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Novel multifunctional acceptor phase additive of water-miscible ionic liquid in hollow-fiber protected liquid phase microextraction

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ABSTRACT

In this paper, water-miscible ionic liquid (IL) such as 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) is introduced for the first time as a novel multifunctional acceptor phase additive in hollow-fiber protected liquid phase microextraction (HF-LPME). For investigating the performances of [BMIM]Cl, it was respectively mixed with NaOH, HCl and deionized water. And their extraction performance was preliminary evaluated with alkaline compounds (clenbuterol, metoprolol, carteolol and propranolol), acidic compounds (diethylstilbestrol, hexestrol, phenol and bisphenol A) and neutral compounds (acenaphthylene, fluorene and fluoranthene). Furthermore, a complete extraction and determination method using IL-three phase HF-LPME and liquid chromatography was established for polycyclic aromatic hydrocarbons (PAHs) in river water. The extraction conditions, such as concentration of IL, extraction temperature, extraction time, stirring speed, ionic strength and the addition of methanol were studied in detail. Under the optimum conditions, the linear ranges of acenaphthylene, fluorene and fluoranthene were 1–100, 1–200 and 1–200 ng mL^{-1}, respectively. Limit of detections (LODs) were lower than 0.25 ng mL^{-1}. The recoveries of PAHs in three kinds of spiked real water are between 90.97 and 109.7% and the precisions are in the range of 2.53–7.01%. Since water-miscible ionic liquids had various forms, similar extraction capabilities to organic solvents and could be conveniently adjusted by acid, alkaline and buffer, this proposed method should have great potentiality in sample preparation of HF-LPME.

1. Introduction

Room-temperature ionic liquids (RTILs) are ionic media resulting from combinations of organic cations and various anions. They have a lot of useful and intriguing physicochemical properties such as no effective vapor pressures, a wide range of viscosities, high stability, and the capacity of undergoing multiple solvation interactions with many types of molecules [1]. ILs can dissolve various organic and inorganic compounds and can be designed to be immiscible or miscible with water and many organic solvents. Since Freemantle effectively launched a renaissance in scientific and engineering interest in ionic liquids [2], researches and applications of ILs were expanded tremendously. There are now over 8000 papers about ionic liquids from solvents, separation to pharmaceuticals and so on [3]. There are also several reviews about the application of ILs in all areas of analytical chemistry [4–8].

Among these reports, ILs are suitable for liquid phase microextraction (LPME) for their unique properties such as high viscosity, minimal vapor pressure and compatibility with high performance liquid chromatography (HPLC) [5]. LPME is an excellent pretreatment method which overcomes many of the disadvantages of liquid liquid extraction (LLE) as well as some of those of solid phase microextraction (SPME) [9]. In various LPME modes, hollow-fiber protected liquid phase microextraction (HF-LPME) is a dazzling one and two extraction modes including two-phase extraction and three-phase extraction (extraction/back extraction) are usually used in HF-LPME [10]. There have been several reviews summarized from extraction principles, historical development, fundamental theory and performance [9–13].

In 2003, Jiang et al. firstly used immiscible ionic liquids as extraction solvents for enriching polycyclic aromatic hydrocarbons (PAHs) in environmental water samples with single drop direct-immersion and headspace liquid-phase microextraction

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[14]. From then on, ILs were introduced to various kinds of LPME methods. There were direct-immersion mode of single-drop liquid-phase microextraction for free benzophenone-3 [15], 4-nonylphenol (4-NP) and 4-tert-octylphenol [16]; headspace liquid-phase microextraction for phenols [17], dichlorodiphenyltrichloroethane and metabolites [18] or chlorinated anilines [19], and dynamic liquid-phase microextraction for anti-inflammatory drugs [20]. *In situ* derivatization with LPME was also adopted for formaldehyde in shiitake mushroom [21]. Based on the solubility of immiscible ionic liquids increasing with the temperature, the method of temperature-controlled ionic liquid dispersive liquid-phase microextraction was established for lead [22], pyrethroid pesticides [23], organophosphorus pesticides [24] and so on. An ionic liquid single-drop in headspace mode under the aid of microwave radiation was also used [25]. Besides, ionic liquid single-drop microextraction coupled with gas chromatography/mass spectrography [26,27] or gas chromatography-electron capture detection [28] has been successfully applied. Since 2007, two literatures have been reported on the hollow fiber used to support immiscible ionic liquid for extraction [29,30].

