



## Faster dispersive liquid-liquid microextraction methods using magnetic ionic liquids as solvents



Honglian Yu<sup>a</sup>, Josias Merib<sup>a,b</sup>, Jared L. Anderson<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, Iowa State University, Ames, IA 50011, USA

<sup>b</sup> Department of Chemistry, Federal University of Santa Catarina, Florianópolis, SC 88040-900 Brazil

### ARTICLE INFO

#### Article history:

Received 28 June 2016

Received in revised form 3 August 2016

Accepted 3 August 2016

Available online 4 August 2016

#### Keywords:

Magnetic ionic liquids

Dispersive liquid-liquid microextraction

High-performance liquid chromatography

Pharmaceuticals

Insecticides

### ABSTRACT

Three hydrophobic magnetic ionic liquids (MILs) containing the tetrachloromanganate(II) ( $\text{MnCl}_4^{2-}$ ) anion, namely, aliquat tetrachloromanganate(II) ( $[\text{Aliquat}^+]_2[\text{MnCl}_4^{2-}]$ ), methyltriocetylammmonium  $[\text{MnCl}_4^{2-}]$  ( $[\text{N}_{1,8,8,8}^+]_2[\text{MnCl}_4^{2-}]$ ), and trihexyltetradecylphosphonium  $[\text{MnCl}_4^{2-}]$  ( $[\text{P}_{6,6,6,14}^+]_2[\text{MnCl}_4^{2-}]$ ) were employed as extraction solvents in DLLME coupled to high-performance liquid chromatography (HPLC) employing UV detection. The MILs were developed with the features of magnetic susceptibility to permit rapid retrieval of the extraction solvent, hydrophobicity to allow for phase separation from water, and mobile phase compatibility with reversed phase HPLC. Additionally, the MILs were customized to minimize hydrolysis of the anionic component in aqueous media as well as reduce absorbance when subjected to HPLC. The three MILs were applied for the extraction of pharmaceutical drugs, phenolics, insecticides, and polycyclic aromatic hydrocarbons. The disperser solvent type, disperser solvent volume, mass of MIL, extraction time, the pH of the sample solution, and salt concentration were studied in order to achieve optimal extraction efficiency for each MIL. The  $[\text{P}_{6,6,6,14}^+]_2[\text{MnCl}_4^{2-}]$  MIL exhibited the best extraction efficiencies for most of the target analytes compared to the other MILs. Good linearity was obtained using this MIL with correlation coefficients (R) varying from 0.997 to 0.999. The limits of detection (LODs) of all analytes ranged from 0.25 to 1.00  $\mu\text{g L}^{-1}$ . The relative recovery was studied in lake water and river water. The relative recovery in lake water varied from 53.8% to 114.7% at a spiked concentration of 20  $\mu\text{g L}^{-1}$  (5  $\mu\text{g L}^{-1}$  for phenanthrene) and from 52.1% to 106.7% at 150  $\mu\text{g L}^{-1}$  (37.5  $\mu\text{g L}^{-1}$  for phenanthrene). In river water, the relative recovery varied from 44.6% to 110.7% at a spiked concentration of 20  $\mu\text{g L}^{-1}$  (5  $\mu\text{g L}^{-1}$  for phenanthrene) and 42.9% to 83.6% at 150  $\mu\text{g L}^{-1}$  (37.5  $\mu\text{g L}^{-1}$  for phenanthrene).

© 2016 Elsevier B.V. All rights reserved.

### 1. Introduction

Recently, much interest has been focused on developing fast and cost-effective sample preparation methods. Dispersive liquid-liquid microextraction (DLLME), a popular sample preparation technique using microliter-volumes of an extraction solvent, was first introduced by Rezaee and co-workers in 2006 [1]. In DLLME, a mixture of a water-immiscible extraction solvent and a water-miscible disperser solvent is added to the aqueous sample to permit dispersion of the extraction solvent into fine droplets. As a result, the surface area of the extraction solvent can be increased providing improved extraction efficiency of the analytes. Agitation [2] or ultrasonication [3] can be performed to enhance the

interaction between extraction solvent and analytes. Centrifugation [4] or decreasing the system temperature [5,6] are commonly used for achieving phase separation between the extraction solvent and the aqueous sample. The low consumption of extraction solvent, good enrichment factors, and simple extraction procedure enable DLLME to be widely applied for the analysis of various analytes within different samples [7–10].

