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Multiple functional ionic liquids based dispersive liquid–liquid microextraction combined with high performance chromatography for the determination of phenolic compounds in water samples

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ABSTRACT

A new mode of ionic liquid based dispersive liquid–liquid microextraction (IL-DLLME) is developed. In this work, [C_6MIm][PF_6] was chosen as the extraction solvent, and two kinds of hydrophilic ionic liquids, [EMIm][BF_4] and [BSO_3HMIm][OTf], functioned as the dispersive solvent. So in the whole extraction procedure, no organic solvent was used. With the aid of SO_3H group, the acidic compound was extracted from the sample solution without pH adjustment. Two phenolic compounds, namely, 2-naphthol and 4-nitrophenol were chosen as the target analytes. Important parameters affecting the extraction efficiency, such as the type of hydrophilic ionic liquids, the volume ratio of [EMIm][BF_4] to [BSO_3HMIm][OTf], type and volume of extraction solvent, pH value of sample solution, sonication time, extraction time and centrifugation time were investigated and optimized. Under the optimized extraction conditions, the method exhibited good sensitivity with the limits of detection (LODs) at 5.5 μg $L^{-1}$and 10.0 μg L^{-1} for 4-nitrophenol and 2-naphthol, respectively. Good linearity over the concentration ranges of 24–384 μg L^{-1} for 4-nitrophenol and 28–336 μg L^{-1} for 2-naphthol was obtained with correlation coefficients of 0.9998 and 0.9961, respectively. The proposed method can directly extract acidic compound from environmental sample or even more complex sample matrix without any pH adjustment procedure.

1. Introduction

Dispersive liquid – liquid microextraction (DLLME) [1] was introduced by Assadi and co-workers in 2006 based on the homogeneous liquid – liquid extraction (HLLE) and cloud point extraction (CPE). In DLLME, the water immiscible extraction solvent is dispersed as fine droplets in sample solution with the effect of water-miscible polar dispersive solvent, and the mass transfer of target analytes is completed in a split second through the infinite large contact area between extraction solvents and sample solution. In the dispersion step, many kinds of external force are used to help the extraction solvent completely disperse into the sample solution including temperature [2], ultrasound [3], and microwave [4]. And most recently, a combination of vortex and ultrasound was first used to enhance the dispersion of extraction solvent [5,6]. All the methods mentioned above increase the extraction efficiency. After dispersion step, phase separation is achieved by centrifugation and then the enriched analytes in the sedimented phase are determined by analytical instrument. This mode has exhibited excellent extraction capability and has been successfully applied in medicinal [7], environmental [8–10], biological field [11–13] and food samples [14,15].

Recently, many researchers have focused on the application of ILs in DLLME [9,16,17] responding to the growing demand for green, environment-friendly techniques. Room-temperature ionic liquids (RTILs), a category of non-molecular ionic solvent with low melting points, are composed of organic cations and various organic or inorganic anions. Owing to the characteristics of low volatility, low toxicity, high thermal stability and good extraction capacity for most organic compounds, ILs are considered as the appropriate replacement for conventional organic solvent. IL-DLLME was first reported in 2008 by Zhou [18], and has received many attentions in recent years. In an IL-DLLME research, types of extraction solvent and the dispersion degree are the most important parameters influencing the extraction efficiency. According to the former researches, the alkylimidazolium hexafluorophosphate-based ILs were most widely used as extraction solvent, so the researches of

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IL-DLLME have focused on the improvement of dispersion degree of extraction solvent. Until now, three types of dispersive methods have been proposed: The first method is with the aid of external force such as temperature [19,20], ultrasound [21,22] and microwave [4] to help the ILs disperse into sample solution; the second approach is in situ IL DLLME [23] involving an in situ metathesis reaction. More recently a completely non-organic solvent IL-DLLME was introduced. In this approach, the hydrophilic ionic liquid [EMIm][BF_4] was used as the dispersive solvent to help the extraction solvent hydrophobic ionic liquid [C_8MIm][PF_6] totally disperse into the sample solution, most importantly of all, no traditional organic solvent was utilized [24]. This method provided a potential mode for IL-DLLME, by which the extraction procedure is completely environment-friendly.

But in the above research, the researchers only used the hydrophilic property of ionic liquid, actually the ILs are known as custom-designed solvent for their selectivity and sensitivity for special kinds of organic compounds by introducing functional groups into the structures, which is the most important advantage comparing to organic solvent during extraction. So in this research, two types of ionic liquids including [EMIm][BF_4] and [BSO_3HMIm][OTf] with a SO_3H group covalently linked through an alkyl chain to the cation were introduced serving as dispersive solvent. According to the reported researches [25], [BSO_3HMIm][OTf] can exhibit acidity in water solution. So [BSO_3HMIm][OTf] used in this research not only act as the dispersive solvent, but also act as a pH modifier. With the volume change of [BSO_3HMIm][OTf], the pH of sample solution will be changed at the same time avoiding extra pH adjustment.

In this research, we aimed to explore the extraction performance and application of the [BSO_3HMIm][OTf] involved multiple functional ionic liquids in dispersive liquid–liquid microextraction. So the target analytes should be acidic to meet the research aim.