As is mentioned above, immiscible ILs have received some development and application. But to the best of our knowledge, most application researches about separation and extraction with ILs are focused on immiscible ILs, which is regrettable. It seems that the water-miscible ILs play subsidiary role. Actually, water-miscible ILs are mutually soluble with water, acidic or alkaline aqueous solutions (such as NaOH or HCl solutions). Moreover, some of them can be seen as Lewis acid or Lewis base that help to adjust ionic forms of analytes in acceptor phase. Furthermore, they have some desired inherent characteristics such as good extraction capability similar to organic solvents. So, we think water-miscible ILs can be expected to be acceptor phase additive of HF-LPME for different natures of compounds.

In this paper, a kind of water-miscible ionic liquids 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) was attempted to be preliminary evaluated as acceptor phase additive in HF-LPME (we defined it as IL-three phase HF-LPME) for extraction of alkaline, acidic or neutral compounds. As a kind of neutral compounds, PAHs cannot be extracted with normal three phase LPME mode which use water or pH adjusted solution. But with the proposed IL-three phase HF-LPME method, it can be extracted well. So an integral extraction and determination method for model compounds of polycyclic aromatic hydrocarbons (PAHs) in river water was established with proposed method. It is hoped that the proposed method will have a great potential in sample preparation of HF-LPME.

2. Experimental procedures

2.1. Chemicals and reagents

Alkaline compounds including clenbuterol, metoprolol, carteolol, propranolol were Chemical Reference Substances and purchased from National Institute for the Control of Pharmaceutical and Biological Products (Beijing, China). Acidic compounds including diethylstilbestrol (purity > 98%), hexestrol (purity > 99%), phenol (purity > 98%) and bisphenol A (purity > 99.3%) were standard substances and obtained from Sigma (St. Louis, MO, USA). Neutral compounds including PAHs acenaphthylene (purity > 99%), fluorene (purity > 99%) and fluoranthene (purity > 99%) were standard substances and purchased from Wako Pure Chemical Industries, Ltd. Water-miscible ionic liquid 1-butyl-3-methylimidazolium chloride ([BMIM]Cl, see Fig. 1, purity > 97%) were obtained from Shanghai Chengjie Chemical Co., Ltd. (Shanghai, China). N-octyl alcohol was analytical reagent and from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

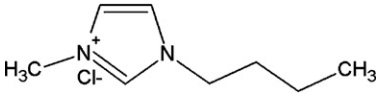

Fig. 1. Structure of [BMIM]Cl.

Stock standard solutions were all prepared in methanol for 1.0 mg mL^{-1} and diluted with ultrapure water, and then stored at 4 °C prior to use.

2.2. Instrumentation

An Agilent 1100 HPLC system (Agilent Technologies Deutschland GmbH, Waldbronn, Germany) equipped with a G1379 degasser and a G1311 quaternary solvent delivery system and a G1314 variable wavelength detector was used in the study.

The homemade HF-LPME device used in the experiments has been reported in our previous work [31]. Accurel Q3/2 polypropylene hollow fiber with a wall thickness of 200 μm (0.2 μm pore size) and an i.d. 600 μm was purchased from Membrana (Wuppertal, Germany) and each piece with effective length 2.0 cm was employed for HF-LPME. Milli-Q ultrapure water (Millipore, Bedford, USA) was used throughout the experiments.

2.3. Sample preparation

PAHs spiked deionized water samples were used in model optimization experiments. Real river water samples were collected from the Minjiang river in Fuzhou, Fujian, China. These samples were all stored at the temperature of 4 °C. Before use, they were filtered with 0.45 μm filter membrane. Real river water samples were used for validation experiments.

2.4. Extraction procedure

During HF-LPME, 5 mL of the water sample and the stirring bar were put in the volumetric flask, and the pH of the solution was adjusted for need.

Before the intake of 10 μL of acceptor phase solution, the microsyringe was respectively rinsed with 25 μL water, 25 μL methanol and 10 μL acceptor phase solution for three times. For each extraction, a new hollow fiber was used in order to avoid any possible contamination. Prior to extraction, a hollow fiber was connected to the tip of the HPLC microsyringe and then immersed in the organic phase (1-octyl alcohol) for 30 s. After that, 10 μL of acceptor solution was injected into the hollow fiber consequently sealed using tweezers. The assembly was then immersed into the sample solution directly. The extraction was carried out at room temperature (ca. 27 °C) under agitation for a certain time. After extraction, the acceptor solution was withdrawn into the syringe, and 5 μL of acceptor solution was injected into the HPLC system for the consequent analysis.

2.5. HPLC analysis

An Agilent Zorbax XDB-C8 column (150 mm length × 4.6 mm i.d., 5 μm particle size) was used for separation in the work. The gradient program of the elution profile and the mobile phase flow rate are presented in Table 1.