Investigations into alternative extraction solvents are important to further advance and improve DLLME. Traditional chlorinated extraction solvents, such as carbon tetrachloride, chloroform, and chlorobenzene, are toxic to the environment and may possess low selectivity towards specific analytes. Ionic liquids (ILs) were first applied as alternative extraction solvents for DLLME in 2008 to address the limitation of traditional organic solvents [5]. ILs are a class of molten organic salts with melting points lower than 100 °C. Their chemical structures can be easily tailored to enhance the selectivity towards various analytes of interest. Furthermore, ILs possess a wide range of viscosities and miscibilities with water and

\* Corresponding author at: Department of Chemistry, Iowa State University, 1605 Gilman Hall, Ames, IA, 50011, USA.

E-mail address: [andersonj@iastate.edu](mailto:andersonj@iastate.edu) (J.L. Anderson).

other organic solvents, making them highly amenable as extraction solvents in DLLME.

Magnetic ionic liquids (MILs) are a subclass of ILs that contain either magnetic cations (e.g., ferrocenium) or magnetic anions (e.g.,  $\text{FeCl}_4^-$ ,  $\text{CoCl}_4^{2-}$ ,  $\text{GdCl}_6^{3-}$ ). The magnetic susceptibility of MILs is obtained by incorporating high-spin transition metals or imparting radical moieties within either the IL cation or anion [11,12]. MILs have recently been introduced as an innovative class of extraction solvents in liquid-liquid extraction [13–18]. MIL-based extraction solvents not only possess the unique properties inherent to conventional ILs but also respond to an external magnetic field. Two studies employing hydrophilic imidazolium-based MILs for the analysis of triazine herbicides in oilseeds and vegetable oils have recently been reported [15,16]. Both studies required hexane to be applied as a diluent for the sample. Additionally, carbonyl iron powder was needed for homogenization with the MIL to increase the magnetic susceptibility of the extraction phase and reduce the phase separation time. These methods also required a second liquid-liquid extraction step using deionized water and ethyl acetate to back-extract the analytes from the MIL phase for analysis.

For aqueous samples, it is necessary to use hydrophobic MILs as extraction solvents to achieve proper phase separation. Hydrophobic phosphonium/ammonium MILs comprised of long aliphatic alkyl chains and the  $\text{FeCl}_4^-$  anion have been applied to analyze various compounds in aqueous samples [14,17]. The hydrophobic trihexyltetradecylphosphonium tetrachloroferate(III) ( $[\text{P}_{6,6,6,14}^+][\text{FeCl}_4^-]$ ) MIL was used for the extraction of phenols [14], while the methyltriocetylammmonium tetrachloroferate(III) ( $[\text{N}_{1,8,8,8}^+][\text{FeCl}_4^-]$ ) MIL was applied for the extraction of phenolic endocrine disrupters and acidic pharmaceuticals [17]. Although these hydrophobic MILs enable the extraction of target analytes in aqueous samples, the  $\text{FeCl}_4^-$  anion is highly susceptible towards hydrolysis in aqueous media [19–21]. This has the potential to lower enrichment factors and may alter the selectivity of the MILs towards target analytes. Therefore, it is necessary to explore alternative magnetic anions that are less susceptible to hydrolysis in order to continually develop suitable MIL-based extraction solvents. In addition to their instability in aqueous samples, MILs containing the  $\text{FeCl}_4^-$  anion exhibit strong UV absorbance which severely limits their compatibility in HPLC when coupled to UV detection.

To address the aforementioned limitations originating from MILs containing the  $\text{FeCl}_4^-$  anion, three tetrachloromanganate(II) ( $\text{MnCl}_4^{2-}$ )-based MILs, namely,  $[\text{Aliquat}^+]_2[\text{MnCl}_4^{2-}]$ ,  $[\text{N}_{1,8,8,8}^+]_2[\text{MnCl}_4^{2-}]$ , and  $[\text{P}_{6,6,6,14}^+]_2[\text{MnCl}_4^{2-}]$ , are applied in this study as alternative extraction solvents in DLLME. Traditional DLLME methods using ILs typically require a heating/cooling and/or centrifugation step in order to recover the extraction solvent. The MIL-based approach described in this study exploits the paramagnetic property of the MIL to enable rapid recovery of the extraction solvent through the aid of a magnet, thereby significantly reducing the overall analysis time. The MILs were used in the extraction of pharmaceutical drugs, phenolics, insecticides, and polycyclic aromatic hydrocarbons followed by chromatographic separation by HPLC. Extraction parameters including disperser solvent type, disperser solvent volume, mass of MIL, extraction time, pH, and salt concentration were optimized as either a single variable or using design of experiment (DOE). The  $[\text{P}_{6,6,6,14}^+]_2[\text{MnCl}_4^{2-}]$  MIL exhibited the best extraction efficiency compared to the other two MILs and was selected for further analysis. The analytical performance including linear range of the calibration curve, limits of detection (LODs), and precision was investigated using the  $[\text{P}_{6,6,6,14}^+]_2[\text{MnCl}_4^{2-}]$  MIL. Additionally, a recovery study was performed in lake water and river water samples to validate the analytical method.

