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Ultra-hydrophobic ionic liquid 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate supported hollow-fiber membrane liquid–liquid–liquid microextraction of chlorophenols

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ABSTRACT

An ultra-hydrophobic ionic liquid, 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([HMIM][FAP]) was immobilized in the pores of a polypropylene hollow fiber for liquid–liquid–liquid microextraction (HF-LLLME) of chlorophenols (CPs) (4-chloro-3-methylphenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol). The analytes were first extracted from 10 ml of water sample into the ionic liquid membrane, and then were extracted back into 5 μ l of sodium hydroxide aqueous solution in the hollow fiber channel. After extraction, the acceptor solution was directly injected into a high-performance liquid chromatographic system for analysis. Extraction parameters such as extraction time, salt concentration in the sample, the pH of the sample and acceptor phase, and stirring rate during extraction were investigated. The relative standard deviations of the analytes varied from 4 to 6%. Limits of detection of < 0.5 ng/ml were obtained for the three analytes. The squared regression coefficients relating to the calibration curve were ≥ 0.9941 . The proposed method was applied to the analysis of CPs in canal water.

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1. Introduction

Sample preparation is a critical step in analytical chemistry, particularly in environmental analysis. In general, liquid–liquid extraction (LLE) [1,2] is one of the most widely used pretreatment procedures. However, it is labor-intensive and time-consuming. In addition, it generally requires a large amount of potentially toxic and high-purity solvents. Over the past 2 decades, miniaturized, microscale sample preparation techniques have been developed as alternatives to LLE, such as liquid-phase microextraction (LPME) [3,6–10] and solid-phase microextraction (SPME) [4,5]. Jeannot and Cantwell developed a liquid-based extraction procedure based on a microdrop of solvent suspended at the tip of a Teflon rod [3]. They referred to the method as solvent microextraction. Later, the same authors [6] and He and Lee [7] developed an approach whereby the organic drop was supported at the tip of a micro-syringe needle. Different types of LPME, as this microscale liquid-based extraction mode is now generally known, have been investigated, such as continuous flow microextraction [8], static LPME [7] (later referred to as single-drop microextraction (SDME)), dynamic LPME [9] and headspace LPME [10]. The technique has

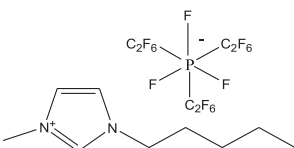
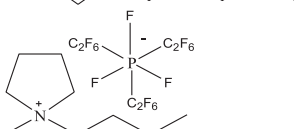
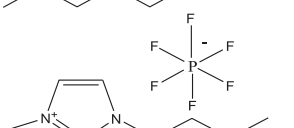
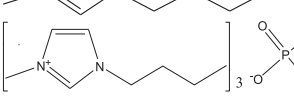
been demonstrated to be a simple, fast, and cost-effective sample pretreatment method [11]. However, the instability of the solvent microdrop, problematic application to complex aqueous samples, relative low precision (when conducted manually), and sensitivity were often encountered [12]. In order to overcome these disadvantages, hollow fiber protected LPME was introduced. One mode of HF-LPME is HF-LLLME [12–14] which is a simple technique in which analytes are extracted into an organic phase from an aqueous donor phase, and subsequently extracted back into an aqueous acceptor phase. For this method, a hollow fiber is used to support the organic phase (held within the wall pores) and acceptor phase (confined within the channel of the membrane). Since the final phase is aqueous, it can be introduced into a reversed-phase high-performance liquid chromatographic (HPLC) system without further treatment. For HF-LLLME, the selection of the organic phase is a critical step to obtain efficient extraction. It should be immiscible with water, relatively less volatile, and be compatible with the hollow fiber. 1-Octanol [13], toluene [15], and undecane [16] are commonly used solvents in HF-LLLME. Since these are volatile organic chemicals, they pose potential risks to users.

Room temperature ionic liquids (ILs) are composed of organic cations and various anions. ILs have some significant advantages over organic solvents, such as low volatility, high thermal stability and the ability to interact with a variety of organic and inorganic

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Table 1
Structures and Physical properties of studied ILs at 20 °C.

