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Screening the extractability of some typical environmental pollutants by ionic liquids in liquid-phase microextraction

The extractability of some typical environmental pollutants in ionic liquids (ILs) was screened by using a simple one-step liquid phase microextraction procedure. It was demonstrated that 1-alkyl-3-methylimidazolium hexafluorophosphate ($[C_nMIM][PF_6]$, $n = 4, 8$), two typical ILs, could effectively extract a set of 45 typical environmental pollutants including BTEX (benzene, toluene, ethylbenzene, and xylene), polycyclic aromatic hydrocarbons, phthalates, phenols, aromatic amines, herbicides, organotin, and organomercury. Analytes in 10 mL sample solution held in a 15 mL vial were extracted by a 5 μ L drop of ILs suspended on the needle of a high-performance liquid chromatography (HPLC) microsyringe; this was followed by HPLC, atomic absorption spectrometry, or cold-vapor atomic fluorescence spectrometry determination. The enrichment factors determined were in the range of 5–168 for 15 min extraction by $[C_4MIM][PF_6]$ and 4–178 for 30 min extraction by $[C_8MIM][PF_6]$, respectively, which indicates that ILs might be considered as potential environmentally benign alternative recyclable solvents for the enrichment of environmental pollutants.

Key Words: Ionic liquids; Separation; Environmental pollutants; Liquid-phase microextraction

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1 Introduction

The development of safe and environmentally benign separation processes plays an important role for the clean manufacturing process and environmental remediation. Room temperature ionic liquids (ILs) have several unique properties (e.g., negligible vapor pressure, low flammability, tunable viscosity, and miscibility in water and other organic solvents by combination of different anions and cations of ILs) which merit their consideration as alternative environmentally benign solvents for synthesis, catalysis, and separation [1, 2].

For metal ion separation, Dai et al. [3] first reported a highly efficient procedure for extraction of Sr^{2+} from aqueous phase into disubstituted imidazolium hexafluorophosphates and bis(trifluoromethyl)sulfonylamides by dicyclohexano-18-crown-6. Later, the extraction of Na^+ , Cs^+ , and Sr^{2+} from aqueous solution into 1-alkyl-3-methylimidazolium hexafluorophosphate ($[C_nMIM][PF_6]$, $n = 4, 6, 8$) ILs by crown ethers [4]; Cd^{2+} , Co^{2+} , Ni^{2+} , and Fe^{3+} from aqueous solution to ILs ($[C_nMIM][PF_6]$, $n = 4, 6$) by various organic and inorganic extractants [5]; and the influence of structural variation in ILs on the selectivity and efficiency

of competitive alkali metal salt extraction by a crown ether were reported. Visser et al. [7] prepared a series of task-specific ILs by appending urea-, thiourea, and thioether-substituted alkyl groups to imidazoles, for liquid-liquid extraction of Hg^{2+} and Cd^{2+} from water. More recently, $[C_4MIM][PF_6]$ was used as an alternative solvent to study liquid/liquid extraction of heavy metal ions from aqueous solution by using dithizone as a metal chelator to form neutral metal-dithizone complexes [8].

ILs were also applied to extract organic compounds such as substituted-benzene derivatives [9], biofuels [10], and erythromycin-A [11] from aqueous solutions. While Abraham et al. [12] studied the partition of some organic compounds between water-ILs systems, Carda-Broch et al. [13] investigated in detail the solvent properties of $[C_4MIM][PF_6]$ and determined the $[C_4MIM][PF_6]$ /water and $[C_4MIM][PF_6]$ /heptane distribution coefficients of a set of 40 compounds, including organic acids, organic bases, amino acids, antioxidants, and neutral compounds.

At present, the extraction capability of ILs for target compounds were performed by determining the distribution coefficient between ILs and water using a traditional procedure, i.e., aliquots of ILs (1–3 mL) were mixed with aqueous solutions and vortexed for the prescribed time, then the mixtures were centrifuged to separate the two phases, and finally the compounds in the two phases were determined and the distribution ratios calculated [4,

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7, 8, 13]. This method suffered from the disadvantages of being time-consuming and tedious, and of consuming relatively large amounts of expensive ILs. Therefore, development of a novel rapid and ILs-saving procedure is of interest. By using two typical ILs ([BMIM][PF₆] and [BMIM]Cl) as gas chromatography stationary phase, Armstrong et al. [14] studied the interactive and retentive behaviors of various compounds with ILs.