For acidic and neutral compounds, Solvent A is water; for alkaline compounds, Solvent A is phosphate solution (50 mmol L^{-1} KH_2PO_4, pH 3.0). All solutions were filtered through a 0.22 μm filter membrane before use. The flow rate of the mobile phase was 1.0 mL min^{-1}. Injection volume was 5 μL. The temperature of the LC column was kept at 27 ± 1 °C.

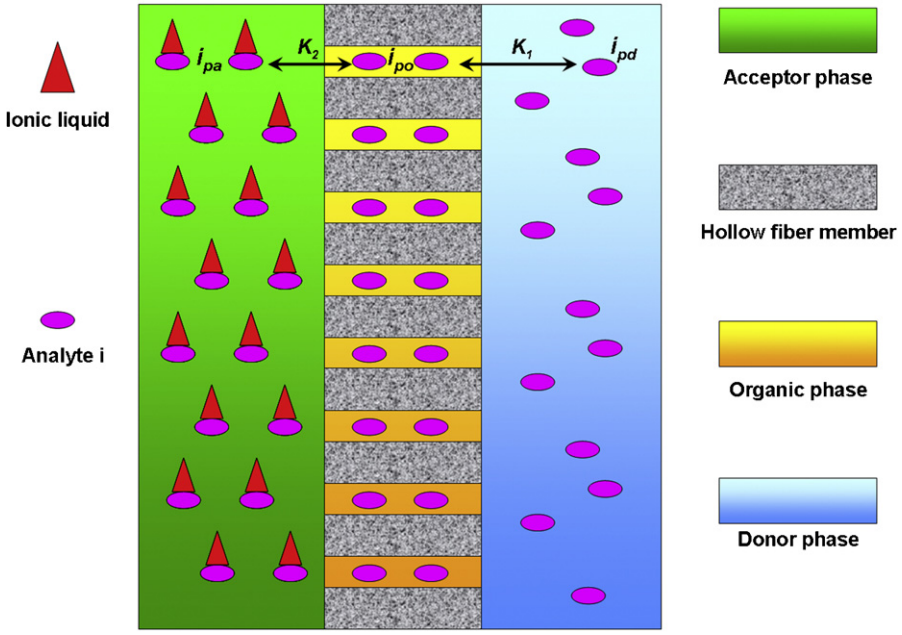

Fig. 2. Schematic diagram of the IL-three phase HF-LPME.

3. Results and discussion

3.1. Theory of IL-three phase HF-LPME

Three phases are involved in this extraction system; they are aqueous donor phase, organic phase and acceptor phase. The schematic diagram of the IL-three phase HF-LPME is shown in Fig. 2.

The extraction process can be represented by the following equation:

$$i_{pa} \overset{K_2}{\longleftrightarrow} i_{po} \overset{K_1}{\longleftrightarrow} i_{pd} \quad (1)$$

In which *i* means the analyte, *pd* is the aqueous donor phase, *po* is the organic phase immobilized in the pores of hollow fiber, and *pa* is the acceptor phase. In the first step of Eq. (1), the analyte *i* in *pd* distributes between *pd* and *po*. The distribution coefficient can be calculated as

$$K_1 = \frac{C_{po,eq}}{C_{pd,eq}} \quad (2)$$

In the second step, *i* distributes between *po* and *pa*. The distribution coefficient is expressed by

$$K_2 = \frac{C_{pa,eq}}{C_{po,eq}} \quad (3)$$

where $C_{pd,eq}$, $C_{po,eq}$, and $C_{pa,eq}$ are the concentrations of *i* in *pd*, *po*, and *pa*, respectively, under equilibrium conditions. The enrichment factor (*EF*) is defined as the ratio of the final concentration of analyte in acceptor phase to the initial concentration of analyte in donor phase ($C_{pd,initial}$).

$$EF = \frac{C_{pa,final}}{C_{pd,initial}} \quad (4)$$

3.2. Preliminary extraction performance of [BMIM]Cl for acidic, alkaline and neutral organics

Four acidic compounds (diethylstilbestrol, hexestrol, phenol and bisphenol A), four alkaline compounds (clenbuterol, metoprolol, carteolol, propranolol) and three neutral compounds (acenaphthylene, fluorene, fluoranthene) were selected to display the extraction performances of water-soluble ionic liquid ([BMIM]Cl). The extraction results were respectively compared with conventional three phase HF-LPME in which 1-octyl alcohol was adopted as organic phase.

