Analytica Chimica Acta 687 (2011) 141–149

Contents lists available at ScienceDirect

Analytica Chimica Acta

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

Role of counteranions in polymeric ionic liquid-based solid-phase microextraction coatings for the selective extraction of polar compounds

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ARTICLE INFO

Article history:
Received 11 October 2010
Received in revised form
21 November 2010
Accepted 22 November 2010
Available online 27 November 2010

Keywords:
Ionic liquids
Polymeric ionic liquids
Solid-phase microextraction
Volatile compounds
Gas chromatography

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 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 $\mu g\,L^{-1}$ for octanoic acid and decanoic acid and 7.5 $\mu g\,L^{-1}$ 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.

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 μm 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

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doi:10.1016/j.aca.2010.11.046

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 μm 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.

2. Experimental

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.

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 $\mu g\,mL^{-1}$. A stock solution mixture of 125 $\mu g\,mL^{-1}$ 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 °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 heptane were also individually prepared for all analytes. A stock solution mixture of 400 $\mu g\,mL^{-1}$ 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 °C. Working solutions were prepared by diluting an appropriate amount of the stock solution up to 10 mL of heptane.

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