The objective of this study is to employ IL-based liquid-phase microextraction (LPME) [15, 16], an inexpensive and simple one-step procedure performed by using a few μL of ILs, for rapid screening of the extractability of some typical environmental pollutants including organic compounds and organometallic compounds by ILs.

2 Experimental

2.1 Reagents

Reagents used for synthesis of ILs, phthalate, aromatic amine, tributyltin, dibutyltin, and monobutyltin chloride were obtained from Acros Organics (Geel, Belgium). Trimethyltin, dimethyltin, monomethyltin, triphenyltin, and dioctyltin chloride were obtained from Aldrich Chem. Co. (Milwaukee, WI, USA). Organomercury standards (methylmercury, ethylmercury, phenylmercury, dimethylmercury and diethylmercury chloride) were purchased from Merck-Schuchardt (Hohenbrunn, Germany). Chlorophenol herbicides, BTEX (benzene, toluene, ethylbenzene, and xylene), and polycyclic aromatic hydrocarbons (PAHs) standards were obtained from Institute for Reference Materials of SEPA (Beijing, China). HPLC-grade methanol and acetonitrile were purchased from Scharlau Chemie SA, Barcelona, Spain. All other chemicals were of analytical grade (Beijing Chemicals Corporation, Beijing, China) and ultrapure water (EASYPure LF) was used throughout.

2.2 IL Synthesis

The synthesis and some physicochemical properties of [C_nMIM][PF₆] ($n = 4, 8$) were described in our previous study [15].

2.3 Apparatus

Organic pollutant determination were performed with an Agilent 1100 LC instrument consisted of a gradient (Bin-Pump) pump, an UV/Vis (VWD) detector, an Agilent ChemStation program for LC systems, and an Agilent Zorbax Eclipse XDB-C₁₈ (150 $\times$ 4.6 mm, particle size 5 μm) analytical column. An atomic absorption spectrometry (Z-5700 Polarized Zeeman atomic absorption spectrometry, Hitachi, Japan) and a cold-vapor atomic fluorescence spectrometry (CVAFS, AF-610A, Beijing Rayleigh Analytical Instrument Corp., China) were employed to deter-

Figure 1. Schematic diagram of the ionic liquids-based liquid-phase micro-extraction. 1, stir bar; 2, sample solution; 3, ILs drop; 4, PTFE tube; 5, septum; 6, microsyringe. (A), direct immersion LPME; (B), head-space LPME.

mine organotin and organomercury compounds, respectively.

2.4 Liquid phase micro-extraction

As shown in **Figure 1**, 10 mL of sample solution was added to a 15 mL vial. For the direct-immersion LPME procedure, 5 μL of ILs is drawn into a 50 μL microsyringe (Agilent) and the microsyringe clamped in place such that the needle of the syringe is immersed in the 10 mL sample solution held in a 15 mL vial. The plunger is depressed to expose a 5 μL ILs drop to the sample solution and the magnetic stirrer is turned on. After stirring for the prescribed time, the ILs drop was retracted for determination. For the headspace LPME procedure, the needle of the microsyringe (holding 5 μL of ILs) is used to pierce the vial septum, and the microsyringe is clamped in place such that the needle of the syringe is located in a consistent position of the headspace. Then the extraction is conducted as described above for direct-immersion LPME.

To suspend a 5- μL ILs drop, the tip of the microsyringe needle was sheathed with a 3 mm long polytetrafluoroethylene (PTFE) tube (0.6 mm ID and 1.8 mm OD).