Ionic liquid	Structure	Density (g/cm ³)	Viscosity (cP)	Surface tension (mN/m)
[HMIM][FAP]		1.557	119	33.2
[BMPL][FAP]		1.589	292	35
[BMIM][PF ₆]		1.36	312	43.21
[BMIM][PO ₄]		–	–	–

compounds [17]. Furthermore, they are considered as environmentally friendlier solvents, and thus serve as alternatives to conventional organic solvents. Since IL was used by Liu et al. in LPME [18], their application has become widespread in the extraction field [19,20]. ILs containing the hexafluorophosphate (PF₆⁻) anion have been applied as supporting liquid for HF-LLLME. For example, 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]) was used in this manner for the extraction of aliphatic and aromatic hydrocarbons [21]. 1-Octyl-3-methylimidazolium hexafluorophosphate ([OMIM][PF₆]) was employed for the extraction of chlorophenols (CPs) [22] and sulfonamides [23]. However, Swatoski et al. reported that these ILs are hydrolytically unstable [24]. It has been found that after 5 min of SDME via direct immersion using [BMIM][PF₆], 50% of the microdrop volume was lost [25]. [OMIM][PF₆] is more hydrophobic; however, it was found that this IL also partially dissolved in aqueous solution after 30 min [18,26]. Recently, ILs containing tris(perfluoroalkyl)trifluorophosphate anion (FAP⁻) have been shown to have excellent hydrolytic, thermal and electrochemical stability. The water uptake of these ILs are more than 10 times less than that of ILs with the PF₆⁻ [27]. Cong et al. have applied FAP-based ILs as SDME extraction solvents [25]. In our previous studies, 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([HMIM][FAP]) was successfully used as extraction solvent in HF-LPME [28] and dispersive liquid–liquid microextraction [29,30] of analytes from aqueous samples.

CPs were used as the analytes in the present work. LPME methods, including ultrasound-headspace LPME [31], dispersive liquid–liquid microextraction (DLLME) [32], single drop LPME [33] and HF-LPME [34] have been applied to extract CPs from environmental water samples. [OMIM][PF₆] as the impregnated IL in the hollow fiber wall pores for HF-LLLME [22] and [BMIM][PF₆] based three-phase liquid–liquid–liquid solvent bar microextraction [35] of CPs from environmental water samples have been reported. In this work, we investigated the FAP-based IL, [HMIM][FAP], as the wall pore-impregnated solvent in HF-LLLME. The influence of HF-LLLME parameters such as extraction time, pH of the donor sample and acceptor phase, stirring rate during extraction, and salt concentration in the sample were optimized and the proposed method, with HPLC, were applied to determine CPs in canal water samples.

2. Experimental

2.1. Chemicals and materials

HPLC grade methanol was purchased from Tedia (Fairfield, OH, USA) and acetone was supplied by Merck (Darmstadt, Germany). 4-Chloro-3-methylphenol (pKa 9.6), 2,4-dichlorophenol (pKa 7.8), and 2,4,6-trichlorophenol (pKa 6.2) were supplied by Aldrich (Milwaukee, WI, USA). Ultrapure water was produced on a Milli-Q water purification system (Millipore, Milford, MA, USA). Sodium chloride was obtained from GCE (Chula Vista, CA, USA). [HMIM][FAP] and 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate [BMPL][FAP] were purchased from Merck. 1-Butyl-3-methylimidazolium phosphate ([BMIM][PO₄]) and [BMIM][PF₆] were bought from Strem Chemicals (Newburyport, MA, USA). The structures and physical properties of the ILs investigated in this study are shown in Table 1. Sodium hydroxide and sodium dihydrogen phosphate were purchased from Merck and orthophosphoric acid (85% purity) was supplied by Carlo Erba (Milan, Italy).

Individual stock solutions of the pure CPs were prepared in methanol at 1 mg/ml concentrations and stored at 4 °C. Working aqueous solutions containing all three CPs at different concentrations were prepared daily. The concentrations of the analytes in the working solutions for the optimization experiments, were 1 µg/ml. Real water samples were collected from a canal in Singapore, and stored at 4 °C until ready for extraction.

Accurel Q3/2 polypropylene hollow fiber membrane with an inner diameter of 600 µm, wall thickness of 200 µm, and wall pore size of 0.2 µm, was obtained from Membrana (Wuppertal, Germany).

2.2. Instrumentation

HPLC analysis was carried out on a Waters (Milford, MA, USA) instrument with a Rheodyne (Cotati, CA, USA) 77251 injector equipped with a 20 µl sample loop, a Degasys DG-2410 degasser, a Waters 1525 µ binary pump and a Waters 2487 dual λ absorbance detector. The detection wavelength was set at 240 nm. Data was collected and processed by Empower version 5.0 (Waters) data analysis software.

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