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Matrix-compatible sorbent coatings based on structurally-tuned polymeric ionic liquids for the determination of acrylamide in brewed coffee and coffee powder using solid-phase microextraction

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ABSTRACT

Nine crosslinked polymeric ionic liquid (PIL)-based SPME sorbent coatings were designed and screened in this study for the trace level determination of acrylamide in brewed coffee and coffee powder using gas chromatography–mass spectrometry (GC–MS). The structure of the ionic liquid (IL) monomer was tailored by introducing different functional groups to the cation and the nature of the IL crosslinker was designed by altering both the structure of the cation as well as counteranions. The extraction efficiency of the new PIL coatings towards acrylamide was investigated and compared to a previously reported PIL sorbent coating. All PIL fibers exhibited excellent analytical precision and linearity. The PIL fiber coating consisting of 50% 1,12-di(3-vinylbenzylbenzimidazolium)dodecane dibis[(trifluoromethyl)sulfonyl]imide as IL crosslinker in 1-vinyl-3-(10-hydroxydecyl)imidazolium bis[(trifluoromethyl)sulfonyl]imide IL monomer resulted in a limit of quantitation of 0.5 $\mu g\,L^{-1}$ with in-solution SPME sampling. The hydroxyl moiety appended to the IL cation was observed to significantly increase the sensitivity of the PIL coating toward acrylamide. The quantitation of acrylamide in brewed coffee and coffee powder was performed using the different PIL-based fibers by the method of standard addition after a quenching reaction using ninhydrin to inhibit the formation of interfering acrylamide in the GC inlet, mainly by asparagine thermal degradation. Excellent repeatability with relative standard deviations below 10% were obtained on the real coffee samples and the structure of the coatings appeared intact by scanning electron microscopy after coffee sampling proving the matrix-compatibility of the PIL sorbent coatings.

1. Introduction

Acrylamide is an unsaturated amide formed primarily through the Maillard reaction when carbohydrate-rich foods are subjected to high temperatures during cooking or thermal processing [1–3]. The toxicological properties of acrylamide are becoming better understood and include neurotoxicity, genotoxicity, carcinogenicity, and reproductive toxicity [4,5]. Acrylamide has been observed in a number of food matrices. Coffee has been of particular high concern because the roasting of coffee beans produces acrylamide levels that are among the highest of food products [6]. The concentration of acrylamide in coffee beans depends on the coffee species as well as the degree of roasting and usually varies within a range of 35–600 $\mu g\,kg^{-1}$ [7]. Lower levels can be expected in coffee beverages due to dilution effects, although acrylamide can easily be transferred from coffee powder to the beverage due to its high water solubility [6,7].

The analysis of acrylamide in food products is still a significant analytical challenge because of its chemical characteristics and its inherent trace-level concentration. The analytical determination of acrylamide is usually performed by high performance liquid chromatography (HPLC) coupled to mass spectrometry (MS) or tandem MS (MS/MS) [8,9], or by gas chromatography-mass spectrometry (GC–MS) [10,11]. The analysis of acrylamide in food always requires several pretreatment/cleanup steps. Conventional extraction techniques use solid phase extraction (SPE) to purify crude sample extracts prior to the analysis [1,9]. However, due to the multiple SPE steps, these methods are often time-consuming and achieve unsatisfactory limits of detection (LOD).

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In a recent study, the authors described a simple and rapid sampling method employing a polymeric ionic liquid (PIL) sorbent coating for in-solution solid-phase microextraction (SPME) coupled to GC–MS for the analysis of acrylamide in brewed coffee and coffee powder [12]. The crosslinked PIL sorbent coating demonstrated superior sensitivity in the extraction of this compound compared to all commercially available SPME coatings. Ninhydrin was employed as a quenching reagent during extraction to inhibit the production of additional acrylamide in the inlet of the gas chromatograph by the extraction of asparagine and glucose within the coffee matrix. The PIL fiber provided a limit of quantitation for acrylamide of 10 μg L^{-1}, thus achieving comparable results to those of the ISO method in the analysis of coffee powder samples.

The ability to design PIL-based coatings to be matrix compatible is of high interest and has led us to explore the effect of their chemical structure on acrylamide extraction efficiency from coffee samples. In this manuscript, we report a series of nine crosslinked PIL-based SPME sorbent coatings designed to increase the extraction efficiency of acrylamide. The structure of the IL monomer was tailored by introducing different functional groups to the cation and the nature of the crosslinker was designed both by modifying the structure of the cation and/or combining it with different counteranions. The extraction efficiency of the new PIL coatings towards acrylamide was investigated and compared to the previously reported PIL sorbent coating. The matrix-compatibility of the PIL-based fibers with complex real-world samples was also proven by quantifying acrylamide in brewed coffee and coffee powder.