2.5 Extractability measurement

Following the extraction, the ILs drop with concentrated organic compounds was retracted into the microsyringe and injected directly into the HPLC system for determination using acetonitrile-water mobile phases; the ILs drop with concentrated organotin was diluted with 50% methanol and then determined with an atomic absorption spectrometry; and the ILs drop with concentrated organomercury was added to an acidic potassium permanganate solution and heated in boiling water for 20 min to oxidize to inorganic mercury and then determined by cold-vapor atomic fluorescence spectrometry. All the concentrations of analytes were quantified by the external standard

Table 1. Enrichment factor of some environmental pollutants obtained by LPME^{a)}. Sample volume, 10 mL; ILs drop volume, 5 μ L; Extraction time, 15 min for [C₄MIM][PF₆], 30 min for [C₈MIM][PF₆].

Compounds	Molecular Weight	Concentration [mg l ⁻¹]	Enrichment factor	
			[C ₄ MIM] [PF ₆]	[C ₈ MIM] [PF ₆]
BTEX				
Benzene	78.1	1	23	27 (30) ^{b)}
Toluene	92.1	1	35	44 (52)
Ethylbenzene	106.2	1	52	
<i>o</i> -Xylene	106.2	1	65	51 (100)
<i>m</i> -Xylene	106.2	1	35	40 (60)
<i>p</i> -Xylene	106.1	1	45	38 (62)
PAHs				
Fluorene	166.2	0.02	75	106
Phenanthrene	178.2	0.02	168	171
Fluoranthene	202.3	0.02	52	91
Benzo[<i>k</i>]fluoranthene	252.3	0.02	25	30
Phthalate				
Diethyl	222.2	0.1	50	
Dipropyl	250.2	0.1	52	71
Di- <i>n</i> -butyl	278.4	0.1	130	178
Dicyclohexyl	330.4	0.1	25	40
Di-(2-ethylhexyl)	390.6	0.1	42	18
Diocetyl	390.6	0.1	42	37
Dinonyl	418.6	1	18	26
Phenol				
3-Chlorophenol	128.6	1	35	
4-Chlorophenol	128.6	1	35	
2,4-Dichlorophenol	163.0	1	40	67
2,4,6-Trichlorophenol	197.4	1	50	
Pentachlorophenol	266.4	1	52	127
4- <i>tert</i> -Octylphenol	206.3	0.025	80	117
4-Nonylphenol	220.4	0.025	125	133
Aromatic amine				
Aniline	93.1	1	13	
3-Methylaniline	107.2	1	34	
3,4-Dimethylaniline	121.2	1	15	
<i>N,N</i> -Dimethylaniline	121.2	1	42	37
2,4-Dichloroaniline	162.0	1	42	77
1-Naphthylamine	143.2	1	78	133
Herbicides				
Atrazine	215.7	0.2	25	
Simazine	201.0	0.2	12	
Organotin chloride				
Monomethyltin	241.5	0.01	28	18
Dimethyltin	220.0	0.01	28	20
Trimethyltin	200.5	0.01	90	161
Monobutyltin	282.2	0.01	12	14
Dibutyltin	303.8	0.01	10	11
Tributyltin	325.5	0.01	15	23
Triphenyltin	385.5	0.01	32	24
Diocetyl	415.0	0.01	35	28
Organomercury chloride				
Methylmercury	251.1	0.1	5	4
Ethylmercury	265.1	0.1	15	13
Phenylmercury	313.2	0.1	40	27
Dimethylmercury	266.1	0.1	15	7
Diethylmercury	294.2	0.1	32	14

^{a)} Whenever no value is reported, this indicates that the solute was not separated by HPLC.^{b)} Data in parentheses are enrichment factors obtained by headspace LPME.

method, and each determination was repeated twice and the mean values were reported.

The extractability of pollutant into ILs was evaluated by enrichment factor (F), which was calculated as following:

$$F = (C_{\text{IL}} - C_{\text{ILO}}) / C_{\text{aq0}}$$

In which C_{IL} , C_{ILO} , and C_{aq0} were the solute concentration in ILs after LPME, ILs blank, and initial aqueous solution, respectively.