Industrial wastewater has been the most urgent problem for environmental protection. The phenolic compounds are the major contaminants presented in environmental water, among which 4-nitrophenol and 2-naphthol, as the intermediates or precursors for the production of insecticides, pharmaceuticals and dyes, have been regarded as the very important ones. Due to the high toxicity and carcinogenicity, 4-nitrophenol is even included in the list of priority pollutants in many countries. According to the present Environmental Quality Standards for Surface Water in China [26], the content of phenolic compounds in surface water should be below 100 $\mu g\ L^{-1}$. So considering low concentration of phenolic compound in aqueous samples, the sample preparation process is necessary before instrumental analysis. Solid-phase extraction (SPE) [27], liquid–liquid extraction (LLE) [28], solid-phase microextraction (SPME) [29,30] and liquid-phase microextraction (LPME) [31,32] have been successively developed for the enrichment of phenolic compounds.

In this research, a new mode of IL-DLLME based on hydrophilic and hydrophobic ionic liquids are developed for the determination of two acidic phenolic compounds, 2-naphthol and 4-nitrophenol, in environmental water. The possible factors affecting extraction efficiency, such as the type of hydrophilic ionic liquids, the ratio of [EMIm][BF_4] to [BSO_3HMIm][OTf], type and volume of extraction solvent, pH value of sample solution, sonication time, extraction time and centrifugation time, were investigated and optimized.

2. Experimental

2.1. Chemicals and reagents

2-naphthol (2-NA) and 4-nitrophenol (4-NP) were obtained from Alfa Aesar (Tianjin, China) and their purities were > 99%. Chromatographic-grade methanol and acetonitrile were purchased from Merck Co. (Darmstadt, Germany). Ionic liquids of 1-butyl-3-methylmidazolium hexafluorophosphate ([C_4MIm][PF_6]), 1-hexyl-3-methylmidazolium hexafluorophosphate ([C_6MIm][PF_6]), 1-octyl-3-methylimidazolium hexafluorophosphate ([C_8MIm][PF_6]), 1-ehthy-3-methylimidazolium tetrafluoroborate [EMIm][BF_4] and 1-sulfobutyl-3-methylimidazolium trifluoromethanesulfate [BSO_3H-MIm][OTf] were obtained from Lanzhou Institute of Chemical Physics of CAS (Lanzhou, China). Other chemicals are of analytical grade and purchased from Tianjin Chemical Reagent Co. (Tianjin, China). Ultrapure water (18.20 MΩ cm, 25 °C) obtained from a OKP-S210 purification system (Shanghai Laikie Instrument Co., Ltd, Shanghai, China) was used for the preparation of mobile phase and sample solution.

2.2. Apparatus

An Agilent 1200 HPLC system comprising a G1312A binary pump, a G1315D diode-array detector and a G1328B manual injector was used for chromatographic analysis. Chromatographic separation of the analytes was performed on a Kromasil C_{18} column (5 μm, 4.6 mm × 250 mm i.d.) (Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China). Agilent ChemStation was employed to acquire and process chromatographic data. The mobile phase was consisted of methanol–water (75:25, v/v) at a flow rate of 1.0 $mL\ min^{-1}$. The column temperature was maintained at 25 °C. The detection wavelengths were set at 313 nm for 4-nitrophenol and 274.5 nm for 2-naphthol.

2.3. Preparation of stock solution and environmental water samples

The stock standard solution of 2-naphthol and 4-nitrophenol were prepared in methanol of HPLC grade with concentration of 0.35 and 0.10 $mg\ mL^{-1}$, respectively, and stored at 4 °C before use. Then the working solutions were prepared freshly by diluting the stock solution with ultrapure water and used immediately for the optimization of IL/IL DLLME procedure and the method validation. Calibration standard solutions containing 2-nathphol and 4-nitrophenol were prepared by ultrapure water over the concentration range of 28–336 and 24–384 $\mu g\ L^{-1}$.

Three local environmental water samples, including tap water, snow water and river water, were collected. The tap water was obtained from our lab, and the snow water was collected in Lanzhou, China. The river water was collected from the Yellow River (Lanzhou, China). These samples were all filtered through a 0.45 μm filter and stocked in amber glass at 4 °C avoiding light.

2.4. Ultrasound-assisted IL/IL-DLLME procedure

First, 5 mL aqueous sample was placed in a 10 mL screwcap glass conical tube without pH adjustment. Then the mixture of 65 μL [C_6MIm][PF_6], 120 μL [EMIm][BF_4], and 30 μL [BSO_3HMIm][OTf] were rapidly injected into the tube and the cloudy solution was formed. Subsequently, the tube was immersed in an ultrasonic water bath (KQ500DB, Kunshan, China), and sonicated at 200 W power for 5 min at room temperature. Then the cooling step was carried out for 20 min, and the phase separation was achieved by 8 min centrifugation. Finally, the upper aqueous phase was disposed by a pipette and the sedimented phase was diluted to 60 μL with methanol. 10 μL filtrates was injected into the HPLC system for analysis.

