparation of polyheterocycle thin films on fiber substrates as sorbent coatings for SPME. [16-19] These initial experiments

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4 demonstrated that a high degree of control of the film thickness, morphology, and deposition rate
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6 was possible using electrodeposition to prepare novel coatings for neutral and ionic analytes.
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8 Further, the addition of an electrochemically-assisted preconcentration step was shown to
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10 enhance extraction selectivity and reduce extraction time. The preparation and applications of a
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12 wide variety of polyheterocycle-based sorbent coatings for SPME and electrochemically-assisted
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14 SPME have been recently reviewed. [20, 21]
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19 While the study of electroactive polymers is still very active, less attention has been paid
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21 toward electrically conductive ILs and their electropolymerization. Recently, thiophene
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23 functionalized ILs have been reported, resulting in molecules that exhibit interesting self-
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25 assembly, solubility, and optical properties with applications in optical sensors. [22-26]
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27 Electrochemical and thermal analysis of the polythiophene-IL systems demonstrated high film
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29 stability, but the steric bulk from the imidazolium head group restricts chain length and increased
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31 the oxidation potential of the thiophene monomer. [22] Regardless, the successful
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33 electropolymerization of these systems, as well as their interesting properties, suggests their
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35 utility for modifying electrode surfaces.
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41 In this study, three thiophene functionalized ILs were synthesized. The
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43 electropolymerization method was applied for the preparation of conducting polymeric ionic
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45 liquid (CPIL)-based thin-films onto macro- and microelectrode substrates. These new CPILs
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47 were then investigated for the selective extraction of analytes for electrochemical
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49 preconcentration and as HS-SPME sorbent coatings in which they demonstrated high thermal
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51 stability and fiber-to-fiber reproducibility.
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2. Experimental

2.1. Reagents

Platinum wire (99.95%, 0.125 mm OD) was purchased from Goodfellow Cambridge, Ltd (Huntington, England). Ni-Ti (Nitinol) wires were provided by Supelco (Bellefonte, PA). Methyl imidazole, vinyl imidazole, benzyl imidazole, 3-methoxythiophene, acetonitrile, toluene, potassium ferricyanide ($K_3Fe(CN)_6$), cobalt(III) sepulchratetrachloride (Co(Sep)), lithium bis[(trifluoromethyl)sulfonyl]imide ($LiNTf_2$), 1-methyl-2-pyrrolodione (NMP), 3-bromothiophene, dichloromethane, 1-octanol, 3-methyl-1-butanol, isopropyl butyrate, benzaldehyde, furfuryl acetate, methyl caprylate, methyl nonanoate, methyl enanthate, methyl tiglate, methyl undecanoate, and methyl tridecanoate were purchased from Sigma-Aldrich (St. Louis, MO). Ethyl heptanoate was purchased from ACROS (Morris Plains, NJ). All esters and fatty acid methyl esters were of analytical grade and used as received. Deionized water ($>18\text{ M}\Omega\cdot\text{cm}$) was used to prepare all aqueous solutions.

2.2. Instrumentation

Electrochemical measurements were carried out in a conventional three-electrode electrochemical cell with either a Bioanalytical Systems (BAS, West Lafayette, IN) 100B or an Epsilon-EC electrochemical analyzer. The working electrode was either a modified or unmodified glassy carbon electrode (GCE, BAS, MF-2012). A platinum wire and Ag/AgCl (3 M NaCl) (BAS, MF-2020) were used as auxiliary and reference electrodes, respectively. When not in use, the reference electrode was stored in 3 M NaCl. All solutions were deoxygenated by an argon purge prior to the electrochemical measurements.

Thermogravimetric analysis and differential scanning calorimetry were performed on a SDT-Q600 Simultaneous TGA/DSC (TA Instruments, New Castle, DE). NMR spectra were

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4 obtained on an Avance III 600 MHz spectrometer (Bruker, Inc., Billerica, MA). All spectra were
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6 referenced to the solvent peak. High resolution mass spectrometric analysis was conducted at the
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8 Mass Spectrometry and Proteomics Facility in the Campus Chemical Instrument Center at the
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10 Ohio State University. Scanning electron microscopy (SEM) was performed with a JEOL JSM-
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12 7500F cold cathode field emission microscope (JEOL USA, Inc., Peabody, MA).
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18 **2.3 *Synthesis of the Thiophene-Based Ionic Liquids***

