CHINESE JOURNAL OF ANALYTICAL CHEMISTRY
Volume 44, Issue 6, June 2016
Online English edition of the Chinese language journal

Cite this article as: Chin J Anal Chem, 2016, 44(6), 942–949.

RESEARCH PAPER

Benzyl Functionalized Ionic Liquid as New Extraction Solvent of Dispersive Liquid-liquid Microextraction for Enrichment of Organophosphorus Pesticides and Aromatic Compounds

WANG Ya-Li, YOU Li-Qin, MEI Yu-Wen, LIU Jian-Ping, HE Li-Jun*
School of Chemistry and Chemical Engineering, Henan University of Technology, Zhengzhou 450001, China

Abstract: A benzyl functionalized ionic liquid, 1-benzyl-3-methylimidazolium bis [(trifluoromethyl) sulfonyl] imide ([BeMIM][Tf_2N]), was synthesized and used as an extraction solvent of dispersive liquid-liquid microextraction (DLLME) for enrichment and determination of 5 kinds of organophosphorus pesticides (phoxim, fenitrothion, chlorpyrifos, phorate and parathion) and 2 kinds of aromatic compounds (chloronaphthalene and anthracene) in environmental water samples by high-performance liquid chromatography (HPLC). [BeMIM][Tf_2N] had higher extraction efficiency than 1-octyl-3-methylimidazolium bis [(trifluoromethyl)sulfonyl] imide and common organic solvents such as carbon tetrachloride and tetrachloroethylene. The extraction was performed using 40 μL of [BeMIM][Tf_2N] as respective extraction solvent and 1 mL of methanol as dispersive solvent with centrifugal time of 5 min. Under the optimal conditions, the proposed method exhibited a good linearity for all analytes with correlation coefficients of 0.9994–0.9998. The precision, described as intra-day and inter-day relative standard deviations (RSDs) of five replicate experiments at three different concentrations of 10, 40 and 100 μg L^{-1}, was 1.1%–4.3% and 0.8%–4.8%, respectively. The limits of detection (LODs) were 0.01–1.0 μg L^{-1} (S/N = 3). The developed method was convenient, rapid and applicable to detection of the analytes in real environmental water samples with satisfactory recovery of 82.7%–118.3% and RSDs of 0.7%–5.6%. Introduction of benzyl group into the imidazolium could considerably elevate the extraction efficiecny of the analytes due to enhanced π-π interaction between [BeMIM][Tf_2N] and analytes. [BeMIM][Tf_2N] was a satisfactory extraction solvent with a high enrichment factor of 339 and extraction efficiency of 81.4%. The partition coefficients of all analytes in [BeMIM][Tf_2N]-DLLME system were determined and the extraction mechanism was discussed.

Key Words: Benzyl functionalized ionic liquid; Dispersive liquid-liquid microextraction; Organophosphorus pesticides; Aromatic compounds

1 Introduction

Sample preparation is the bottleneck in the whole process of analysis and has become the key for improving analytical performance. Thus simple, sensitive and quick sample preparation method is really desired. Ionic liquid-based dispersive liquid-liquid microextraction (IL-DLLME) is an environmentally friendly sample preparation technique[1–3], which combines the distinct properties of ionic liquid, including low vapor pressure and tunable physicochemical properties, and the advantages of DLLME such as short extraction time, simple operation, high enrichment factor (EF),

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Received 24 December 2015; accepted 7 March 2016

*Corresponding author. Email: lijunhe@haut.edu.cn

This work was supported by the National Natural Science Foundation of China (Nos. 21577031, 20905020), the Plan for Scientific Innovation Talent of Henan Province, China (No. 124100510005) and the Plan of Nature Science Fundamental Research in Henan University of Technology, China (No. 2014JCYJ06).

DOI: 10.1016/S1872-2040(16)60937-4

and low solvent consumption. This technique has been widely applied to extract and enrich organic pollutants, metal ions and biological molecules in environmental, food, and biological samples[4–9].