3. Results and discussion

3.1. Optimization of ultrasound assisted IL/IL-DLLME

The present work focused on finding the optimum extraction conditions for the phenols in environmental water samples using hydrophilic ionic liquid as dispersive solvent. In order to obtain the best extraction efficiency, several influencing factors including the type of dispersive solvent, the volume ratio of [EMIm][BF_4] to [BSO_3HMIm][OTf], the type and volume of extraction solvent, ultrasound time, cooling time, and centrifugation time were evaluated. 5 mL working solution containing 100 μg L^{-1} 2-naphthol and 4-nitrophenol were used for the optimization and all the experiments were carried in triplicate.

3.1.1. Selection of dispersive solvent and volume ratio of [EMIm][BF_4] to [BSO_3HMIm][OTf]

In conventional DLLME, polar organic solvent such as methanol, acetonitrile, acetone, ethanol and tetrahydrofuran are used as dispersive solvent. But in IL/IL DLLME procedure, the hydrophilic IL is utilized as the dispersive solvent avoiding the usage of organic solvent. Besides that, the acid hydrophilic IL was added acting as a pH modifier avoiding additional pH adjustment.

Three polar organic solvent methanol, acetonitrile and acetone, along with two kinds of hydrophilic ILs [BSO_3HMIm][OTf] and [EMIm][BF_4] were separately selected as potential dispersive solvents, and their effects on the extraction recoveries were compared. In this procedure, the pH value of working solution was adjusted to 2.0. According to the obtained results (Fig. 1), methanol, acetone, and [EMIm][BF_4] achieved similar high recoveries, which suggest it is workable using hydrophilic ionic liquids as dispersive solvent. However, the extraction recovery provided by [BSO_3HMIm][OTf] was very low, which could be contributed to its acidity. After adding 0.15 mL [BSO_3HMIm][OTf], the solution pH value decreased to below 1.0, and at such a pH value, the cloudy state could not formed. So [BSO_3HMIm][OTf] could not be used alone as dispersive solvent. Afterwards, 0.15 mL mixture of [EMIm][BF_4] and [BSO_3HMIm][OTf] at a ratio of 4:1 was tested in working solution ($pH=7.0$) without additional pH adjustment. After injecting the mixture, the solution pH value was changed to 2.02 and the highest recovery was obtained compared with those provided by organic solvent or single [EMIm][BF_4]. Even more noteworthy is that the use of [BSO_3HMIm][OTf] avoids the pH adjustment and simplifies the operation steps. Therefore, the mixture of [EMIm][BF_4] and [BSO_3HMIm] [OTf] was selected as the dispersive solvent.

The volume of dispersive solvent and the ratio of [EMIm][BF_4] to [BSO_3HMIm][OTf] were subsequently optimized. The volume of dispersive solution directly influences the dispersion degree of the extraction solvent and, subsequently, the extraction efficiency. As shown in Fig. 1, the highest recovery for both 4-NP and 2-NA could be achieved when the volume of dispersive solvent is 0.15 mL. When the volume was less than 0.15 mL, the extraction solvent could not be completely dispersed resulting poor cloudy state. When the volume exceeded 0.15 mL, the solubility of ionic liquids in the aqueous solution increased leading to small volume of sediment, which will decrease the extraction recovery as well. So the volume of dispersive solvent was fixed to 0.15 mL. The volume ratios of [EMIm][BF_4] to [BSO_3HMIm][OTf] ranging from 60/90 to 135/15 were also investigated. After injection of different ratios of mixture, the pH values changed in the range of 1.41–3.12 (Fig. 3a), and the highest recoveries were achieved at 120/30 when pH was 2.02 (Fig. 3b). At this pH value, the target analytes were kept in molecular form and prone to migration into the extraction phase. Finally, 0.15 mL mixture of [EMIm][BF_4] and [BSO_3HMIm] [OTf] at a volume ratio of 120/30 was used as the dispersive solvent to replace the traditional organic solvent in this research.

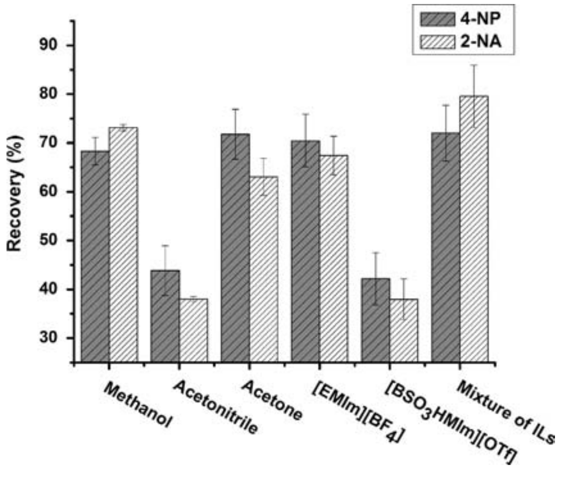

Fig. 1. Effect of dispersive solvent on the recovery of 2-naphthol (2-NA) and 4-nitrophenol (4-NA) ($n=3$). Extraction conditions: extraction solvent, 65 μL [C_6MIm][PF_6]; volume ratio of [EMIm][BF_4] to [BSO_3HMIm][OTf], 120/30; sonication time, 5 min; cooling time, 20 min; centrifugation time, 8 min at 3000 rpm.