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20 The synthetic scheme used was adapted from a previous report of the preparation of
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22 thiophene-functionalized IL monomers [26] and is presented in Scheme 1. In general, 3-(6-
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24 chlorohexyloxy)thiophene (0.20 g, 2.4 mmol) and 1.08 equivalents of the 1-substitued imidazole
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26 derivative were placed in a dry 25 mL round bottom flask, followed by acetonitrile (10 mL). The
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28 flask was equipped with a water-cooled condenser and the mixture was heated at 90 °C for 1 day.
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30 The solvent was removed on a rotary evaporator and the residue was triturated with diethyl ether
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32 (3 x 10 mL) to produce a reddish solid. The solid was further washed with toluene and dried
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34 under vacuum.
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40 Detailed synthetic procedures and analytical data for all ILs and precursors are provided
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42 in the Supplementary Materials section.
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47 **2.4 *CPIL Modified Electrode Fabrication***

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49 Glassy carbon electrodes (GCEs) were polished using alumina gamal (<0.1 μm),
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51 sonicated for 2 min in a Branson model 1210 ultrasonic bath, and then thoroughly rinsed with
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53 deionized water before use. CPIL modified electrodes were prepared by potential cycling a
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55 freshly polished GCE in a 0.04 M solution of monomer in CH₂Cl₂ between -0.2 and +1.3 V (vs.
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57 Ag/AgCl) at a scan rate of 100 mV/s until a dark film was visible on the electrode surface and
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the voltammetric peaks increased indicating the formation and growth of a CPIL film. The CPIL modified GCE was washed thoroughly with deionized water and immediately used for electrochemical experiments.

2.5 *Fabrication of SPME Fibers*

Laboratory-made SPME fibers were constructed according to a modification of previously reported procedures using platinum wire as the substrate. [27] Once constructed, the SPME fibers were electrochemically pretreated in a 0.5 M H₂SO₄ solution by applying a constant anodic potential of +1.5V for 25 minutes. The fibers were then removed from the solution, rinsed with acetone, and allowed to completely dry. The CPIL modified Pt wires were prepared by potential cycling the fibers 60 times between +0.1 and +2.2 V in a 0.04 M solution of monomer in 3:1 (v:v) CH₂Cl₂:toluene. The SPME fibers were removed from solution, washed with deionized water, and examined by optical microscopy to ensure complete coverage of the fiber as evident by a visibly dark film on the fiber.

2.6 *HS-SPME Analysis*

Standard solutions were prepared by dissolving the individual analyte in acetonitrile to obtain concentrations ranging from 25 to 250 µg mL⁻¹. Working solutions at concentrations between 50 to 500 ng mL⁻¹ were prepared by spiking a certain amount of the standard solution into 15 mL of deionized water within a 20 mL sampling vial. Extractions were performed in headspace mode and the solution was stirred at 800 rpm. Desorption was performed by exposing the fiber in the GC inlet at 250 °C for 5 minutes. Evaluation of the extraction efficiency was performed using an Agilent 7890 gas chromatograph coupled to a 5975C inert XL MSD with a Triple Axis detector (GC/MS) (Santa Clara, CA). Detection of all analytes via single ion

monitoring (SIM) mode was accomplished by monitoring 3 m/z fragment ions for each analyte. Helium was used as the carrier gas and maintained at a constant flow rate of 1 mL min⁻¹. Separation was performed using a SLB-5ms (30 m × 250 μm × 0.25 μm) column purchased from Supelco (Bellefonte, PA). The GC inlet was maintained at 250 °C and the GC oven was operated with a separation temperature program from 60 to 160 °C at 5 °C/min, followed by a ramp of 20 °C/min to 250 °C. An 85 μm polyacrylate (PA) fiber was obtained from Supelco (Bellefonte, PA) for comparison purposes.

3. Results and Discussion

3.1 *Ionic Liquid Synthesis and Thermal Stability*

Three organic cations were developed using different alkyl-imidazole head groups prior to quaternization. The imidazolium head groups are summarized in Figure 1. During electropolymerization of the ILs containing a chloride counter ion, the polymer films were undesirably water soluble and not stable on a platinum wire. This is in agreement with previously reported literature of polypyrrole coated SPME fibers. [28] Therefore, the chloride anion was exchanged for [NTf₂]⁻ in order to increase hydrophobicity. The metathesis product was confirmed by ¹H NMR by a shift in the most acidic imidazolium proton from ~11 to ~8.8 ppm (see supplementary material).