2. Experimental

2.1. Materials

Acrylamide (99.9%), ninhydrin, menthol (99%), acrylonitrile (99%), 1-chlorohexadecane (95%), 1,12-dibromododecane (98%), 4-vinylbenzyl chloride (90%), 10-bromodecanoic acid (95%), 10-chloro-1-decanol (90%), 1-vinylimidazole (≥99%), imidazole (≥99%), vinyltrimethoxysilane (VTMS) (98%), and 2-hydroxyl-2-methylpropiophenone (DAROCUR 1173) (>96%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Acetonitrile, acetone, methanol, ethanol, isopropanol, ethyl acetate, chloroform, and dimethylsulfoxide were also purchased from Sigma–Aldrich with purities equal to or higher than 99%. Hydrogen peroxide (30%, w/w), glacial acetic acid, hydrochloric acid, silver nitrate, ammonium hydroxide (28–30% solution in water), hexafluoroacetylacetone (99%), and sodium hydroxide were purchased from Fisher Scientific (Fair Lawn, NJ, USA). Lithium bis[(trifluoromethyl)sulfonyl]imide ($LiNTf_2$) was purchased from SynQuest Laboratories (Alachua, FL, USA). Deuterated dimethylsulfoxide and deuterated chloroform were purchased from Cambridge Isotope Laboratories (Andover, MA, USA). Nitinol wire with a diameter of 128 μm was purchased from Nitinol Devices & Components (Fremont, CA, USA). Deionized water (18.2 MΩ cm) was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA).

A commercial blend of roasted coffee beans was purchased from a local market and subsequently ground with a commercial coffee grinder.

2.2. Synthesis of ionic liquid monomers and crosslinkers and fabrication of PIL-based SPME fibers

Table 1 lists the IL monomer/crosslinker composition of the crosslinked PIL-based SPME fiber coatings that were evaluated in this study. 1-Vinylbenzyl-3-hexadecylimidazolium bis[(trifluoromethyl)sulfonyl]imide [VBHDIM] [NTf_2], 1-vinyl-3-(10-hydroxydecyl)imidazolium bis[(trifluoromethyl)sulfonyl]imide [$VC_{10}OHIM$] [NTf_2], and 1,12-di(3-vinylbenzyl-imidazolium)dodecane dibis[(trifluoromethyl)sulfonyl]imide [$(VBIM)_2C_{12}$] 2[NTf_2] were prepared according to previously published methods [13,14]. The synthesis of 1-vinyl-3-(9-carboxy nonyl)imidazolium bis[(trifluoromethyl)sulfonyl]imide [$VC_9COOHIM$] [NTf_2], 1,12-di(3-vinyl benzylimidazolium)dodecane dihexafluoroacetylacetonate [$(VBIM)_2C_{12}$] 2[F_6-acac] and 1,12-di(3-vinylbenzylbenzimidazolium)dodecane dibis[(trifluoromethyl)sulfonyl]imide [$(VBBIM)_2C_{12}$] 2[NTf_2] is reported in the Supporting Information. All IL monomers and crosslinkers were fully characterized by ^{1}H NMR and the spectral data are reported in the Supporting Information. ^{1}H NMR spectra were collected in deuterated dimethyl sulfoxide using a Bruker DRX 500 MHz nuclear magnetic resonance (NMR) spectrometer (Billerica, MA, USA).

All PIL-based fibers, composed of a coating mixture consisting of IL monomer, IL crosslinker (50% by weight with respect to the monomer), and DAROCUR 1173 photoinitiator (3% by weight with respect to the coating mixture), were prepared on derivatized NiTi wires as described previously [12,13]. A coating length of 1.3 cm was maintained for all fibers examined in this study. The approximate film thickness of the PIL sorbent coatings, examined using a JEOL JSM-6060 LV low vacuum scanning electron microscope (SEM), was determined on at least 5 segments for each fiber and is reported in Table 1.

2.3. Standard and sample preparation

Individual stock solutions of acrylamide and menthol (used as an internal standard) were prepared in a 20 mL sealed vial by dissolving 2 mg of the pure standard in deionized water to obtain a concentration of 100 mg L^{-1}. Working standards of acrylamide were prepared by pipetting appropriate amounts of the stock standard and 10 μL of the menthol internal standard stock solution (final concentration 50 μg L^{-1}) into a 20 mL sealed vial and further diluted with deionized water to obtain a final volume of 20 mL. A 2% (w/v) ethanolic ninhydrin solution was prepared in a 20 mL sealed vial by dissolving 400 mg of pure ninhydrin in 20 mL of ethanol.

Brewed coffee samples were prepared using a household American coffee maker from 35 g of ground coffee extracted with 600 mL of tap water. Before analysis, a 19 mL aliquot of the brewed coffee was mixed with 10 μL of the menthol internal standard stock solution (final concentration 50 μg L^{-1}) and 1 mL of 2% (w/v) ethanolic ninhydrin solution in a 20 mL sealed vial. Roasted coffee powder samples were prepared by transferring 2 g of ground roasted coffee into a 20 mL sealed vial containing 17 mL of deionized water. Subsequently, 10 μL of the menthol internal standard stock solution and 1 mL of 2% (w/v) ethanolic ninhydrin solution were added to the suspension. Reaction quenching by ninhydrin was carried out for both brewed coffee and coffee powder by placing the solution vial into a water bath thermostated at 80 °C (with constant agitation at 1500 rpm) for 10 min. Sampling was performed immediately after the reaction.

2.4. Sampling and quantitation of acrylamide in brewed coffee and coffee powder

Sampling was carried out by directly immersing the PIL fiber into the sample solution under the following conditions: solution temperature: 25 °C, extraction time: 30 min; sample agitation: 1500 rpm. A temperature of 25 °C was selected to prevent the formation of new acrylamide in the sample at higher temperatures. The extraction time was optimized by sampling a 2.5 μg L^{-1} solution of acrylamide with Fiber **1** (see Table 1) at 5, 15, 30, 45 and 60 min. The analytes were then desorbed in the GC inlet at