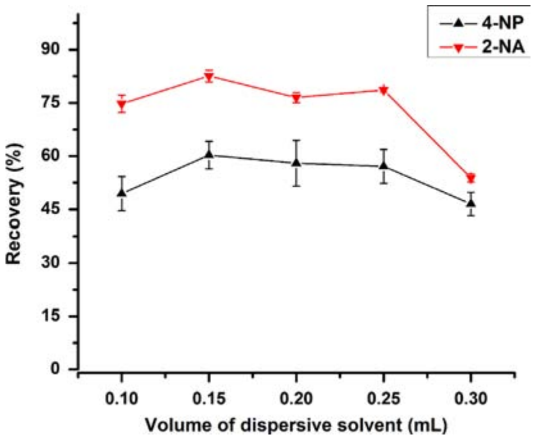

Fig. 2. Effect of the volume of dispersive solvent on the recovery of 2-naphthol (2-NA) and 4-nitrophenol (4-NA) ($n=3$). The other extraction conditions are the same as Fig. 1.

3.1.2. Selection of extraction solvent and effect of extraction solvent volume

In DLLME, the appropriate type and volume of extraction solvent are the major parameters for extraction efficiency. Hydrophobic ILs are selected to replace the traditional organic chlorinated solvents on the basis of their environment-friendly, low solubility in water, good extraction capability to target analytes and good chromatographic behavior. In this researches, three kinds of alkylimidazolium hexafluorophosphate-based ILs: [C_4MIm][PF_6], [C_6MIm][PF_6] and [C_8MIm][PF_6] were chosen. Their physical and chemical properties including the viscosity and solubility in water, which has huge effects on the formation of emulsion and volume of sedimented phase, change with the changes of the alkyl chain length. In this optimization procedure, 65 μL ILs was added into the aqueous sample solution and the obtained sediment were all diluted to 60 μL by methanol. As shown in the Fig. 4a, [C_6MIm][PF_6] exhibited the best extraction efficiency. For [C_4MIm][PF_6], its solubility in water was high (1.88 g/100 mL) causing little sediment, subsequently, low recovery. And the high viscosity of [C_8MIm][PF_6] hindered the dispersion in the aqueous sample solution which also resulted low recoveries. So [C_6MIm][PF_6] was selected as the extraction solvent. This may be contributed to the similar polarity between extraction solvent and target analytes.

The volume of extraction solvent directly influenced the volume of sediment phase thereafter affected the enrichment factor. Therefore, the optimal volume of extraction solvent should ensure both relative high enrichment factor and large enough

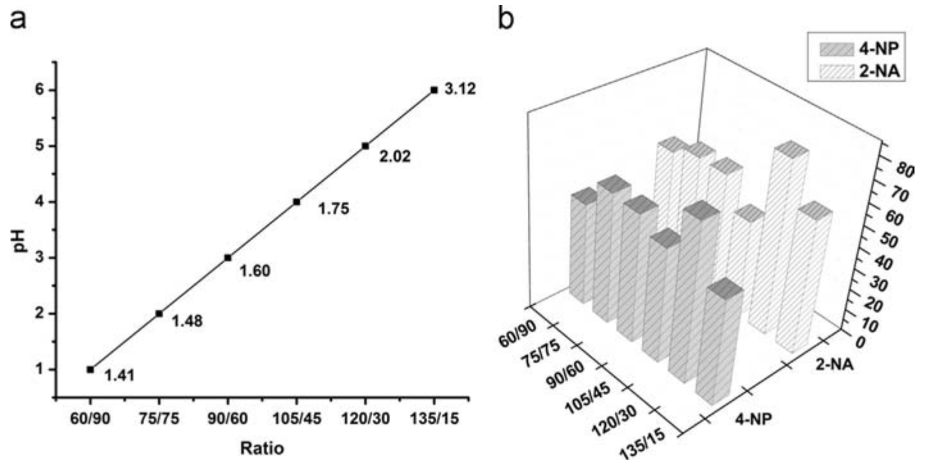

Fig. 3. Effect of (a) pH value and (b) ratio of [EMIm][BF_4] to [BSO_3HMIm][OTf] on the recovery of 2-naphthol (2-NA) and 4-nitrophenol (4-NA) ($n=3$). The other extraction conditions are the same as Fig. 1.

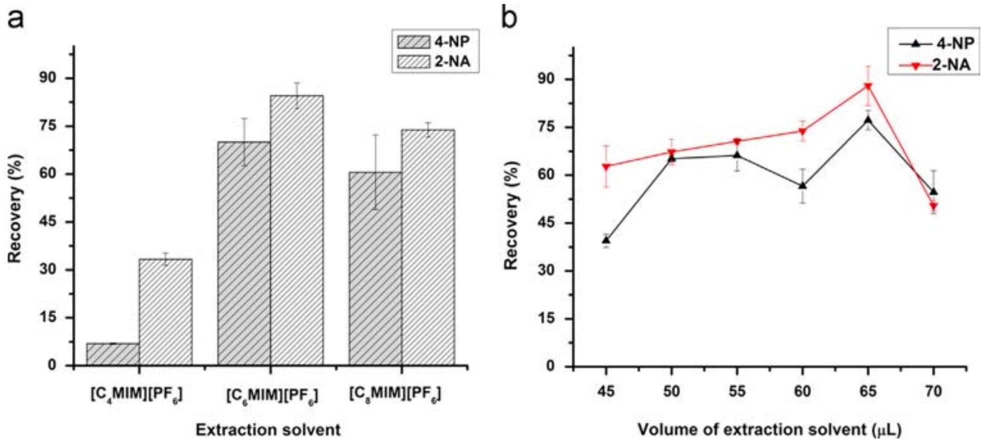

Fig. 4. Effect of (a) extraction solvent and (b) volume of extraction solvent on the recovery of 2-naphthol (2-NA) and 4-nitrophenol (4-NA) ($n=3$). The other extraction conditions are the same as Fig. 1.

