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Crosslinked polymeric ionic liquids as solid-phase microextraction sorbent coatings for high performance liquid chromatography

Honglian Yu, Josias Merib, Jared L. Anderson*

Department of Chemistry, Iowa State University, Ames, IA 50011, USA

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ABSTRACT

Neat crosslinked polymeric ionic liquid (PIL) sorbent coatings for solid-phase microextraction (SPME) compatible with high-performance liquid chromatography (HPLC) are reported for the first time. Six structurally different PILs were crosslinked to nitinol supports and applied for the determination of select pharmaceutical drugs, phenolics, and insecticides. Sampling conditions including sample solution pH, extraction time, desorption solvent, desorption time, and desorption solvent volume were optimized using design of experiment (DOE). The developed PIL sorbent coatings were stable when performing extractions under acidic pH and remained intact in various organic desorption solvents (i.e., methanol, acetonitrile, acetone). The PIL-based sorbent coating polymerized from the IL monomer 1-vinyl-3-(10-hydroxydecyl) imidazolium chloride [$VC_{10}OHIM$][Cl] and IL crosslinker 1,12-di(3-vinylbenzylimidazolium) dodecane dichloride [$(VBIM)_2C_{12}$] 2[Cl] exhibited superior extraction performance compared to the other studied PILs. The extraction efficiency of pharmaceutical drugs and phenolics increased when the film thickness of the PIL-based sorbent coating was increased while many insecticides were largely unaffected. Satisfactory analytical performance was obtained with limits of detection (LODs) ranging from 0.2 to 2 $\mu g\,L^{-1}$ for the target analytes. The accuracy of the analytical method was examined by studying the relative recovery of analytes in real water samples, including tap water and lake water, with recoveries varying from 50.2% to 115.9% and from 48.8% to 116.6%, respectively.

1. Introduction

Solid-phase microextraction (SPME) has gained tremendous popularity since its introduction in the early 1990s [1]. SPME is a solvent free, cost-effective, and high throughput method that combines sampling and sample preparation into one step. SPME has been widely applied in different areas including environmental [2], food [3], bioanalytical [4], and clinical analysis [5]. This technique is typically performed in either the headspace or direction immersion mode but can be performed using a combination of these modes [6]. The extraction is based on the adsorption and/or partitioning between a sorbent coating and the analytes within the sample matrix. The desorption of analytes from the sorbent coating is performed by either thermal or solvent desorption. SPME is compatible with different separation techniques including gas chromatography (GC) and high performance liquid chromatography (HPLC).

Even though SPME is a mature technique, the continual development of new sorbent coating materials can greatly expand its applicability to a broader range of analytes and matrices. There are a number of commercially-available SPME coatings possessing a wide range of polarity that are currently available on the market. However, the selectivity of these coatings towards target classes of analytes may be inadequate which can severely limit the overall sensitivity of the method. Polymeric ionic liquids (PILs) were first introduced as SPME sorbent coatings for GC and can provide higher selectivity compared to some of the more traditional sorbent coatings [7]. The selectivity of these materials have been progressively improved through the tailoring of the chemical structure within the cation component and by creating unique combinations of cations and anions [8–16].

An area of intense study in SPME involves the extraction of polar analytes from aqueous sample solutions. Due to their high affinity towards the sample matrix, these analytes are typically extracted in the direct immersion mode. For analytes that are not sufficiently volatile, the development of HPLC-compatible SPME coatings is crucial. The coupling of PIL-based SPME to HPLC requires that the coatings be highly robust when exposed to organic desorption solvents and not slough from the support material. Crosslinked PIL-

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* Corresponding author at: Department of Chemistry, Iowa State University, 1605 Gilman Hall, Ames, IA 50011, USA.
E-mail address: andersoj@iastate.edu (J.L. Anderson).