Fig. 3 shows that using 1.0 mM HCl mixed with 15% (v/v) saturated [BMIM]Cl solution as acceptor has a little better extraction performance for alkaline compounds than conventional three phase HF-LPME with 1.0 mM HCl in acceptor phase.

For extraction acidic compounds, 100 mM NaOH mixed with 15% (v/v) saturated [BMIM]Cl solution was used as acceptor phase in IL-three phase HF-LPME. It can be seen from Fig. 4 that conventional three phase HF-LPME with 100 mM NaOH in acceptor phase

Table 1
Gradient program of the elution profile.

	Gradient elution program			Detection program	
	Time (min)	Solvent A	Solvent B	Time (min)	Ultraviolet wavelength (nm)
Acidic	0.00	Water (40%)	Methanol (60%)	0.00	270
	5.00	Water (20%)	Methanol (80%)	3.90	230
Neutral	0.00	Water (20%)	Methanol (80%)	0.00	270
				3.20	230
				4.00	254
				4.90	235
Alkaline	0.00	Phosphate solution (80%)	Methanol (20%)	0.00	370
	10.00	Phosphate solution (40%)	Methanol (60%)	3.20	220

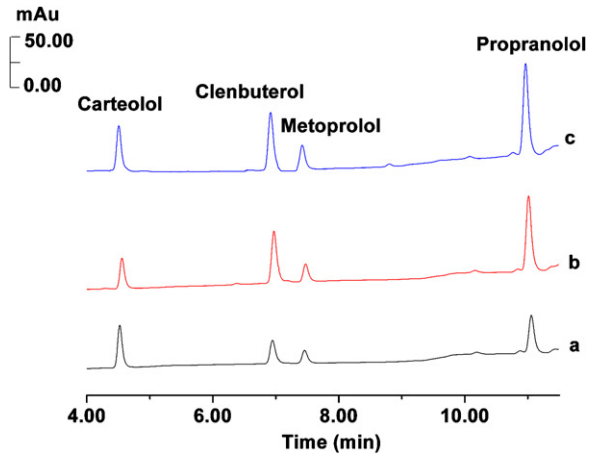

Fig. 3. Comparison of extraction performance for alkalinous compounds. (a) Direct injection 10 μg/mL standard solutions, (b) conventional three phase HF-LPME with 1.0 mM HCl in acceptor phase, and (c) 1.0 mM HCl + 15% saturated ionic liquid in acceptor phase. Conditions for a and b: analytes 0.4 μg/mL, respectively; stirring speed 600 rpm; extraction temperature 30 °C; extraction time 10 min; no salt; donor phase pH 11.00.

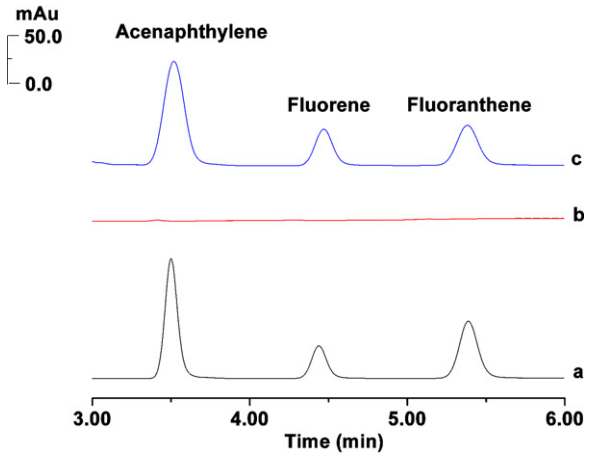

Fig. 5. Comparison of extraction performance for neutral compounds. (a) Direct injection 10 μg/mL standard solutions, (b) Water in acceptor phase, and (c) 4.5 mol L^{-1} ionic liquid in acceptor phase. Conditions for a and b: analytes 0.4 μg/mL, respectively; stirring speed 1050 rpm; extraction temperature 30 °C; extraction time 10 min; no salt.

exhibits better extraction performance for hexestrol while IL-three phase HF-LPME is better for phenol.

For the neutral compounds, it can be seen from Fig. 5 that the IL-three phase HF-LPME used 4.5 mol L^{-1} [BMIM]Cl as acceptor phase exhibits good extraction performance, while conventional three phase LPME is ineffective for neutral compounds. It illustrated the extractions of neutral compounds are because of the partition between organic solvent (1-octyl alcohol) and [BMIM]Cl.

Therefore, it can be concluded that water-soluble ionic liquid [BMIM]Cl is a kind of effective multifunctional extract acceptor phase additive for acidic, alkaline and neutral organics and the extraction efficiency is partly depended on the properties of target analytes.

