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Use of Ionic Liquid-filled Semipermeable Membrane for Extraction of Polycyclic Aromatic Hydrocarbons in Water

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Abstract: A novel and facile sample preparation method was developed for the extraction of polycyclic aromatic hydrocarbons (PAHs) in aqueous sample solution using 1-butyl-3-methylimidazolium hexafluorophosphate ([C_4MIM][PF_6]) – filled semipermeable membrane. For 24 hrs extraction of naphthalene, 1-methylnaphthalene, 2-chloronaphthalene, phenanthrene, the result showed that the extraction efficiency, correlation coefficient (R^2) and RSD (n=5) were in the range of 67-102 %, 0.9870-0.9962, and 2.1-5.3 %, respectively.

Keyword: Ionic liquid, semipermeable membrane, extraction, polycyclic aromatic hydrocarbons.

Ionic liquids (I Ls） have aroused interest for their promising role as alternative green solvents. They are ionic media formed from combination of organic cations and various anions and may be liquid at room temperature. I Ls have several unique properties that make them useful in a variety of chemical process[1-3]. For example, they are nonvolatile, nonflammable, and good solvents for a wide rang of both organic and inorganic compounds. Recently, I Ls were considered as attractive water-immiscible phase in liquid-liquid extraction[4, 5]. The aim of this study is to exploit the potentiality of I L in sample preparation replacing traditional solvents. Considering that dense semipermeable membrane which permit diffusional-jump transfer of organic contaminants were successful used for monitoring of aquatic contaminant[6], we developed a novel and facile sample preparation method for the extraction of polycyclic aromatic hydrocarbons (PAH) in water using 1-butyl-3-methylimidazolium hexafluorophosphate ([C_4MIM][PF_6]) (**Scheme 1**) – filled semipermeable membrane.

In the experiment, 0.5 mL [C_4MIM][PF_6] were enclosed in semipermeable membrane(15 cm x 2 cm, 75 μm thickness, low-density polyethylene tubing) and exposed to 500 mL stirred four PAHs compounds (naphthalene, 1-methylnaphthalene,

Scheme 1

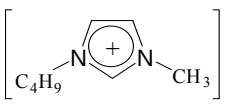

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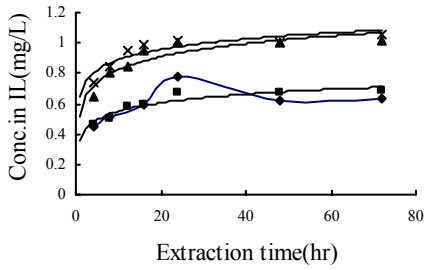
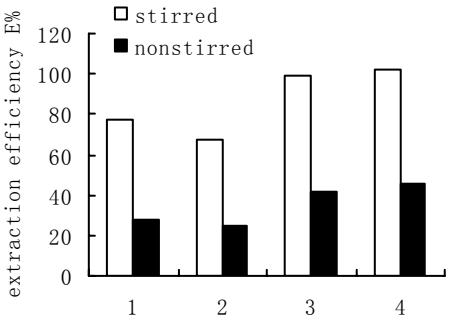
Figure 1 Uptack curve of four PAHs compounds [a]



a. 0.5 mL [C_4MIM][PF_6]-filled semipermeable membrane exposed to stirred 1 μg/L PAHs sample solution. ◆ naphthalene, ■ 1-methylnaphthalene, ▲ 2-chloronaphthalene, × phenanthrene

Figure 2 Extraction efficiency of four PAHs compounds in stirred sample solutionand and in nonstirred sample solution [b]



b. conditions: 1 μg/L PAHs sample solution were extracted using 0.5 mL IL filled semipermeable membrane. 1. naphthalene, 2. 1-methylnaphthalene, 3. 2-chloronaphthalene, 4. phenanthrene.

2-chloronaphthalene, phenanthrene) sample aqueous solution. After extraction for the prescribed time, the I L were aspirated by microsyringe and injected into the HPLC for separation and detection, using mixture of acetonitrile and water (4:1) as mobile phase at a flow rate of 1 mL/min, C_{18} column (200 × 4.6 mm) separation and FLU detection (xλ 280 nm, eλ 355 nm).

Figure 1 show uptake curve of 4 PAHs by I L [C_4MIM][PF_6]-filled semiper- meable membrane exposed to 500 mL stirred 1 μg/L solution. After about 24 hrs, an apparent equilibrium was established between the concentration of the substance in the I L and that in aqueous solution, so in the following study, the extraction time was set to 24 hrs. As can be seen, the pattern of uptake was similar for 1-methylnaphthalene, 2-chloro-naphthalene and phenanthrene. For the extraction of naphthalene, however, the uptake curve have decrease trend after 24 hrs, which probably is due to the volatility of naphthalene.

A comparison of extraction efficiency in stirred sample solution with in nonstirred sample solution for 24 hrs was made. The results in **Figure 2** indicated that the recovery of 4 PAHs in the stirred solution were almost 2-fold of that in the nonstirred solution. It means that stirring can accelerate the partition equilibrium of PAHs between the I L and water.

To evaluate [C_4MIM][PF_6]-filled semipermeable membrane extraction method, some parameters such as linearity, reproducibility and extraction efficiency for naphthalene, 1-methylnaphthalene, 2-chloronaphthalene, phenanthrene were determined under above condition. Linearity was investigated over a concentration range of 0.5~10 μg/L. The reproducibility was determined by five repeated extraction of a 1 μg/L water sample. The results in **Table 1** indicated that, for the studied 4 PAHs, good linearity with correlation coefficients ranging from 0.9870 to 0.9962 was obtained. The relative standard deviations (RSD) were between 2.1 and 5.3%. The extraction efficiency for naphthalene, 1-methylnaphthalene, 2-chloronaphthalene, phenanthrene was 78%, 67%, 99%, and 102%, respectively. The result is due to relative solubility of PAHs in the [C_4MIM][PF_6], which probably can be explained by the local electrostatic PAH-IL interactions.

The unique property of nonvolatility, adequate viscosity and surface tension allow I L to be contained in the semipermeable membrane without losing in the extraction process. The method proposed in this paper is a one-step extraction technique with only a spot of I L, avoiding harmful organic solvent. Furthermore, by a judicious combination of cations and anions, it is possible to adjust the I L properties in order to suit the certain requirement. The I L-filled semipermeable membrane extraction method will have a broad potential in sample preparation, although much more details studies regarding both the theoretical and practical aspects should be conducted.

Table 1 Extraction efficiency, linearity and reproducibility for extraction of 4 PAHs by 0.5 mL [C_4MIM][PF_6]-filled semipermeable membrane exposed to 500 mL sample aqueous solution

Analyte	Extraction efficiency(%)	Corre coeff(R^2)	Reproducibility (RSD,%,n=5)
naphthalene	78	0.9870	4.3
1-methylnaphthalene	67	0.9892	3.4
2-chloronaphthalene	99	0.9946	2.1
phenanthrene	102	0.9962	5.3

Acknowledgments

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