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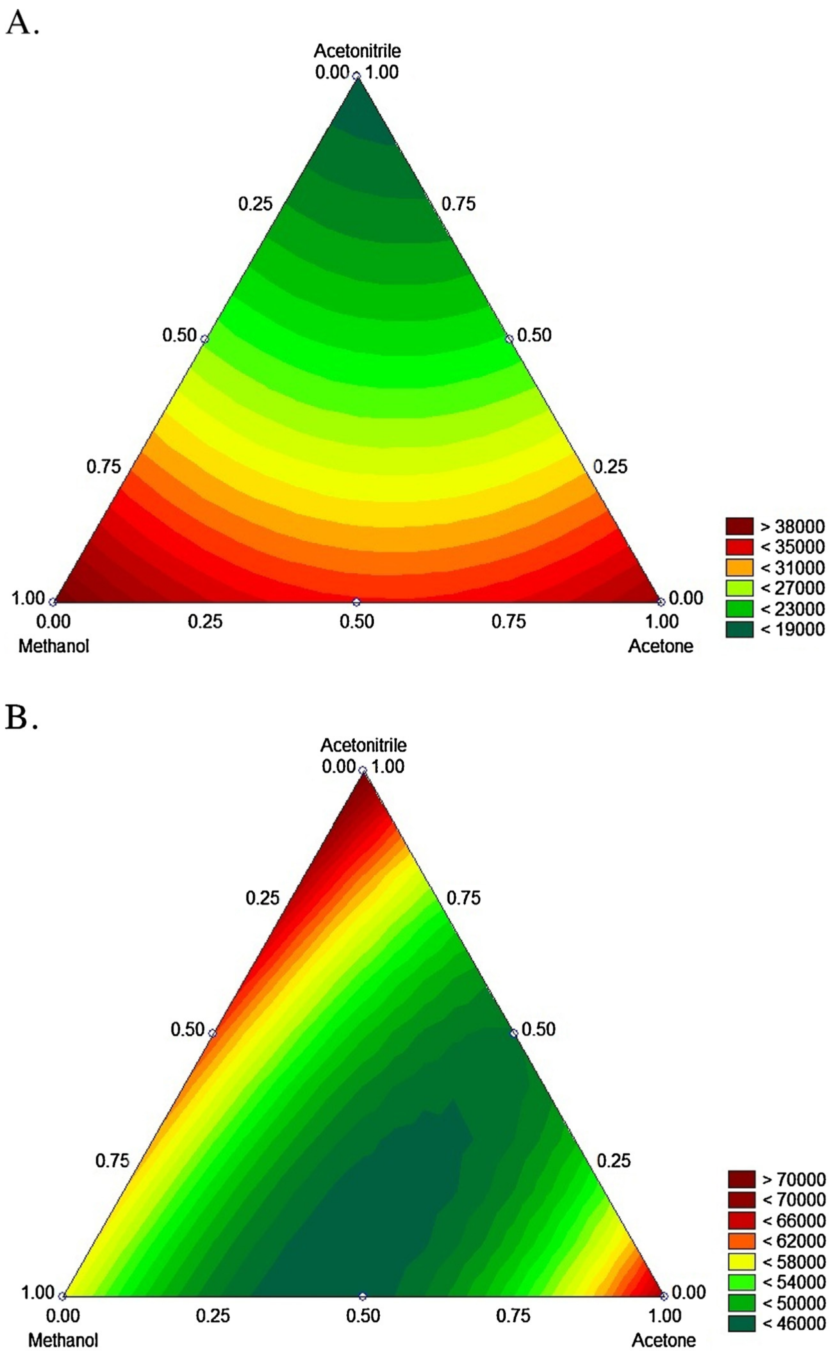

Fig. 1. Triangular surface responses obtained from the mixture design for optimizing the desorption solvent type using (A) Fiber 1 and (B) PDMS/DVB fiber. Concentration of analytes: 400 μg L^{-1}; Extraction time: 30 min; Desorption time: 15 min; Desorption solvent volume: 50 μL.

based sorbent coatings have been recently developed to address this limitation [11]. By crosslinking the PILs, the durability of the sorbent coating can be significantly enhanced, leading to a robust extraction system [13,17–19]. Hybrid materials polymerized from an IL monomer and an organic/inorganic crosslinker have been applied as sorbent coatings for the analysis of various analytes in aqueous samples using SPME-HPLC [19–22]. A PIL-based monolith and its graphene oxide derivative were developed as SPME sorbent coatings for the analysis of polar endocrine disrupting chemicals and phenolic compounds with HPLC [23,24]. These materials were prepared by azobisisobutyronitrile (AIBN)-initiated polymerization which requires high temperatures, lengthy reaction times (12–24 h), and the use of reaction solvents. Recently, a UV-initiated "on-fiber" polymerization method was introduced to prepare crosslinked PIL-based SPME sorbent coatings that can be immobilized to nitinol supports [17]. This approach is solvent-free and the ensuing polymerization can be achieved within 30 min to 2 h through photo-polymerization. Compared to the aforementioned sorbent coating fabrication techniques, this method is simple and efficient. Additionally, the use of sorbent coatings based on neat crosslinked PILs can further enhance the selectivity towards target analytes while imparting necessary structural integrity to the polymeric material when subjected to various organic solvents often used in HPLC.

For the first time, we report the use and development of HPLC compatible neat crosslinked PIL-based SPME sorbent coatings for the analysis of pharmaceutical drugs, phenolics, and insecticides. Six structurally diverse PIL-based sorbent coatings were immobi-

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