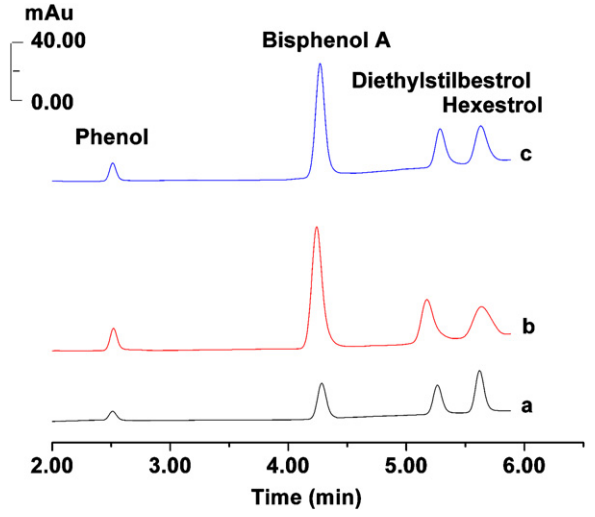

Fig. 4. Comparison of extraction performance for acidic compounds. (a) Direct injection 10 μg/mL standard solutions, (b) conventional three phase HF-LPME with 100 mM NaOH in acceptor phase, and (c) 100 mM NaOH + 15% saturated ionic liquid in acceptor phase. Conditions for a and b: analytes 0.4 μg/mL, respectively; stirring speed 600 rpm; extraction temperature 30 °C; extraction time 10 min; no salt; donor phase pH 3.00.

3.3. Optimization of IL-three phase HF-LPME conditions for PAHs

In this paper, PAHs (acenaphthylene, fluorene and fluoranthene) were chosen as model compounds to establish a complete extraction and analysis system with this IL-LPME and HPLC method. The effects of concentrations of IL, extraction temperature, stirring speed, salt concentration, extraction time and concentration of methanol were optimized. This IL-LPME method was then evaluated on the basis of enrichment factor, reproducibility and linearity for the PAHs in real river samples.

The effect of concentration and viscosity of [BMIM]Cl on the extraction performance was investigated in the range of 1.8–5.4 mol L^{-1}, and the result was shown in Fig. 6a. It can be seen that the response of three PAHs is increased with the increase of [BMIM]Cl from 1.8 to 4.5 mol L^{-1}, which is probably because the higher concentration of [BMIM]Cl can extract more analytes. When [BMIM]Cl exceeded 4.5 mol L^{-1}, the peak areas of PAHs are declined and it is perhaps due to the fact that the high viscosity of [BMIM]Cl would affect mass transfer and diffusion of PAHs. So, 4.5 mol L^{-1} [BMIM]Cl is chosen in the subsequent experiment.

Temperature could have significant effects on efficiency of extraction process, because it would affect both kinetics and thermodynamics of the diffusion process of analytes during extraction. Besides, high temperature would raise loss of organic phase and decrease precision [32]. The effect of temperature was studied under 30, 35, 40, 45, 50 and 55 °C, respectively, and 40 °C was found to be the best temperature for further work.

The extraction of the analytes from the water sample into the organic phase and then into the acceptor phase can be described as a slow equilibrium processes. Hence, the extraction time is expected to play an important role in the extraction efficiency of the process. It was found from Fig. 6b that acenaphthylene, fluorene and fluoranthene could reach equilibrium after 15 min; therefore, the extraction time of 15 min was used for all subsequent experiments.

Mass transfer of target compounds through the organic solvent which resides in the pores of the fiber can be improved by agitation. With agitation, a new and fresh interface between aqueous phase and organic phase will be provided continuously, thereby increasing the extraction efficiency.

The effect of stirring speed on the extraction efficiency was investigated in a range of 600–1200 rpm. It was found that the extraction efficiency of acenaphthylene, fluorene and fluoranthene had good peak responses at 1050 rpm. Then they showed obviously