volume of sediment for subsequent analysis. Out of this consideration, the volume of extraction solvent was evaluated from 45 to 70 μL at the interval of 5 μL. The results (Fig. 4b) showed that the recoveries of target analytes kept increasing with the increase of volume, but the highest enrichments factor were obtained at 65 μL, so it was chosen for the following optimization.

3.1.3. *Effect of sonication time*

In DLLME procedure, the equilibrium state of target analytes are quickly achieved through the large surface area between the extraction solvent and the aqueous sample. But the high viscosity of ILs would hinder the dispersion procedure and make poor formation of cloudy solution, subsequently decrease the extraction efficiency. So the sonication was introduced to help the hydrophobic ionic liquids disperse completely in the aqueous sample solution and form an excellent cloudy solution. The effect of sonication time was optimized in the range of 1–9 min at 200 W power at 25 °C. The results shown in Fig. 5a indicated that the recoveries of 2-naphthol and 4-nitrophenol increased from 1 min to 5 min, and achieved the maximum at 5 min, and then decreased slightly with the continuous increase of sonication time. This may be explained as follows: enough time could ensure ILs disperse entirely into the sample solution, but too long sonication time would cause the generation of heat, which increased the solubility of ILs in the sample solution. Hence, 5 min were chosen as the sonication time for the subsequent experiments.

3.1.4. *Effect of extraction time*

In DLLME, the surface area between extraction solvent and aqueous phase is infinitely large, through which the transfer of target analytes from aqueous sample solution to extraction solvent was achieved instantaneously. So the extraction time is defined as an interval between the finish of sonication and the beginning of centrifugation. In this moment, the conical tube was placed in the ice-water bath to help the ILs separated out from the aqueous sample solution so the extraction time could also be called cooling time. So the extraction time ranging from 5 to 25 min was investigated. As Fig. 5b shown, the recoveries of both 2-naphthol and 4-nitrophenol scarcely changed from 5 min to 20 min, but exceeding 20 min, the viscosity of IL increased with cooling time extending, and a few ILs could not be separated from aqueous phase in the subsequent centrifugation.

3.1.5. *Effect of centrifugation time*

Centrifugation is a crucial procedure that separates the IL phase from aqueous phase. Theoretically, a longer centrifugation time will cause more sediment and higher recoveries. But the evaluation of centrifugation time in the range of 2–14 min (Fig. 5c) shows that the best recoveries were obtained at 8 min. This can be

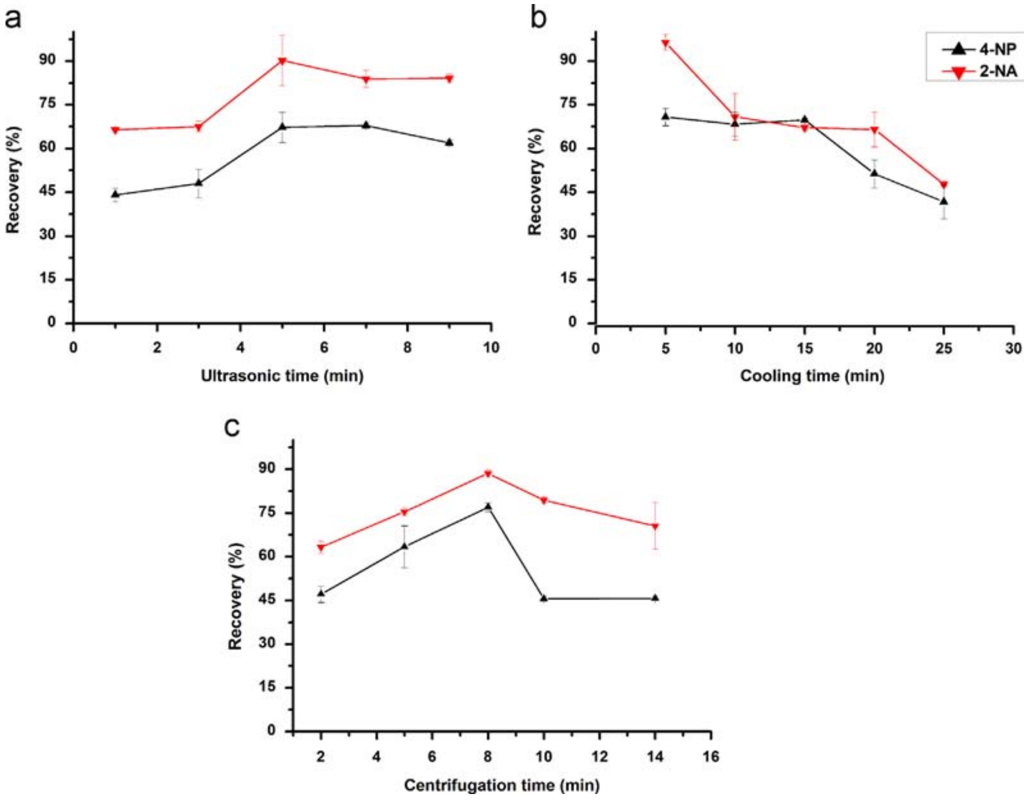

Fig. 5. Effect of (a) sonication time, (b) cooling time, (c) centrifugation time on the recovery of 2-naphthol (2-NA) and 4-nitrophenol (4-NA) (n=3). The other extraction conditions are the same as Fig. 1.

