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Conductive polymeric ionic liquids for electroanalysis and solid-phase microextraction

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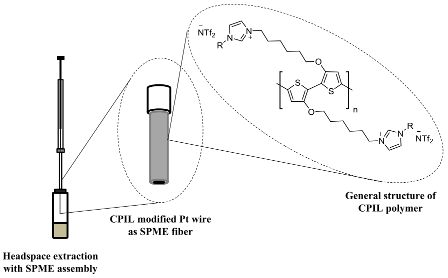
HIGHLIGHTS

- Synthesis, characterization, and electropolymerization of thiophene-based ionic liquids on electrode surfaces.
- Application of conductive polymer ionic liquids for electroanalysis and solid-phase microextraction.
- Selective extraction of polar analytes by solid-phase microextraction.

GRAPHICAL ABSTRACT



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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 ($[NTf_2]^-$) analogs 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-C_6MIm][NTf_2]-based sorbent coating exhibited higher extraction efficiency compared to an 85 μm polyacrylate fiber and excellent

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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 demonstrated that a high degree of control of the film thickness, morphology, and deposition rate was possible using electrodeposition to prepare novel coatings for neutral and ionic analytes. Further, the addition of an electrochemically-assisted preconcentration step was shown to enhance extraction selectivity and reduce extraction time. The preparation and applications of a wide variety of polyheterocycle-based sorbent coatings for SPME and electrochemically-assisted SPME have been recently reviewed [20,21].

While the study of electroactive polymers is still very active, less attention has been paid toward electrically conductive ILs and their electropolymerization. Recently, thiophene functionalized ILs have been reported, resulting in molecules that exhibit interesting self-assembly, solubility, and optical properties with applications in optical sensors [22–26]. Electrochemical and thermal analysis of the polythiophene-IL systems demonstrated high film stability, but the steric bulk from the imidazolium head group restricts chain length and increased the oxidation potential of the thiophene monomer [22]. Regardless, the successful electropolymerization of these systems, as well as their interesting properties, suggests their utility for modifying electrode surfaces.

In this study, three thiophene functionalized ILs were synthesized. The electropolymerization method was applied for the preparation of conducting polymeric ionic liquid (CPIL)-based thin-films onto macro- and microelectrode substrates. These new CPILs were then investigated for the selective extraction of analytes for electrochemical preconcentration and as HS-SPME sorbent coatings in which they demonstrated high thermal stability and fiber-to-fiber reproducibility.

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) sepulchrate trichloride (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 MΩ 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 0.5 mm diameter 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 obtained on an Avance III 600 MHz spectrometer (Bruker, Inc., Billerica, MA). All spectra were referenced to the solvent peak. High resolution mass spectrometric analysis was conducted at the Mass Spectrometry and Proteomics Facility in the Campus Chemical Instrument Center at the Ohio State University. Scanning electron microscopy (SEM) was performed with a JEOL JSM-7500F cold cathode field emission microscope (JEOL USA, Inc., Peabody, MA).

2.3. Synthesis of the thiophene-based ionic liquids

The synthetic scheme used was adapted from a previous report of the preparation of thiophene-functionalized IL monomers [26] and is presented in Scheme 1. In general, 3-(6-chlorohexyloxy)