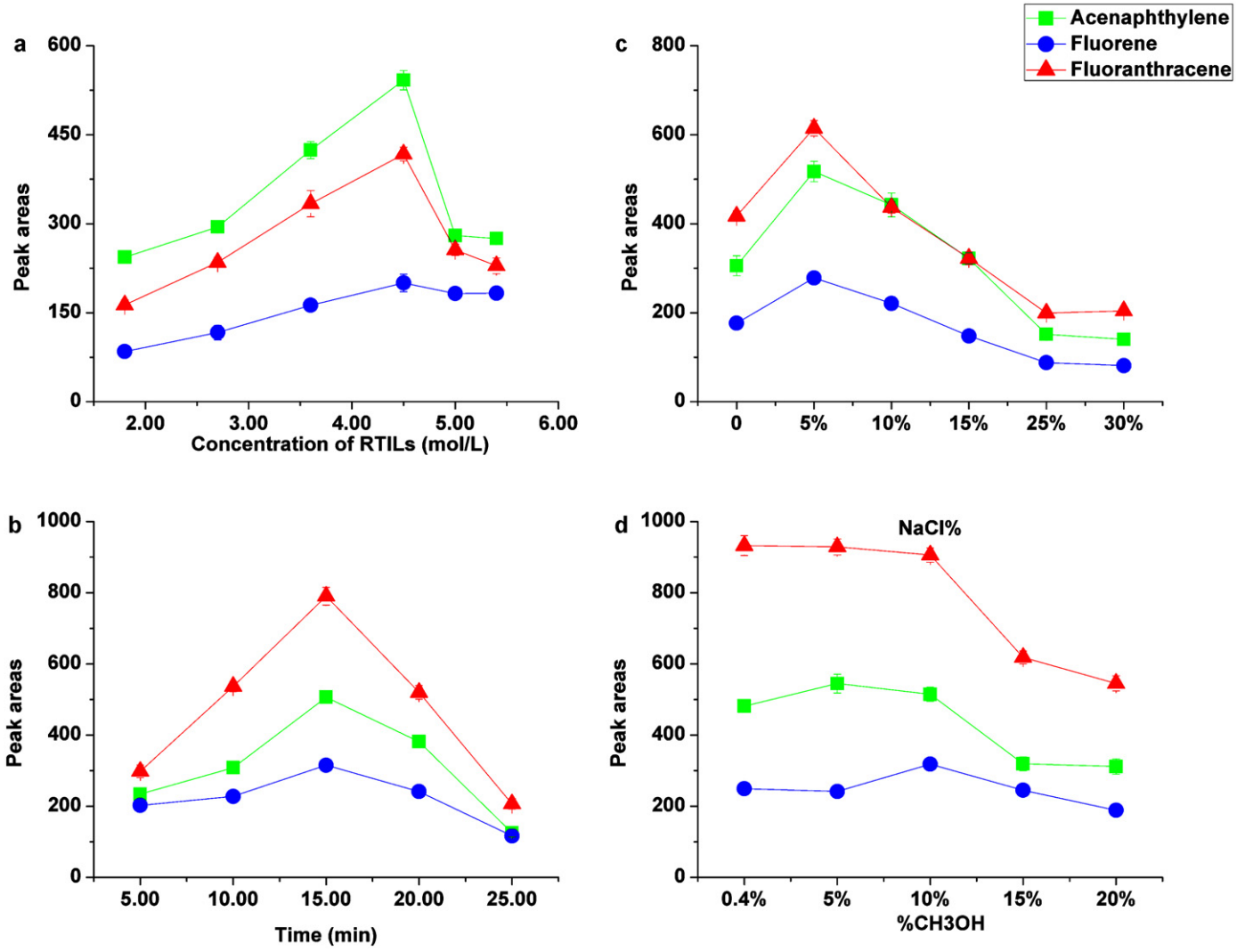

Fig. 6. Optimization of extraction process. Conditions: analytes 0.4 μg/mL, respectively; stirring speed 1050 rpm; extraction temperature 40 °C.

decreasing trend with increasing stirring speed up to 1200 rpm. Hence the stirring speed was set at 1050 rpm in subsequent experiments.

PAHs are a kind of neutral materials, so pH of donor phase does not affect the extraction results and does not be adjusted. Increasing the ionic strength of the sample solution has been shown to decrease the affinities of the analytes for the aqueous matrix and results in enhancing the extraction effect. So, spiked water samples with various concentrations of NaCl in the range of 0–30% (w/v) were tested. It was observed from Fig. 6c that 5% NaCl (w/v) yielded the most extracted amounts of three PAHs.

Because of the adsorption of PAHs onto the vessel surface and the low aqueous solubility of PAHs, it is necessary to add organic solvent such as methanol, acetonitrile or 2-propanol into the sample solution [33]. In this work, the effect of different concentration of methanol for extracting PAH was studied in Fig. 6d. From 0.4 to 10% of methanol, response of three PAHs were stable and then methanol concentration increased the dissolved amount of the 1-octyl alcohol liquid membrane in the sample solution, leading to low analytical response for the PAHs. So, 0.4% (v/v) methanol was used in the following studies.

