Journal of Chromatography A, 1344 (2014) 15–22

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Polymeric ionic liquid bucky gels as sorbent coatings for solid-phase microextraction

Cheng Zhang[a], Jared L. Anderson[a,b,*]

[a] *Department of Chemistry, The University of Toledo, Toledo, OH 43606, USA*
[b] *School of Green Chemistry and Engineering, The University of Toledo, Toledo, OH 43606, USA*

ARTICLE INFO

Article history:
Received 24 February 2014
Received in revised form 3 April 2014
Accepted 4 April 2014
Available online 13 April 2014

Keywords:
Ionic liquid
Polymeric ionic liquids
Multi-walled carbon nanotubes
Solid-phase microextraction
Polycyclic aromatic hydrocarbons
Gas chromatography

ABSTRACT

Novel cross-linked polymeric ionic liquid (PIL) bucky gels were formed by free-radical polymerization of polymerizable ionic liquids gelled with multi-walled carbon nanotubes (MWCNT) and used as sorbent coatings for solid-phase microextraction (SPME). The combination of PIL with MWCNTs significantly enhanced the π–π interaction between the sorbent coatings and the aromatic analytes. Compared to the neat PIL-based sorbent coating, the PIL bucky gel sorbent coatings demonstrated higher extraction efficiency for the extraction of polycyclic aromatic hydrocarbons (PAHs). A partitioning extraction mechanism was observed for the PIL/MWCNT-based sorbent coatings indicating that the addition of MWCNTs did not seem to affect the extraction mechanism of the sorbent coating. The analyte-to-coating partition coefficients ($\log K_{fs}$) were estimated and the limits of detection (LOD) for selected PIL bucky gel sorbent coating were determined to be in the range of 1–2.5 ng L^{-1}. Recovery studies were also performed for PAHs in river and tap water to validate the applicability of the developed method.

1. Introduction

Solid-phase microextraction (SPME) has become a popular sampling and pre-concentration technique since its introduction by Pawliszyn and co-workers in the early 1990s [1]. This technique is based on the adsorption or partitioning of analytes to a thin sorbent coating film, which is physically coated or chemically immobilized on a support. The simple design of SPME fibers allow for quick and cost effective extractions in which analytes can be easily delivered to various chromatographic systems. Currently, there are a number of commercial sorbent coatings available including polydimethylsiloxane (PDMS), polyacrylate (PA), PDMS–divinylbenzene (PDMS–DVB) and carboxen–PDMS. Based on their respective polarities, these coatings are applicable for a broad spectrum of analytes [2–5]. However, these coatings still lack the selectivity needed in the extraction of specific classes of analytes. As a result, there has been increasing interest in developing new coating materials to achieve better sensitivity and selectivity while expanding the lifetime of the SPME fiber [6–8].

Carbon nanotubes (CNTs) have fascinated the scientific community since their discovery by Iijima [9]. Based on the number of layers of graphene sheets that are rolled up within their structures, these compounds can be classified as single-walled carbon nanotubes (SWCNTs) or multi-walled carbon nanotubes (MWCNTs). CNTs possess high surface areas, high mechanical strength, and high thermal stability. The characteristic structures of CNTs allow them to interact strongly with certain classes of organic molecules through π–π interactions, electrostatic forces, and dispersion interactions [10]. Due to the aforementioned advantages of CNTs, they have been successfully applied in sample preparation as solid-phase extraction (SPE) sorbents and SPME sorbent coatings for the analysis of a variety of organic compounds, such as phenols, polycyclic aromatic hydrocarbons (PAHs), polybrominated diphenyls, phthalate esters and organochlorine pesticides [11–17].

Various approaches have been previously employed to immobilize CNTs on a SPME support. These techniques include organic binders [15], physical deposition [16], electrochemical deposition [17], as well as exploiting sol–gel technology [18]. However, these methods of preparing SPME fibers can be time consuming or complicated. Additionally, the prepared coatings may exhibit low extraction efficiency and stability, which limits the applicability of the CNTs in SPME. Thus, it is necessary to find new materials to address these challenges.