explained as that the ILs could not be separated completely and the volume of sediment was small with insufficient centrifugation time, but excessive time would generate heat causing loss of ILs and lose sensitivity. Considering this, 8 min was chosen as the centrifugation time.

3.2. Evaluation of method performance

A series of experiments were performed under the optimal experimental conditions for obtaining linear ranges, intra-and inter-day precision, and the limits of detection (LODs) and limits of quantification (LOQs). All the experiments were performed in triplicate.

Enrichment factor (EF) is calculated according to the following equation: $EF = C_{\text{dil}}/C_{\text{o}}$, where C_{dil} is the concentration of analyte in the diluents for HPLC analysis, and C_{o} is the concentration of analyte originally presented in the sample solution. Under the optimum conditions, and the EFs for 2-naphthol and 4-nitrophenol were 70 and 62 fold, respectively.

The calibration standard working solutions were extracted under the optimized DLLME procedure, and then analyzed by HPLC. The calibration curves were constructed by plotting the peak area (Y) against the original concentration (X) in the working solution by the corresponding five concentrations in triplicate. The linear equations are $Y = 2454.7X + 13773.9$ for 4-nirophenol in the range of 24–384 $\mu g\ L^{-1}$, and $Y = 1169.6X - 15977.8$ for 2-naphthol in the range of 28–336 $\mu g\ L^{-1}$. The correlation coefficients are 0.9998 for 4-nitrophenol and 0.9961 for 2-naphthol, respectively. The LODs were obtained by using a criterion signal equal to 3 times baseline noise and ranged from 5.5 $\mu g\ L^{-1}$ (4-nitrophenol) to 10.0 $\mu g\ L^{-1}$ (2-naphthol). The LOQs were 12.3 $\mu g\ L^{-1}$ for 4-nitrophenol and 25.4 $\mu g\ L^{-1}$ for 2-naphthol using a criterion of a signal-to-noise ratio of 10.

The precision of the instrument was evaluated by performing intra-day (n=5) and inter-day assays (n=5) replicate injection of 2-NA standard solution. Intra-assay precision was measured for continuous injections during the same day whereas inter-assay precision was measured on 5 days in two weeks. The RSD values of peak area were 1.08% for intra-day precision, and 2.31% for inter-day precision.

Nine replicate experiments of the environmental water samples spiked with 100 $\mu g\ L^{-1}$ 2-naphthol and 4-nitrophenol were performed under optimal conditions in one day to give relative standard deviations of 4.72% and 6.92%, respectively.

3.3. Method comparison

The present method was compared with the other reported methods for the determination of 4-nitrophenol and 2-naphthol in terms of extraction solvent, linearity, LOD, LOQ and recovery and the results are listed in Table 1. As what can be concluded, the present work could provide similar or even better extraction efficiency in a relatively short extraction time and no organic solvent is used in the whole extraction procedure.

3.4. Interference study

As the members of phenolic compound, phenol, 2-aminophenol, and 2-chlophenol are thought to be the most common pollutes contained in the environmental water. So the influences of phenol, 2-aminophenol, 2-chlophenol, and some inorganic species on the 4-nitrophenol and 2-naphthol signals were tested, and the results are shown in Table 2. Most of them showed no interference on 4-nitrophenol and 2-naphthol with the relative standard deviations less than 5.0% for triplicate experiments.

Table 1
Comparison of IL/IL DLLME with other methods for the determination of 4-nitrophenol and 2-naphthol.

Method	Compound	Extraction solvent	Linear range ($\mu g\ L^{-1}$)	LOD ($\mu g\ L^{-1}$)	LOQ ($\mu g\ L^{-1}$)	Recovery (%)	Reference
SPE-HPLC	4-nitrophenol	–	5–1000	1.1	–	92–106	[33]
SPME-HPLC	4-nitrophenol	Methanol	100–2500	18	–	–	[34]
HF-LPME-CE	4-nitrophenol	1-Octanol	50–300	40	160	88.9–90.3	[35]
Flow-through optosensor spectrofluorimetric system	2-naphthol	–	5–20	–	–	70–110	[36]
On-line clean-up column-switching liquid chromatography-fluorescence detection	2-naphthol	Acetonitrile and water	3–360	0.5	–	96–102	[37]
IL/IL DLLME	4-nitrophenol	$[C_6MIm][PF_6]$	24–384	5.5	12.3	87–104	This
	2-naphthol	$[C_6MIm][PF_6]$	28–336	10.8	25.4	98–107	method

Table 2
Influences of inorganic and organic species on the determination of 4-nitrophenol and 2-naphthol ($n=3$).