Thermogravimetric analysis was performed for all three newly synthesized thiophene-based ILs (A-C) at 10 °C/min under air (Figure 2). While all three ILs demonstrated thermal stability up to at least 300 °C, suggesting they may be used in high-temperature applications, [thioph-C₆MIIm][NTf₂] exhibited greater thermal stability up to approximately 370 °C. Upon reaching their maximum temperatures for thermal stability, decomposition appears to take place

in multiple steps for all three ILs. DSC analysis under the same conditions shows an exothermic heat flow transition at about 500 °C resulting in complete decomposition of the ILs. This value is consistent with literature reports of similar ILs. [22]

3.2 *Electrochemical Characterization*

The electrochemical behavior of all three thiophene-based ILs was investigated by cyclic voltammetry. The [thioph-C₆ViIm][NTf₂] and [thioph-C₆MIm][NTf₂] CPILs readily electropolymerized onto the GCE in CH₂Cl₂ solution. As an example, the electropolymerization of [thioph-C₆ViIm][NTf₂] is shown in Figure 3. The scan was initiated at -0.20 V and cycled multiple times between +1.30V at 100 mV/s. Electropolymerization and film growth were clearly observed as evident by the increase in peak current during successive cycles.

The final cycle is shown in Figure 4 from the electrodeposition of the methyl and vinyl functionalized ILs. Voltammograms for both the methyl and vinyl CPIL exhibited two peaks during the reduction sweep at +0.265 and +0.457 V and +0.259 and +0.457 V, respectively. The corresponding re-oxidation peaks occur at +0.368 and +0.527 V and +0.394 and +0.646 V, respectively, during the positive potential sweep. This is consistent with two one-electron oxidation processes typically observed in the electropolymerization of thiophenes. [14] Peak separations (ΔE_p) of 135 and 189 mV were observed for the vinyl CPIL and 103 and 70 mV for the methyl analogue. Similarly, formal potentials ($E^{\circ'}$) were observed at +0.327 and +0.552 V for the vinyl CPIL, whereas the methyl CPIL exhibited $E^{\circ'}$ values at +0.317 and +0.492 V. The benzyl functionalized IL did not show appreciable growth during successive cycles in CH₂Cl₂ and likely did not polymerize or passivated the electrode after one cycle. The accessible electrochemical potential window was enhanced by switching the solvent to acetonitrile. It was found that [thioph-C₆BzIm]⁺ did not show any electrochemical activity at a platinum electrode

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4 until approximately +2.0 V. Two oxidation peaks were apparent (Figure 5), however, only one
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6 (at +1.98 V) appears reversible. The reversible redox couple was observed with an $E^{\circ'}$ estimated
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8 to be +1.94 V. In contrast to the methyl and vinyl derivatives, the benzyl derivative does not
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10 appear to polymerize even after reaching this higher potential.
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14 After electrodeposition, the electrodes were removed from the monomer solution, rinsed
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16 with water, and allowed to dry. The electrodes were then placed in a solution containing only 0.1
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18 M tetrabutylammonium tetrafluoroborate in acetonitrile and scan rate studies were performed.
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20 For both vinyl and methyl CPILs, a plot of the peak cathodic current as a function of scan rate
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22 was observed to be linear, indicating a surface confined species consistent with
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24 electropolymerization onto the electrode surface.
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28 The similar redox behavior for both the vinyl and methyl versions of the IL suggests the
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30 vinyl group is not involved in the polymerization process under the conditions used. Reductive
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32 electropolymerization of vinyl groups has been reported when the vinyl group is accompanied by
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34 a conductive center such as ruthenium. [29] An attempt to electropolymerize $[C_6ViIm]^+$, which
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36 contains only a vinyl substituent on the imidazole and not a thionyl tail, under electrochemically
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38 reducing conditions was conducted and resulted in an insulating film on the surface of the
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40 electrode with no visually apparent film growth. This suggests the formation of a small amount
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42 of non-conducting polyvinyl IL at the electrode surface. Electropolymerization at negative
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44 potentials was similarly attempted with $[thioph-C_6ViIm][NTf_2]$ and resulted in an irreversible
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46 reduction at -1.65 V in the voltammogram and limited growth on successive cycles. Thus, it was
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48 evident that crosslinking via vinyl electropolymerization was not a productive route for coating
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50 formation and a thionyl group was necessary to produce a conductive polymer film and provide
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52 significant film growth.
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3.3 Selectivity of the CPIL Modified Electrode