To sum up, the optimum conditions of extraction were as follows: in 5 mL spiked water solution including 5% (w/v) NaCl and 0.4% (v/v) methanol, 2.0 cm hollow fiber was used. 1-Octyl alcohol was used as organic phase, while 4.5 mol L^{-1} [BMIM]Cl as acceptor phase and the extraction process was performed in 40 °C for 15 min with 1050 rpm stirring.

Fig. 7 shows the typical chromatograms of 10 μg/mL standards by direct injection and 0.4 μg/mL analytes under the optimum conditions. It can be seen that the three PAHs have been well extracted with obvious peaks and sharp profiles.

3.4. Method validation

For evaluating the proposed IL-LPME method, real water samples from Minjiang river (Fuzhou, Fujian, China) were adopted for method validation. Since there are no PAHs in the water, spiked real river water is analyzed. Some characters of the proposed method such as linear range, correlation coefficients, limits of detection (LODs), limits of quantitation (LOQs), the intra-day precision ($n = 5$) and the inter-day precision ($n = 3$) were all investigated by enriching 5 mL of the spiked river water samples and compared with direct injection procedure of 5 μL PAHs standard solution (see Table 2).

The linearity was good for all analytes in the whole range of tested concentrations ($R^2 > 0.9956$) with a detection limit (S/N = 3) of 0.25 ng mL^{-1} for all analytes, while the detection limit of direction injection without IL-three phase HF-LPME pre-concentration

Table 2
Regression equations, linear ranges, correlation coefficients, limits of detection and enrichment factors.

Analytes[a]		Linear range (ng mL^{-1})	R^2	LOQs (ng mL^{-1})	LOD[b] (ng mL^{-1})	Enrichment factor[c]	Intra-day precision (n = 5)[d]	Inter-day precision (n = 3)[d]
Acenaphthylene	Direct injection	25–1000	0.9997	25	10	54	–	–
	After LPME	1–100	0.9991	1	0.25		5.21	5.54
Fluorene	Direct injection	25–1000	0.9999	25	10	53	–	–
	After LPME	1–200	0.9989	1	0.25		6.70	5.25
Fluoranthene	Direct injection	25–1000	0.9987	25	10	45	–	–
	After LPME	1–200	0.9956	1	0.25		5.88	4.93

–, did not calculated.
[a] The same experimental conditions as in Fig. 7.
[b] S/N = 3.
[c] 20 ng mL^{-1} in donor phase, respectively.
[d] 10 ng mL^{-1} in donor phase, respectively.

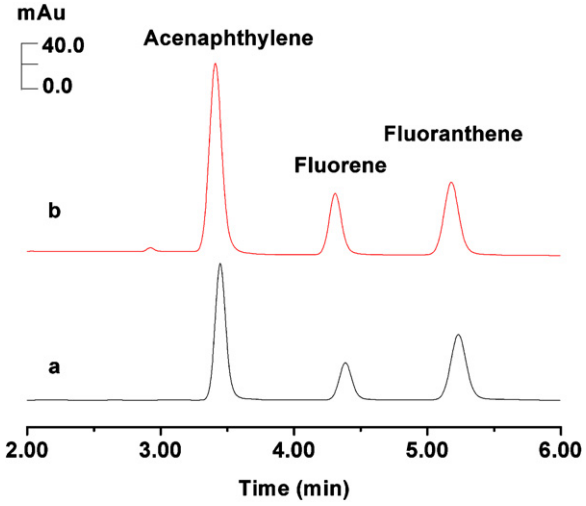

Fig. 7. Typical chromatograms of three PAHs before and after extraction. (a) Before extraction, 10 μg/mL, respectively and (b) after extraction, 0.4 μg/mL, respectively. Conditions: IL concentration 4.5 mol L^{-1}; stirring speed 1050 rpm; extraction temperature 40 °C; extraction time 15 min; 5% NaCl; 0.4% CH_3OH.