In 2003, imidazolium-based ionic liquid (IL) monomers were used as a new class of dispersants for CNTs by Fukushima and co-workers [19]. After being mixed and ground with SWCNTs, the IL monomer forms a viscous gel. The gel can then

---

* Corresponding author at: Department of Chemistry, The University of Toledo, 2801 W. Bancroft Street, MS 602, Toledo, OH 43606, USA. Tel.: +1 4195301508; fax: +1 4195304033.
E-mail address: Jared.Anderson@utoledo.edu (J.L. Anderson).

http://dx.doi.org/10.1016/j.chroma.2014.04.013

be polymerized using 2,2′-azobis (2-methylpropionitrile) (AIBN) via thermal-initiated polymerization. This feature of the IL monomer/CNT-based composite provides potential advantages over previously reported approaches in the immobilization of CNTs onto the SPME support due to the fact that the gel can be synthetically designed with appropriate IL monomers and then be polymerized on a SPME support.

Our group first utilized polymeric ionic liquids (PILs) as sorbent coatings for SPME and found that they can exhibit high thermal stability, good analytical performance, and often extended coating lifetimes [20–23]. More importantly, the PIL-based coating can be appropriately functionalized to provide the desired selectivity and sensitivity in the extraction of target analytes. The success of these approaches provides indications that with modification, the IL/CNT-based gel can be employed for the preparation of PIL/CNT-based SPME sorbent coatings.

For the first time, we report the development and application of cross-linked PIL bucky gel sorbent coatings for SPME analysis. These sorbent coatings were prepared by an on-fiber copolymerization of 1-vinyl-3-butylimidazolium bis[(trifluoromethyl)sulfonyl]imide ([VC_4IM] [NTf_2]) with a IL cross-linker, namely, 1,12-di (3-vinylimidazolium) dodecane bis[(trifluoromethyl)sulfonyl]imide ([$(VIM)_2C_{12}$] 2[NTf_2]) in the presence of AIBN. Various polycyclic aromatic hydrocarbons (PAHs) were selected as model analytes to validate the new method and evaluate the extraction efficiency, selectivity and analytical performance of the sorbent coatings. The effect of MWCNTs on the resulting extraction efficiencies was also compared between different sorbent coatings by varying the amount of MWCNTs in the PIL bucky gel sorbent coatings. Since the addition of MWCNTs into the PIL-based coating has the potential to alter the morphology and rigidity of the SPME sorbent coating, the extraction mechanism of the PIL bucky gel sorbent coating in direct immersion mode was studied. To better understand the selectivity and sorption behavior of the homemade SPME sorbent coatings, the analyte-to-coating partition coefficients were estimated. The LOD of all analytes were determined in order to demonstrate the applicability of the PIL bucky gel sorbent coatings for the extraction of PAHs at trace levels. Additionally, method validation was performed via recovery studies in river and tap water.

2. Experimental

2.1. Chemicals and reagents

PAH standards of naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene and chrysene were obtained from Supelco (Bellefonte, PA, USA). MWCNTs (>98% carbon basis, O.D. × L 6–13 nm × 2.5–20 μm), 1-octanol, vinyltrimethoxysilane (VTMS), ammonium hydrogen difluoride, 1-vinylimidazole, 1-bromobutane, and 2,2′-azobis (2-methylpropionitrile) (AIBN) were purchased from Sigma–Aldrich (Milwaukee, WI, USA). Lithium bis[(trifluoromethyl)sulfonyl]imide was purchased from SynQuest labs (Alachua, FL, USA). Chloroform, acetonitrile, isopropanol, ethyl acetate, and hexane (HPLC grade) were purchased from Fisher Scientific (Fair Lawn, NJ, USA). A 100 μm PDMS fiber was obtained from Supelco. Deionized water was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA) and was used in the preparation of aqueous solutions.