3 Results and discussion

3.1 Selection of extraction parameters

For equilibrium LPME, the major parameters that affected the enrichment factor were the volume ratio of solvent drops to sample, the solute partition coefficient, and the solvent solubility in sample solution. Because no extraction equilibrium was reached for most LPME, however, the solute diffusion rate also influences the enrichment factor. Therefore, for non-equilibrium LPME, the enrichment factor is the complex result of the interaction of various parameters, including the partition coefficient and diffusion coefficient of solute, solubility of extraction solvent, volume and viscosity of both sample solution and solvent. Thus, the enrichment factor of non-equilibrium LPME by ILs does not represent the real partition coefficient of the target compound between ILs and water, but can approximately show the extraction capability of ILs for the target compound.

The effect of some parameters such as sample volume and extraction time on LPME of PAHs were optimized in our previous study [15]. In this present study, a 5- μL ILs drop was used as extraction solvent for LPME of 10-mL sample solution, and the enrichment times adopted were 15 min for $[\text{C}_4\text{MIM}][\text{PF}_6]$ and 30 min for $[\text{C}_8\text{MIM}][\text{PF}_6]$, respectively. The analytical performance parameters of determination were not studied in detail since as many as 45 different compounds were extracted in this study. According to our previous studies [15, 16], however, the precision (relative standard deviation) of the proposed LPME procedure should be better than 15%.

3.2 Screening

The above-described LPME method was applied to determine the enrichment factor, and thus to screen the extractability of a set of 45 environmental pollutants in ILs.

As shown in **Table 1**, the enrichment factor of some organic compounds by $[\text{C}_4\text{MIM}][\text{PF}_6]$ or $[\text{C}_8\text{MIM}][\text{PF}_6]$ could not be obtained because the analytes could not be separated from the huge solvent ($[\text{C}_4\text{MIM}][\text{PF}_6]$ or $[\text{C}_8\text{MIM}][\text{PF}_6]$) peak. This was confirmed by the very similar residence times of the analytes and ILs obtained when they were injected into the HPLC system. Furthermore,

no analyte peak was obtained when ILs spiked with high concentration of analytes were injected into the HPLC system, thus indicating that this phenomenon did not occur because the amount of analytes extracted was too low to be detected.

As shown in Table 1, all these compounds can be effectively extracted by ILs with enrichment factors in the range of 5–168 for 15 min extraction by $[\text{C}_4\text{MIM}][\text{PF}_6]$ and 4–178 for 30 min extraction by $[\text{C}_8\text{MIM}][\text{PF}_6]$, respectively. Table 1 also indicates that although the extraction time by $[\text{C}_4\text{MIM}][\text{PF}_6]$ was only half of that by $[\text{C}_8\text{MIM}][\text{PF}_6]$, the obtained enrichment factor for $[\text{C}_4\text{MIM}][\text{PF}_6]$ was similar to or even higher than that for $[\text{C}_8\text{MIM}][\text{PF}_6]$. This is probably because the viscosity of $[\text{C}_4\text{MIM}][\text{PF}_6]$ is much lower than that of $[\text{C}_8\text{MIM}][\text{PF}_6]$, which gives rise to a higher solute diffusion coefficient and thus a higher extraction efficiency in $[\text{C}_4\text{MIM}][\text{PF}_6]$. It is clear from Table 1 that the enrichment factor of headspace LPME (data in parentheses) was higher than that of direct-immersion LPME for the volatile BTEX. The reason is that headspace LPME has a higher extraction rate because the extract does not have to be transported through a liquid-liquid interface, which is the rate determining step in the direct-immersion procedure.

4 Conclusion

By using a simple one-step LPME procedure, the extractability of some environmental pollutants in ILs was screened. This study demonstrated that two typical ILs, $[\text{C}_4\text{MIM}][\text{PF}_6]$ and $[\text{C}_8\text{MIM}][\text{PF}_6]$, can effectively extract a set of 45 environmental pollutants including BTEX, PAHs, phthalate, phenol, aromatic amine, herbicides, organotin, and organomecury. Since ILs have several unique properties, including negligible vapor pressure, low flammability, tunable viscosity, and miscibility in water and other organic solvents by combination of different anions and cations, they might be considered as potential environmentally benign alternative recyclable media for separation and enrichment of environmental pollutants.

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