3.3.1 Analyte Preconcentration and Analysis

Cyclic voltammograms were recorded for both the methyl and vinyl CPILs in the presence of cationic (Co(Sep)) or anionic ($\text{K}_3\text{Fe}(\text{CN})_6$) redox probes (see Figure S1). In the presence of $[\text{Fe}(\text{CN})_6]^{3-}$, a reversible redox couple was seen similar to the redox behavior at a bare GCE. In contrast, the response for Co(Sep) was effectively muted. This is likely due to the positive charge associated with the imidazolium cation tethered to the polythiophene-based IL, which creates a charge barrier to reject the cationic probe similar to the selective rejection observed by a polymer IL (PIL) gold composite electrode. [30] It is reasonable to suggest that the thiophene-based CPILs once polymerized on an electrode surface may be useful to selectively block cationic interferences.

Because of the inherent affinity for anionic species, it was hypothesized that the CPIL coating might be useful for the selective extraction of anionic analytes. To test this, the accumulation of ferricyanide was studied by repeated cycling from +0.80 to -0.20V in a 1 mM $\text{K}_3\text{Fe}(\text{CN})_6$ solution. The peak current for the reduction of ferricyanide increased upon scanning indicating accumulation occurred, but the peak current only approached that of the bare GCE. The electrode was then removed from the ferricyanide solution, rinsed thoroughly with deionized water, placed in a 0.1 M KNO_3 solution, and subjected to the same cycling regimen. In this experiment, the maximum current observed in the accumulation experiment decayed with time. The process of accumulation of $[\text{Fe}(\text{CN})_6]^{3-}$ and decay of the signal was repeatable suggesting reversibility of the interaction. These results indicate accumulation does not occur to the extent that preconcentration is observed to enhance analytical sensitivity. This conclusion was further supported by a scan rate study of $[\text{Fe}(\text{CN})_6]^{3-}$ after accumulation and subsequent desorption in

aqueous KNO_3 until a stable response was achieved. A plot of peak current vs scan rate and square root of scan rate both produced non-linear correlations, but a plot of log current vs log scan rate produced a linear correlation with a slope of 0.68. A log-log plot with a slope of 1 would indicate surface confined redox chemistry, while a slope of 0.5 indicates a diffusion controlled process. [31] A slope in-between suggests the redox reaction is influenced both by diffusion and surface confined processes.

3.3.2 Deposition of CPILs on Microelectrode Substrates for Solid-Phase Microextraction

ILs possess unique solvation characteristics that make them particularly interesting compounds for microextraction applications. However, their propensity to flow from the fiber support at high GC inlet temperatures makes their application in SPME challenging. To overcome this drawback, polymeric ionic liquids (PILs) have been shown to be useful sorbent coatings when coated or immobilized on substrates for SPME by direct immersion or head space sampling. [32] To engineer additional structural rigidity to the coatings, Anderson and co-workers have pioneered the development of PILs for a wide range of environmental and pharmaceutical SPME analyses. PILs were developed by photochemically-induced free-radical polymerization of IL-based monomers and crosslinkers. [27,33,34] The properties of PILs can be controlled by the structure and quantity of the crosslinker and the substituents appended to the IL monomers. Moreover, another challenge in the current method is to produce SPME sorbent coatings with controllable film thickness and high fiber-to-fiber reproducibility, which is a limitation of dynamic coating methods. To resolve this problem, electropolymerization was investigated for the preparation of CPIL-based sorbent coatings.

Microelectrode materials have similar diameters to SPME fibers and can be readily modified by electrodeposition to deposit uniform thin films. A fiber substrate must be carefully chosen such that it possesses a diameter of approximately 100 μm , high conductivity and a sufficiently high tensile modulus. In addition, the modified fiber must be capable of withstanding the high temperature conditions of the GC inlet, where desorption of the analytes retained on the SPME sorbent coating occurs. Carbon, platinum, nitinol, and copper microelectrode materials were examined and after consideration of the necessary characteristics, a 125 μm Pt fiber was chosen as the substrate that provided the best CPIL films.