The type of ionic liquid is the most important factor influencing the extraction efficiency in IL-DLLME. 1-Alkyl-3-methylimidazolium-based ionic liquid was frequently used as extraction solvent for extraction and enrichment of target analytes[1,10–12]. Various 1-alkyl-3-methylimidazolium hexafluorophosphate based DLLME system were developed to extract and enrich organophosphorus pesticides (OPPs), polycyclic aromatic hydrocarbons, and nitrite ion in our previous works[13–15]. A novel symmetrical ionic liquid, 1,3-dibutylimidazolium hexafluorophosphate, was also reported as extraction solvent for extraction and preconcentration of OPPs from water and fruit samples by DLLME combined with high-performance liquid chromatography (HPLC)[16]. Compared with other common organic solvents, the main advantage of ionic liquid was that their physicochemical properties were designable and controllable. Two pathways were frequently used to improve extraction efficiency by changing the type of ionic liquid. One was to enhance hydrophobicity of ionic liquid. For example, the extraction efficiency increased with increasing the length of subsituitive alkyl chain of imidazolium. An additional change in the extraction efficiency of the ionic liquid was obtained by introducing strong hydrophobic anion such as bis [(trifluoromethyl) sulfonyl] imide into the ionic liquid. The other one was to strengthen the interactions between ionic liquid and analytes. For example, the extraction efficiency could be improved by introducing special functional groups to ionic liquid, providing hydrogen bonding and π-π interactions besides hydrophobic interaction, subsequently improving extraction performance. Hydroxy functionalized ionic liquid was employed in extraction and enrichment of polar DNA, phenolic compounds, and phenoxy carboxylic acid herbicides[9,17–18]. In light of the diversity and complexity of various target analytes, the development of new functionalized ionic liquid is beneficial for IL-DLLME.

In this study, a benzyl functionalized ionic liquid, 1-benzyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ([BeMIM][Tf_2N]), was synthesized and characterized, and used as extraction solvent for enrichment and determination of 5 OPPs and 2 aromatic compounds in environmental water samples by DLLME-HPLC. It was anticipated that the extraction efficiency of [BeMIM][Tf_2N] for the analytes could be improved by introduction of benzyl group into imidazolium ring to provide π-π interaction between extraction solvent and the target analytes. Furthermore, [Tf_2N^-] with more uniform charge distribution and lower symmetry had stronger hydrophobicity than [PF_6^-] and [BF_4^-], and was favorable to boost extraction. Some extraction parameters influencing [BeMIM][Tf_2N]-DLLME were investigated and optimized, and the developed [BeMIM][Tf_2N]-DLLME-HPLC method was applied to three real samples. The partition coefficients (K) of analytes in [BeMIM][Tf_2N]-DLLME system were determined and the extraction mechanism was discussed.

2 Experimental

2.1 Instruments and chromatographic conditions

All chromatographic tests were performed on a Shimadzu system (Tokyo, Japan) equipped with a LC-10AT VP Plus pump, a SPD-10A VP Plus UV-vis detector and CBM-10A VP Plus chromatographic station. A Rheodyne (Cotati, CA, USA) 7725i injector with 20 µL sample loop was used. 80-1 centrifuge was purchased from Huayan Medical Apparatus and Instruments Company (Shanghai, China). Separations were carried out on a Shimadzu ODS column (250 mm×4.6 mm I.D, 5 µm) using methanol-water (80:20, V/V) as mobile phase. All the test mixtures were analyzed at room temperature at a flow rate of 1.0 mL min^{-1} with UV detection at 254 nm.

2.2 Reagents and samples

Phoxim, fenitrothion, chlorpyifos, phorate and parathion were purchased from Agro-Environmental Protection Institution (Beijing, China). Chloronaphthalene and anthracene were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). The stock solutions of each analyte were prepared in methanol at the concentration of 0.10 g L^{-1} for anthracene and 1.0 g L^{-1} for other analytes, and stored at 4 °C. The working solutions were prepared by diluting the stock solutions with doube-distilled water.

Lithium bis[(trifluoromethyl)sulfonyl]imide ($LiTf_2N$) was obtained from Henan Wanxiang Chemical Co., Ltd. (Zhengzhou, China). 1-Methylimidazole and benzyl bromide were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). 1-Octyl-3-methylimidazolium bis[(trifluoromethyl)-sulfonyl]imide ([OMIM][Tf_2N]) was synthesized in our laboratory[14]. Tap water and rain water were collected from the campus of Henan University of Technology (Zhengzhou, China), and the Yellow River water was collected from Zhengzhou City (China). Other reagents, including methanol, acetone, acetonitrile, ethanol, carbon tetrachloride (CCl_4) and tetrachloroethylene (C_2Cl_4) were of HPLC grade. Double-distilled water was used throughout this work.

2.3 Synthesis and characterization of [BeMIM][Tf_2N]

[BeMIM][Tf_2N] was synthesized according to literature[19] with a minor modification. 1-Methylimidazole (0.2 mol) and excess of benzyl bromide were dissolved in 100 mL of acetonitrile. The mixture was stirred for 72 h at room