## 2. Experimental

### 2.1. Reagents and materials

The reagent trihexyltetradecylphosphonium chloride ( $[\text{P}_{6,6,6,14}^+][\text{Cl}^-]$ ) (97.7%) was purchased from Strem Chemicals (Newburyport, MA, USA). Aliquat<sup>®</sup> 336 (average molecule weight: 442.00) and 2-nitrophenol (99%) were purchased from Acros Organics (Pittsburgh, PA, USA). Manganese (II) chloride tetrahydrate ( $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ) (98.0%) was purchased from Alfa Aesar (Ward Hill, MA, USA). Dichloromethane (99.9%), glacial acetic acid (99.9%), hydrochloric acid (12 N), sodium hydroxide ( $\geq 97.0\%$ ), and sodium chloride (NaCl) were purchased from Fisher Scientific (Fair Lawn, NJ, USA). Acetaminophen (99.0%), sulfamethoxypyridazine (99.6%), phenacetin ( $\geq 98\%$ ), hexaflumuron (99.1%), chlorfenapyr (98.8%), flufenoxuron (98.1%), chlorfluazuron (98.9%), and  $\tau$ -fluvinalinate (99%) were purchased from Sigma Aldrich (St. Louis, MO, USA). Acetonitrile, acetone, and methanol were also purchased from Sigma Aldrich with purities equal to or higher than 99.9%. Phenanthrene (99.9%), fluoranthene (98.2%), and pyrene (96.6%) were purchased from Supelco (Bellefonte, PA, USA). Ultrapure water ( $18.2\text{ M}\Omega\text{ cm}$ ) was obtained from a Milli-Q water purification system (Bedford, MA, USA). A neodymium magnetic rod ( $B=0.66\text{ T}$ ) was purchased from K&J Magnetics (Pipersville, PA, USA). All DOE data was analyzed using the *Statsoft Statistica* 8.0 program.

Chemical structures of the 13 analytes are shown in Table 1. An individual stock solution for each analyte was prepared at a concentration of  $5000\text{ mg L}^{-1}$  in different organic solvents. The stock solution of phenacetin was prepared in methanol. The stock solutions of hexaflumuron, flufenoxuron, and chlorfluazuron were prepared in acetone, while all other stock solutions were prepared in acetonitrile. Intermediate stock solutions containing all the analytes were prepared in acetonitrile at three concentrations including  $200\text{ mg L}^{-1}$ ,  $20\text{ mg L}^{-1}$ , and  $2\text{ mg L}^{-1}$ , with the exception of phenanthrene ( $50\text{ mg L}^{-1}$ ,  $5\text{ mg L}^{-1}$ , and  $0.5\text{ mg L}^{-1}$ , respectively). Aqueous standard samples were prepared by spiking an aliquot of the analyte stock solution into ultrapure water containing NaCl (30%, w/v).

### 2.2. Instrumentation

A Shimadzu LC-20A HPLC (Tokyo, Japan) was used for the separation and analysis of all extracted components. The HPLC was equipped with a Rheodyne manual injector, two LC-20AT pumps, a DGU-20A<sub>3</sub> degasser, and a SPD-20 UV/Vis detector. Separation was performed using a Restek C<sub>18</sub> column ( $5.0\ \mu\text{m}$ ,  $4.6\text{ mm} \times 250\text{ mm}$ , State College, PA, USA). The gradient method initially applied 60% of mobile phase A (0.1% acetic acid in water, v/v) and 40% of mobile phase B (0.05% acetic acid in acetonitrile, v/v). The percentage of mobile phase B was linearly increased from 40% to 70% over 15 min and from 70% to 85% over an additional 15 min. The mobile phase composition was then held at 85% for 10 min. The total flow rate of mobile phase was kept constant at  $1\text{ mL min}^{-1}$ . All analytes were detected at 254 nm.

### 2.3. Synthesis and characterization of magnetic ionic liquids

The synthesis of all MILs was carried out according to previously published studies [24,25]. For the synthesis of  $[\text{P}_{6,6,6,14}^+]_2[\text{MnCl}_4^{2-}]$ ,  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (0.5 equiv.) was added to a solution of  $[\text{P}_{6,6,6,14}^+][\text{Cl}^-]$  (1 equiv.) in dichloromethane. The reaction was performed for 24 h at room temperature under constant agitation. Afterwards, the dichloromethane solvent was removed by rotary evaporation. The obtained product was dried

Download English Version:

<https://daneshyari.com/en/article/1198326>

Download Persian Version:

<https://daneshyari.com/article/1198326>

[Daneshyari.com](https://daneshyari.com)