Sample solutions were prepared by dissolving the PAHs individually in acetonitrile to prepare standard solutions with concentrations of 500 or 2000 $\mu g\, mL^{-1}$. Standard stock solutions containing all of the analytes at a concentration of 20 $\mu g\, mL^{-1}$ was prepared using the individual stock solutions. Working solutions were prepared by spiking a certain amount of the standard stock solution into 10 mL of deionized water within a 10 mL sampling vial.

2.2. Instrumentation

Thermal initiated polymerization of the IL monomer/MWCNT-based gel was performed using an Agilent 5890 gas chromatograph. Helium was used as the carrier gas and maintained at a constant flow rate of 1 $mL\, min^{-1}$. The GC inlet was maintained at 80 °C to enable polymerization of the IL monomer.

Evaluation of the extraction efficiency and analyte-to-fiber partition coefficients for all coatings was performed using an Agilent 6850 N gas chromatograph employing flame ionization detection (FID). Helium was used as the carrier gas and maintained at a constant flow rate of 1 $mL\, min^{-1}$. All separations were performed via splitless injection mode using a HP-5 capillary column (30 m × 250 μm × 0.25 μm) purchased from Agilent Technologies (Santa Clara, CA, USA). The following temperature program was used for the separation of PAHs: initial temperature was set to 80 °C, held for 2 min, followed by a ramp of 10 °C/min to 200 °C. The temperature was then held for 3 min and increased to 300 °C at a ramp of 25 °C/min and held for 10 min.

Evaluation of the extraction mechanism and analytical performance of the PIL bucky gel sorbent coating was performed using an Agilent 7890 gas chromatograph coupled to a 5975C inert XL MSD with a Triple Axis detector (GC/MS). Detection of all analytes via single ion monitoring (SIM) mode was accomplished by monitoring 3 relevant m/z fragment ions for each analyte. Helium was used as the carrier gas and maintained at a constant flow rate of 1 $mL\, min^{-1}$. For the extraction mechanism studies, separation was performed using a CP-Wax 57-CB (50 m × 250 μm × 0.20 μm) column purchased from Agilent Technologies. The following temperature program was used for the separation of naphthalene and 1-octanol: initial temperature was set to 70 °C and held for 2 min, followed by a ramp of 20 °C/min to 150 °C. The temperature was then increased to 225 °C at a ramp of 10 °C/min and held for 10 min.

Scanning electron microscopy (SEM) images were acquired on a JEOL JSM-7500F field emission scanning electron microscope.

2.3. Synthesis of IL monomer and cross-linker and preparation of SPME fibers

The [VC_4IM] [NTf_2] IL monomer and the [$(VIM)_2C_{12}$] 2[NTf_2] IL cross-linker were synthesized following previously reported procedures [21,26]. Detailed synthesis procedures, ^1H NMR spectra, and electrospray ionization (ESI) mass spectra of the [VC_4IM] [NTf_2] IL monomer are presented in Figures S1 and S2 (Supplementary Information).

Homemade SPME fibers were prepared according to previous procedures [21]. The bare fused silica support was etched and derivatized to enhance the overall mechanical stability of the SPME fiber. As shown in Fig. 1, a mixture containing 200 mg of the [VC_4IM] [NTf_2] IL monomer, 30 mg of the [$(VIM)_2C_{12}$] 2[NTf_2] IL cross-linker, and a specific weight percentage of MWCNT (3%, 5%, or 8% (w/w)) was ground in an agate mortar for 1 h. Subsequently, 6.9 mg of AIBN (3%, w/w) was added to the resulting gel. The mixture was further ground for 1 min to ensure complete mixing of all components. The IL monomer/MWCNT-based gel was then evenly applied to the fused silica fiber via dip-coating. The coated fiber was carefully exposed to a GC injector at 80 °C under helium for 10 h. Finally, a black, solid-like sorbent coating was obtained. Following polymerization, each fiber was conditioned five times at 280 °C for 5 min. The composition of each prepared coating and their respective naming system are provided in Table 1. In order to confirm the