[thioph-C₆MIm][NTf₂] was used as the prototype monomer for electropolymerization due to its superior thermal stability demonstrated during thermogravimetric analysis. The electrodeposition conditions also readily translated from the larger GCE to the 125 μm Pt fiber. As shown in the SEM images (Figure 6A and B), deposition of the CPIL was clearly visible by the significant difference in surface morphology between the bare Pt wire and the CPIL coated wire. As proposed, electrodeposition provided a uniform coating over the length of the wire. Determination of an accurate film thickness was difficult because the platinum fiber was easily deformed while cutting a cross-sectional specimen. However, the CPIL film thickness was estimated to be 5 μm . Attempts were made to increase film thickness by increasing the number of cycles during polymerization. However, no noticeable increase of the film thickness was achieved, which was in good accordance with the previous reported literature. [35] This result may be due to the increased resistance in the film as a function of thickness, where after the deposition of a coating of ~ 5 μm a significant overpotential may be necessary to sustain electropolymerization. After electropolymerization, all coated fibers were conditioned in a GC inlet at 250 $^{\circ}\text{C}$ for 5 min. This process was repeated 5 times to eliminate all solvents and

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4 impurities on the fiber. SEM images were taken after conditioning and compared to the freshly
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6 coated fibers (Figure 6B and C). The similarity between the unconditioned and conditioned
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8 fibers revealed the fibers do not appear to be affected by the conditioning methods and further
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10 confirms their thermal stability.
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15 16 **3.3.3 HS-SPME Analysis of Polar Analytes** 17

18 Proof of concept HS-SPME analysis was conducted on a suite of polar analytes in order
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20 to probe the extraction efficiency of the poly[thioph-C₆MIm][NTf₂]-based SPME sorbent coating
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22 (Figure 7). To identify the equilibration time for each analyte on the SPME sorbent coating,
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24 sorption-time profiles were generated by performing the headspace extraction at various time
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26 intervals. As shown in Figure S2, equilibration was quickly reached in approximately 30 minutes
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28 for most analytes. Based on this result, an extraction time of 30 minutes was applied for all
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30 subsequent studies. For comparison, extraction of the same analytes was performed
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32 simultaneously with a commercial PA fiber. As shown in Figure 7, the PA fiber exhibited much
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34 higher extraction efficiencies for all analytes compared to the poly[thioph-C₆MIm][NTf₂] fiber.
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36 However, it should be noted that the film thickness of the PA fiber is 85 μm , which is
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38 significantly higher than the estimated film thickness of the poly[thioph-C₆MIm][NTf₂] fiber of
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40 $\sim 5 \mu\text{m}$. The high extraction efficiency obtained for PA fiber is attributed to its higher sorbent
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42 coating volume. As discussed previously, it is difficult to prepare a thiophene-based CPIL fiber
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44 that possesses similar sorbent coating volume. In order to better evaluate the extraction
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46 efficiencies of commercial PA fiber and poly[thioph-C₆MIm][NTf₂] fiber, the peak areas for all
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48 extracted analytes were normalized by dividing the peak areas with the film thickness of the
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50 sorbent coating. [36, 37] It is also worth noting that the normalization can only be rationalized
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52 when the mechanism of extraction for SPME coatings are absorption-based. The PA and PIL-
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4 based coatings are known to extract analytes through an absorption mechanism. [38] Therefore
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6 after normalization, the poly[thioph-C₆MIm][NTf₂] fiber exhibited much higher extraction
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8 efficiency compared to the PA fiber for most analytes (Figure 8). The poly[thioph-
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10 C₆MIm][NTf₂] fiber also showed lower standard deviations compare to the PA fiber. The fiber-
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12 to-fiber reproducibility was also investigated by preparing two poly[thioph-C₆MIm][NTf₂] fibers
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14 using the same electropolymerization conditions. After being tested under the same extraction
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16 conditions, the peak areas for all analytes extracted by two fibers were found to be almost
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18 identical (Figure 9). The high fiber-to-fiber reproducibility for these two fibers demonstrated the
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20 utility of using the electropolymerization method for the preparation of HS-SPME sorbent
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22 coatings.
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31   **4.   Conclusions**