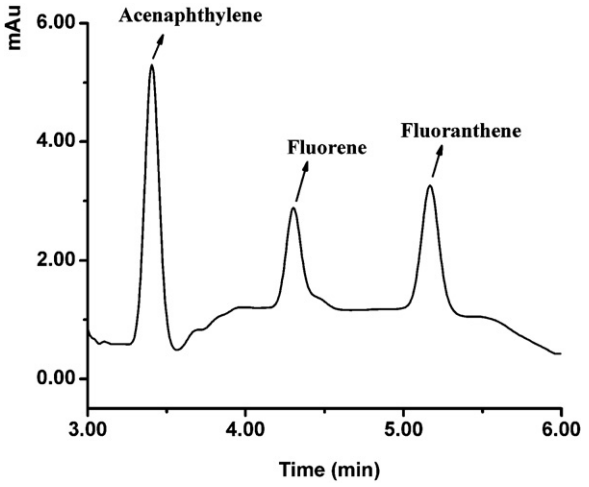

Fig. 8. Typical chromatograms of three PAHs in spiked river water sample. Conditions: analytes 20 ng mL^{-1}, respectively; IL concentration 4.5 mol L^{-1}; stirring speed 1050 rpm; extraction temperature 40 °C; extraction time 15 min; 5% NaCl; 0.4% CH_3OH.

was 10 ng mL^{-1} for all analytes. Obviously, after the pretreatment, LODs of PAHs have been improved greatly. The typical chromatogram of the spiked Minjiang river water sample after HF-LPME and analysis by HPLC under the optimum conditions is shown in Fig. 8.

The enrichment factor (EF) was defined as the ratio of analyte concentration in acceptor phase after HF-LPME to initial concentration of analyte in donor phase. The proposed HF-LPME method provided good enrichment factors, which were 54-fold for acenaphthylene, 53-fold for fluorene and 45-fold for fluoranthene, respectively. Under optimum conditions, the intra-day precisions of this LPME–HPLC method (n = 5) are in the range of 5.21–6.70% and the inter-day precisions (n = 3) are in the range of 4.93–5.54%.

3.5. Application

Finally, the developed method was applied to the analysis of real water samples that were collected from Minjiang river, Wulong Jiang river and rain water. Since all the samples are free of PAHs, the samples are spiked with two concentration of PAHs (10 ng mL^{-1} and 100 ng mL^{-1}, respectively). The analytical results of the recoveries and precisions (R.S.D.) for the spiked samples (n = 3) were given in Table 3. The back-calculated average concentrations of PAHs in acceptor phase were also given. As could be seen, acenaphthylene, fluorene and fluoranthene in the three kinds of real water did not show significant differences. The recoveries are in the range of 90.97–109.7% and the precisions are in the range of 2.53–7.01%.

Table 3
Method recoveries (PAHs concentration in accptor phase) and precisions of spiked river water samples by IL-three phase HF-LPME[a] (n = 3).

	$C_{i,pd}$ (ng mL^{-1})	Recoveries% ($C_{i,pa}$, ng mL^{-1}) Precisions (RSD%)		
		Acenaphthylene	Fluorene	Fluoranthene
Minjiang river water	10	100.3% (542.6) 4.07	105.7% (560.7) 3.97	90.97% (409.3) 4.47
	100	103.8% (5604) 2.53	100.5% (5327) 4.08	108.6% (4888) 4.13
Wulong Jiang river water	10	96.61% (521.7) 5.63	102.4% (542.6) 5.42	98.56% (443.5) 4.60
	100	94.34% (5094) 5.33	109.7% (5814) 4.79	105.2% (4732) 5.28
Rain water	10	101.5% (548.0) 6.99	106.1% (562.5) 7.01	99.72% (448.7) 6.46
	100	109.3% (5902) 6.55	111.3% (5900) 6. 27	108. 8% (4896) 7.00

[a] The same experimental conditions as in Fig. 7.

4. Conclusions

Water-miscible ionic liquids are a kind of ideal multifunctional acceptor phase additive because they have extraction capacity similar to organic solvents. Besides, they can be mixed with NaOH, HCl or deionized water; some of them can even be regarded as Lewis acid or alkali and help adjusting ionic forms of analytes in acceptor phase. And the using of hollow fiber could well protect water-miscible ionic liquid and reduces interference of matrices.

In this paper, water-miscible ionic liquid was the first time used as a novel multifunctional acceptor phase additive in hollow fiber protected liquid phase microextraction. The extraction performances of the proposed extraction method towards alkaline, acidic and neutral compounds were studied and the extraction efficiency was depended on the kinds of IL, concentration of IL and NaOH/HCl, and the property of target analytes. For application of the proposed method, model compounds polycyclic aromatic hydrocarbons (PAHs) were determined in spiked Minjiang river water samples using HPLC-UV detector and LODs were lower than 0.25 ng mL^{-1}. The enrichment factor were found to be 54-fold for acenaphthylene, 53-fold for fluorene and 45-fold for fluoranthene (20 ng mL^{-1} in donor phase), respectively. Since water-miscible ionic liquids have various forms and can be conveniently adjusted by acid, alkali and buffer, the proposed method should have a great potential in sample preparation of liquid phase microextraction.

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