Interference	Concentration ($mol\ L^{-1}$)	Compound	Signal change (%)	RSD (%)
2-aminophenol	10^{-5}	4-nitrophenol	2.1	3.1
		2-naphthol	2.3	2.8
2-chlophenol	10^{-5}	4-nitrophenol	2.8	4.7
		2-naphthol	2.9	4.1
phenol	10^{-5}	4-nitrophenol	0.3	2.5
		2-naphthol	0.2	3.2
Fe^{3+}	10^{-5}	4-nitrophenol	−1.1	2.4
		2-naphthol	−1.3	3.6
Pb^{2+}	10^{-5}	4-nitrophenol	−1.8	2.8
		2-naphthol	−2.1	2.7
Cd^{2+}	10^{-5}	4-nitrophenol	−0.5	1.1
		2-naphthol	−0.9	1.9
Mn^{2+}	10^{-5}	4-nitrophenol	1.4	2.1
		2-naphthol	1.1	2.1
Zn^{2+}	10^{-5}	4-nitrophenol	−2.3	3.8
		2-naphthol	−3.1	2.8
Cl^-	10^{-5}	4-nitrophenol	−1.1	2.6
		2-naphthol	−1.5	1.9
CO_3^{2-}	10^{-5}	4-nitrophenol	−2.1	4.5
		2-naphthol	−2.7	3.9
NO_3^-	10^{-5}	4-nitrophenol	−1.4	4.4
		2-naphthol	−0.9	4.3

3.5. Application in real sample

The proposed IL/IL-DLLME-HPLC method was applied to determined 4-nitrophenol and 2-naphthol in water samples. 5 mL water sample was directly placed in a 10 mL screwcap glass conical tube without pH adjustment. Then 65 μL $[C_6MIm][PF_6]$ and 0.15 mL dispersive solvent composing of $[EMIm][BF_4]$ and $[BSO_3HMIm][OTf]$ in the ratio of 120/30 were injected into the tube and sonication for 5 min. Then the tube was transferred into ice-water for 20 min and phase separation was achieved by 8 min centrifugation. Three sets of water samples including Yellow River water, tap water and snow water were all spiked at three different concentration levels of 45 μg L^{-1}, 98 μg L^{-1} and 140 μg L^{-1}, respectively. The results were illustrated in Table 3. And the chromatograms of blank yellow river sample and yellow river sample spiked with 25 μg L^{-1} 2-naphthol and 4-nitrophenol are shown in Fig. 6.

Table 3
Spiked recoveries in environmental water by proposed method ($n=3$).

Sample	Compounds	Added ($\mu g\ L^{-1}$)	Found ($\mu g\ L^{-1}$)	RR[a] (%)	RSD (%)
Yellow river water	4-nitrophenol	45	39	87	3.2
		98	97	99	4.1
		140	132	94	3.7
	2-naphthol	45	47	104	3.4
		98	92	94	3.9
		140	139	99	4.3
Tap water	4-nitrophenol	45	42	93	2.5
		98	98	100	3.1
		140	137	98	3.1
	2-naphthol	45	44	98	2.8
		98	96	98	2.7
		140	137	98	3.0
Snow water	4-nitrophenol	45	46	102	3.2
		98	99	101	4.1
		140	139	99	3.9
	2-naphthol	45	48	107	4.5
		98	97	99	3.0
		140	140	100	4.6

[a] is defined as the relative recovery.

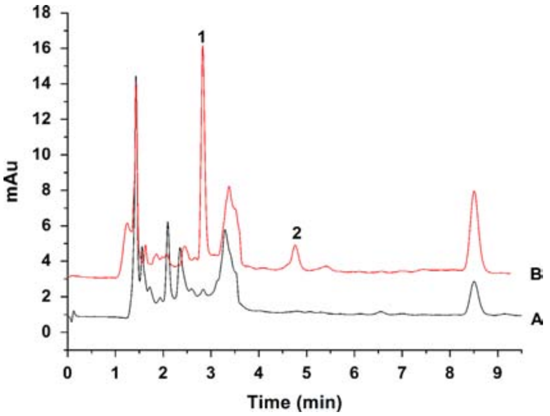

Fig. 6. Chromatograms of (A) blank water samples from yellow river and (B) water samples from yellow river spiked with 25 μg L^{-1} 2-naphthol and 4-nitrophenol extracted by DLLME.

4. Conclusion

In this study, a new mode of ionic liquid based DLLME was developed. It provided a potential way to realize direct extraction of acid compound from untreated environmental water samples by using the functional ionic liquid. The hydrophilic ionic liquid used here not only acted as dispersive solvent but also as the pH modifier. According to the present research, the acidic compounds could be extracted by introducing the SO_3– group; moreover, by introducing the functional group, some other kinds of compounds can be selectively extracted. Compared to the reported IL DLLME, this method has the unique extraction capacity for special kind of compound. On the basis of extraction mechanism of IL/IL DLLME method, this method should be suitable to other chemical families or other contaminants by specific functional group.