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33   Thiophene-based conducting polymeric ILs were prepared by electrodeposition of the
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35 corresponding monomer ILs onto macro- and microelectrode substrates. Uniform thin-films of
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37 methyl and vinyl imidazolium derivatives showed unique electrochemical properties including
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39 an affinity for anionic redox probes while rejecting cationic ones in solution. The controlled
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41 electrodeposition conditions also provided concentrically coated fibers for use in HS-SPME
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43 analysis. Poly[thioph-C₆MIm][NTf₂]-coated SPME fibers were thermally stable and allowed for
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45 the extraction of polar analytes by headspace analysis. The poly[thioph-C₆MIm][NTf₂]-based
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47 sorbent coating exhibited better extraction efficiencies for polar analytes compared to a
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49 commercial polyacrylate fiber after normalization for differences in film thickness. Further
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51 efforts are underway to create poly[thioph-C₆MIm][NTf₂] sorbent coatings with greater
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53 extraction volumes and selective extraction characteristics. The fiber-to-fiber reproducibility for
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55 two fibers using this approach was excellent owing to the controlled electrochemical fabrication
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process. In conclusion, the controlled electrodeposition of uniform CPIL coatings provides a new approach for the development of new and unique sorbent coatings for HS-SPME analysis.

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Figure and Scheme Legends

Scheme 1. Synthetic route for the thiophene-based ILs.

Figure 1. Structures of the IL cations (A) [thioph-C₆MIm]⁺, (B) [thioph-C₆ViIm]⁺, (C) [thioph-C₆BzIm]⁺, and (D) [C₆ViIm]⁺. The corresponding anion is either Cl⁻ or [NTf₂]⁻.

Figure 2. TGA of the three thiophene-based conducting ILs under air.

Figure 3. Electropolymerization of 0.04 M [thioph-C₆ViIm][NTf₂] onto a GCE in CH₂Cl₂. Scan was initiated at -0.20 V and swept to +1.30V. Scan rate: 100 mV/s.

Figure 4. Comparison of final cyclic voltammograms of 0.04 M [thioph-C₆ViIm][NTf₂] and 0.04 M [thioph-C₆MIm][NTf₂] during electropolymerization in CH₂Cl₂. Scan rate: 100 mV/s.

Figure 5. Cyclic voltammogram of 0.04 M [thioph-C₆BzIm][NTf₂] in acetonitrile during successive cycling. Scan rate: 100 mV/s.

Figure 6. SEM images of (A) bare 125 μm Pt wire, (B) Pt fiber coated with [thioph-C₆MIm][NTf₂], and (C) fiber in B after exposure to 250 °C in the GC inlet.

Figure 7. Comparison of the response (TIC, total ion count) from a poly[thioph-C₆MIm][NTf₂]-coated fiber to a commercial PA fiber for the extraction of various polar analytes. Concentration of analytes tested in this study: 3-methyl-1-butanol: 500 ng mL⁻¹; isopropyl butyrate: 200 ng mL⁻¹; Benzaldehyde: 500 ng mL⁻¹; Furfuryl acetate: 500 ng mL⁻¹; Methyl enanthate: 50 ng mL⁻¹; 1-octanol: 500 ng mL⁻¹; Ethyl heptanoate: 50 ng mL⁻¹; Methyl caprylate: 50 ng mL⁻¹; Methyl nonanoate: 50 ng mL⁻¹; Methyl tiglate: 50 ng mL⁻¹; Methyl undecanoate: 50 ng mL⁻¹; Methyl tridecanoate: 50 ng mL⁻¹.

Figure 8. Comparison of the response (TIC) from a poly[thioph-C₆MIm][NTf₂]-coated fiber to a commercial PA fiber after normalization to film thickness. Concentration of analytes is shown in Figure 7.

Figure 9. Fiber-to-fiber reproducibility for identically prepared poly[thioph-C₆MIm][NTf₂]-coated fibers. Concentration of analytes is shown in Figure 7.

Figure

Scheme 1

Figure 1

Figure 2

Figure 3

Figure 4

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Figure 6

Figure 7

Figure 8

Figure 9