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References

[1] M. Rezaee, Y. Assadi, M.R.M. Hosseinia, E. Aghaee, F. Ahmadi, S. Berijani, J. Chromatogr. A 1116 (2006) 1–9.
[2] J. Cao, S. Liu, W. Bai, J. Chen, Q. Xie, Anal. Lett. 46 (2013) 1342–1354.
[3] A. Bidari, M.R. Ganjali, P. Norouzi, M.R.M. Hosseini, Y. Assadi, Food Chem. 126 (2011) 1840–1844.
[4] X. Xu, R. Su, X. Zhao, Z. Liu, D. Li, X. Li, H. Zhang, Z. Wang, Talanta 85 (2011) 2632–2638.
[5] G. Cinelli, P. Avino, I. Notardonato, A. Centola, M.V. Russo, Anal. Chim. Acta 769 (2013) 72–78.
[6] G. Cinelli, P. Avino, I. Notardonato, M.V. Russo, Anal. Methods 6 (2014) 782–790.
[7] J.-N. Sun, Y.-P. Shi, J. Chen, J. Chromatogr. B 879 (2011) 3429–3433.
[8] Y. Liu, E. Zhao, W. Zhu, H. Gao, Z. Zhou, J. Chromatogr. A 1216 (2009) 885–891.
[9] Y.C. Fan, Z.L. Hu, M.L. Chen, C.S. Tu, Y. Zhu, Chin. Chemi. Lett. 19 (2008) 985–987.
[10] M. Luo, D. Liu, Z. Zhou, P. Wang, Chirality 25 (2013) 567–574.
[11] J.-N. Sun, Y.-P. Shi, J. Chen, Anal. Methods 5 (2013) 1427–1434.
[12] M. Behbahani, F. Najafi, S. Bagheri, M.K. Bojdi, M. Salarian, A. Bagheri, J. Chromatogr. A 1308 (2013) 25–31.
[13] X. Wang, J. Liu, Q. Liu, X. Du, G. Jiang, Talanta 116 (2013) 906–911.
[14] L.M. Ravelo-Pérez, J. Hernández-Borges, M. Asensio-Ramos, M.Á. Rodríguez-Delgado, J. Chromatogr. A 1216 (2009) 7336–7345.
[15] L.B. Abdulra'uf, A.Y. Sirhan, G.Huat Tan, J. Sep. Sci. 35 (2012) 3540–3553.
[16] L. He, X. Luo, H. Xie, C. Wang, X. Jiang, K. Lu, Anal. Chim. Acta 655 (2009) 52–59.
[17] X. Jiang, H. Zhang, X. Chen, Microchim. Acta 175 (2011) 341–346.
[18] Q. Zhou, H. Bai, G. Xie, J. Xiao, J. Chromatogr. A 1177 (2008) 43–49.
[19] Y. Li, J. Zhang, B. Peng, S. Li, H. Gao, W. Zhou, Anal. Methods 5 (2013) 2241–2248.
[20] J. Zhang, H. Gao, B. Peng, S. Li, Z. Zhou, J. Chromatogr. A 1218 (2011) 6621–6629.
[21] A.M. Carro, P. Gonzalez, R.A. Lorenzo, J. Chromatogr. A 1319 (2013) 35–45.
[22] X. You, S. Wang, F. Liu, K. Shi, J. Chromatogr. A 1300 (2013) 64–69.
[23] C. Yao, J.L. Anderson, Anal. Bioanal. Chem. 395 (2009) 1491–1502.
[24] S. Gao, X. Yang, W. Yu, Z. Liu, H. Zhang, Talanta 99 (2012) 875–882.
[25] G. Aridoss, K.K. Laali, Eur. J. Org. Chem. 2011 (2011) 2827–2835.
[26] GB3838-2002, Environmental Quality Standards for Surface Water, State Environmental Protection Administration, China, 2002.
[27] R.-S. Zhao, X. Wang, J.-P. Yuan, L.-L. Zhang, Microchim. Acta 165 (2009) 443–447.
[28] D.L. Venter, I. Nieuwoudt, J. Chem. Engin. Data 46 (2001) 813–822.
[29] K.J. James, M.A. Stack, Fresenius J. Anal. Chem. 358 (1997) 833–837.
[30] C.L. Arthur, J. Pawliszyn, Anal. Chem. 62 (1990) 2145–2148.
[31] M.A. Jeannot, A. Przyjazny, J.M. Kokosa, J. Chromatogr. A 1217 (2010) 2326–2336.
[32] H. Faraji, S.W. Husain, M. Helalizadeh, J. Sep. Sci. 35 (2012) 107–113.
[33] S. Zhu, W. Niu, H. Li, S. Han, G. Xu, Talanta 79 (2009) 1441–1445.
[34] M. Guidotti, G. Ravaioli, M. Vitali, J. High. Resolut. Chromatogr. 22 (1999) 628–630.
[35] M.M. Sanagi, M. Miskam, W.A. Wan Ibrahim, D. Hermawan, H.Y. Aboul-Enein, J. Sep. Sci. 33 (2010) 2131–2139.
[36] S. Ortega-Algar, N. Ramos-Martos, A. Molina-Díaz, Talanta 60 (2003) 313–323.
[37] R. Preuss, J. Angerer, J. Chromatogr. B 801 (2004) 307–316.